Nitrosation by Alkyl Nitrites. Part 2.[1] Kinetics of Reactions in Aqueous Acid Solution with Isopropyl and t-Butyl Nitrites

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The rates of reaction of isopropyl nitrite with sulphamic acid, hydrazoic acid, thioglycolic acid, cysteine, *N*-methylaniline, and thiourea are markedly reduced by the addition of propan-2-ol. A detailed kinetic analysis of the results is as expected for a mechanism where hydrolysis of isopropyl nitrite occurs rapidly (and reversibly) and the released nitrous acid effects nitrosation. The analysis yields values for the equilibrium constant for isopropyl nitrite hydrolysis and also for the rate constants for nitrous acid nitrosation (for a range of substrates), which are in good agreement with the literature values obtained by direct measurement. For t-butyl nitrite the extent of hydrolysis is so great (and the reaction is so rapid) that the kinetics are identical with those obtained using nitrous acid. Under most of the experimental conditions employed the rate-limiting step is the reaction of $H_2NO_2^+$ with the substrate, but at high [substrate] for the more reactive species, the rate-limiting step changes to that of hydrolysis of RONO. This is particularly true for t-butyl nitrite, where it is easier for the nitrosation of the substrate by nitrous acid to compete with the re-nitrosation of the alcohol, since the rate of the latter reaction is much smaller for a tertiary alcohol than it is for a secondary alcohol. Further experimental measurements on the $\mathrm{ROH + HNO_2 \longrightarrow RONO}$ system, for both isopropyl and t-butyl nitrites, confirm these mechanistic ideas.

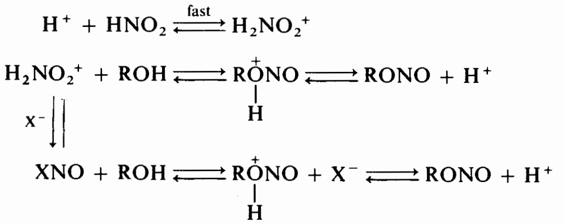
Alkyl nitrites have been and are much used synthetically as nitrosating agents, both in aqueous solution (under acidic and also alkaline conditions) and in non-aqueous solvents. In this series of papers we set out to establish the detailed mechanistic features of such reactions, which hitherto have not been defined. This part deals with reactions in aqueous acid solution; in Part 1[1] reactions in alcohol as solvent, also under acidic conditions, were studied.

In aqueous acid solution, alkyl nitrites readily undergo hydrolysis to give equilibrium concentrations of nitrous acid and the corresponding alcohol. Hydrolysis has been examined mechanistically by several workers, notably by Allen,[2] usually with dioxane–water as solvent. More recently the situation has been examined kinetically (in water) starting from the alcohol and nitrous acid.[3] This treatment allows values of the rate constant for the forward and reverse reactions [equation (1)]

$$\mathrm{ROH + HNO_2 \underset{H^+}{\overset{H^+}{\rightleftharpoons}} RONO + H_2O} \qquad K \quad (1)$$

to be determined. Recently the equilibrium constants K for alkyl nitrite formation have also been determined directly[4] by spectrophotometry, and also indirectly by another kinetic technique,[4] for a range of aliphatic alcohols. Formation of alkyl nitrites in this way (which is the standard preparative procedure) is the best known example of electrophilic *O*-nitrosation. Both forward and reverse reactions are acid-catalysed and are also catalysed by nucleophiles X^- such as halide ion and thiocyanate ion.[3] The overall situation is summarised in Scheme 1.

The question associated with nitrosation by alkyl nitrite in aqueous acidic solution then is, do alkyl nitrites react directly or *via* the nitrous acid formed on hydrolysis? The indications are that the latter is the case. One study[5] of nitrosations of sulphanilamide with cyclohexyl nitrite and with nitrous acid concludes that a common nitrosating agent is involved. Rate reductions of amine nitrosations by added alcohols[4,6] have been interpreted in terms of the formation of equilibrium concentrations of alkyl nitrites, which are not reactive. On the other hand there is evidence that under different experimental conditions alkyl nitrites do act directly, *e.g.* in aqueous alkali,[7] in alcoholic solvents,[8] and in non-protic solvents such as chloroform and acetonitrile.[9] Tertiary nitrites are claimed to have major advantages as synthetic reagents,[9,10] so we have examined the kinetics of nitrosation by t-butyl nitrite as well as by a secondary nitrite, isopropyl nitrite. We have covered a range of typical substrates: sulphamic acid, hydrazoic acid, thioglycolic acid, cysteine, *N*-methylaniline, thiourea.



$$\begin{array}{l}
\mathrm{H^+ + HNO_2 \overset{fast}{\rightleftharpoons} H_2NO_2^+} \\
\mathrm{H_2NO_2^+ + ROH \rightleftharpoons \underset{\displaystyle H}{\underset{|}{R\overset{+}{O}NO}} \rightleftharpoons RONO + H^+} \\
\quad \mathrm{X^-} \downarrow\uparrow \\
\mathrm{XNO + ROH \rightleftharpoons \underset{\displaystyle H}{\underset{|}{R\overset{+}{O}NO}} + X^- \rightleftharpoons RONO + H^+}
\end{array}$$

Scheme 1.

Experimental

Both alkyl nitrites were prepared and purified by the standard procedure,[11] from the corresponding alcohol and nitrous acid. Fresh t-butyl nitrite solutions were made up frequently (about every 2 h during use) as they showed significant signs of decomposition over 24 h. All other reagents used were of AnalaR grade except for t-butyl alcohol and *N*-methylaniline, which were distilled before use. Fresh solutions of sodium nitrite were made up daily as required.

Most of the kinetic measurements were carried out (in aqueous solution at 25 °C) in a stopped-flow spectrophotometer; the slower reactions of *N*-methylaniline were followed in a coventional spectrophotometer. The nitrosation reactions of t-butyl alcohol and of propan-2-ol were followed at 290 and 285 nm, respectively, by noting the increasing absorbance due to the alkyl nitrite. Some nitrosation experiments with RONO were followed at 375.5 ($\mathrm{Bu^tONO}$) or at 370 nm ($\mathrm{Pr^iONO}$), by measuring the disappearance of the absorbance due to RONO; in other cases it was more covenient to follow the appearance of the nitrosation product at 330 (for thioglycolic acid), 285 (for *N*-methylaniline), 330 (for cysteine), or 420 nm (for thiourea).

Table 1. Values of $k_1/[H^+]$ (dm^6 mol^{-2} s^{-1}) and $k_{-1}/[H^+]$ (dm^3 mol^{-1} s^{-1}) for the nitrosation of Pr^{i}OH and Bu^{t}OH at 25 °C

	Pr^{i}OH		Bu^{t}OH	
$[H^+]$/M	$k_1/[H^+]$	$k_{-1}/[H^+]$	$k_1/[H^+]$	$k_{-1}/[H^+]$
0.020	108	585	?	890
0.040	108	563		
0.106	128	570	?	880

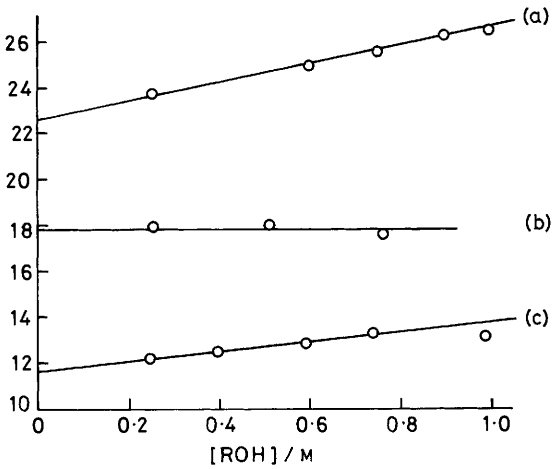


Figure 1. Plot of k_0 as a function of added [ROH] in the nitrosation of Pr^{i}OH and Bu^{t}OH with HNO_2/H^+: (a) Pr^{i}OH at $[H^+]$ 0.040M, (b) Bu^{t}OH at $[H^+]$ 0.020M, (c) Pr^{i}OH at $[H^+]$ 0.020M

All the reactions of alkyl nitrites were carried out under first-order conditions with [substrate] $\gg$ [RONO]; the nitrosations by nitrous acid of t-butyl and isopropyl alcohols were similarly carried out with [ROH] $\gg$ $[HNO_2]$. Good first-order behaviour was noted throughout and the rate constants k_0 (defined by $-d[HNO_2]/dt = k_0[HNO_2]$) were obtained from the integrated rate equation, using a measured infinity value. Each reported k_0 value is the mean of at least five separate determinations, and the quoted error is the standard deviation within a set, typically 2—3%.

Results and Discussion

(a) *Nitrosation of t-Butyl and Isopropyl Alcohols with Nitrous Acid.*—These reactions have previously been studied kinetically[3] at 0 °C, but have now been repeated at 25 °C, so that the derived rate constants may be used [in sections (b) and (c)] for the reactions of t-butyl and isopropyl nitrites, all of which were measured at 25 °C. We have used the same procedure as before, with [ROH] $\gg$ $[HNO_2]$ and measuring k_0 as a function of [ROH]. The observed rate constant k_0 is then given by equation (2), and the rate constants for the forward (k_1)

$$k_0 = k_1[\mathrm{ROH}] + k_{-1} \qquad (2)$$

and reverse (k_{-1}) reactions can be obtained from plots of k_0 *vs.* [ROH]. It is not easy to obtain accurate values of k_1 for these alcohols, as is evident from the data in Figure 1. The slopes for Pr^{i}ONO at both acidities are quite small, so the error in k_1 is large; it is impossible even to estimate a k_1 value for Bu^{t}ONO at 0.02M H^+ [graph (b)] and also at 0.106M H^+ (not shown) since the slopes are so close to zero in both cases. Values of k_{-1} (from the intercepts) are more reliable. The combined data are shown in Table 1. It is evident that the rate constant for the nitrosation of Bu^{t}OH at 25 °C (although we cannot put a value to it) is much less than that for the nitrosation of Pr^{i}OH. This is exactly the same conclusion as was found for reactions at 0 °C, where the order of alcohol reactivity is primary > secondary $\gg$ tertiary, and has been attributed to a steric effect.

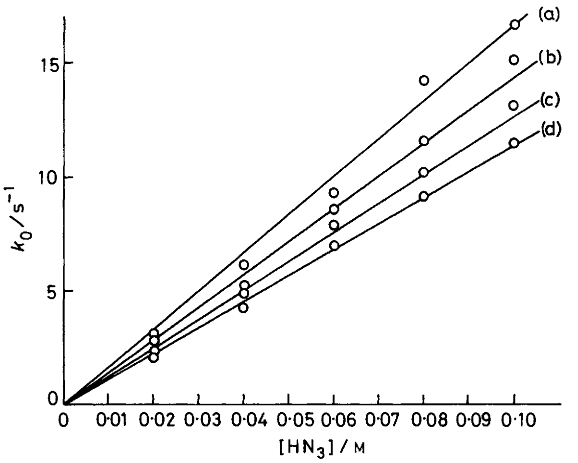


Figure 2. Dependence upon $[HN_3]$ and added [Pr^{i}OH] in the nitrosation of HN_3 by Pr^{i}ONO at $[H^+]$ = 0.538M: (a) [Pr^{i}OH] = 0, (b) [Pr^{i}OH] = 0.191M, (c) [Pr^{i}OH] = 0.402M, (d) [Pr^{i}OH] = 0.607M

(b) *Nitrosation with Isopropyl Nitrite.*—Sulphamic acid, hydrazoic acid, thioglycolic acid, cysteine, and *N*-methylaniline all reacted rapidly in dilute aqueous acid solution at 25 °C with Pr^{i}ONO to give the usual nitrosation products. Rate constants were mostly obtained by stopped-flow spectrophotometry under first-order conditions with [substrate] $\gg$ [Pr^{i}ONO]. Plots of k_0 *vs.* [substrate] were linear, passing through the origin. The reaction rates were reduced by the addition of Pr^{i}OH. The results for the reaction of hydrazoic acid in 0.5M-acid are shown in Figure 2. Acid catalysis occurs for the reactions of HN_3 but not for *N*-methylaniline. These results suggest that hydrolysis of the nitrite occurs, and that the nitrous acid formed is responsible (in its protonated form) for nitrosation of the substrate *S*, as outlined in Scheme 2. For the RONO hydrolysis we use the same rate constant nomenclature as in part (a) for ROH nitrosation; *K* is the equilibrium constant for RONO formation. We define *k* as the third-order rate constant for nitrous acid nitrosation of *S* (rate = $k[HNO_2][S][H^+]$). When the substrate is not significantly protonated under the reaction conditions (*e.g.* for HN_3 and $HSCH_2CO_2H$) it is clear that overall acid catalysis should occur, but where *S* is significantly protonated (as in $NH_2SO_3^-$ and PhNHMe), then such acid catalysis is offset by the protonation of *S*. If the rate-limiting step is the nitrosation of *S* by nitrous acid and the equilibrium formation of nitrous acid is maintained, then the expression for k_0 expected from Scheme 2 is given by equation (3) when *S* is not protonated, and by equation (4) if significant

$$\mathrm{RONO} + \mathrm{H_2O} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{ROH} + \mathrm{HNO_2}$$

$$\left.\begin{array}{l} \mathrm{HNO_2} + \mathrm{H^+} \rightleftharpoons \mathrm{H_2NO_2^+} \\ \mathrm{H_2NO_2^+} + S \longrightarrow \text{nitrosation products} \end{array}\right\} k$$

Scheme 2.

$$k_0 = \frac{k[S][\mathrm{H^+}]}{1 + K[\mathrm{ROH}]} \qquad (3)$$

$$k_0 = \frac{k[S][\mathrm{H^+}]K_a}{(K_a + [\mathrm{H^+}])(1 + K[\mathrm{ROH}])} \qquad (4)$$

Table 2. Values of K and k derived from plots of k_0^{-1} *vs.* [Pr^{i}OH] for reactions of Pr^{i}ONO with substrates S

S	$[H^+]$/M	K/dm^3 mol^{-1}	k^a/dm^6 mol^{-2} s^{-1}	k^b/dm^6 mol^{-2} s^{-1}
HN_3	0.100	0.71 ± 0.1	220 ± 13	214^c
HN_3	0.538	0.71 ± 0.1	300 ± 10	360^c
$NH_2SO_3^-$	0.522	0.67 ± 0.1	2 050 ± 40	1 130^d
$HSCH_2CO_2H$	0.203	0.71 ± 0.1	2 460 ± 70	2 630^e
$HSCH_2CH(\overset{+}{N}H_3)CO_2H$	0.052	0.62 ± 0.1	330 ± 10	340^e

[a] From this work. [b] Literature value measured directly using HNO_2. [c] Ref. 13. [d] Ref. 12. [e] P. A. Morris and D. L. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1988, in the press.

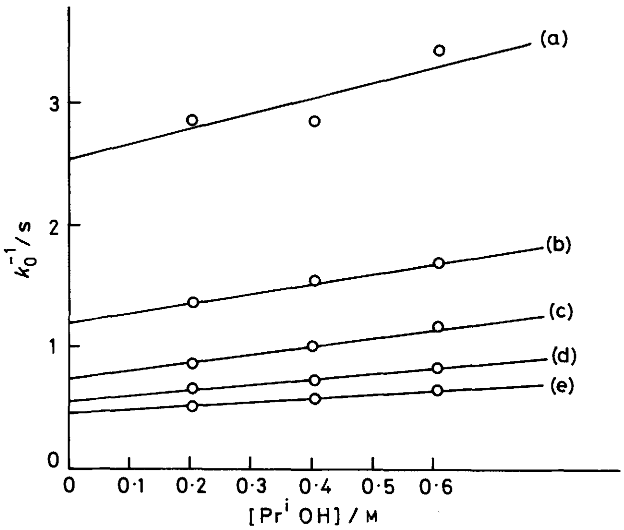


Figure 3. Reciprocal plot for the nitrosation of HN_3 by Pr^{i}ONO at $[H^+]$ = 0.100M (a) $[HN_3]$ = 0.02M, (b) $[HN_3]$ = 0.04M, (c) $[HN_3]$ = 0.06M, (d) $[HN_3]$ = 0.08M, (e) $[HN_3]$ = 0.10M

protonation of S occurs. K_a is the dissociation constant of SH^+ and $[S]$ is the total stoicheiometric concentration of the substrate. Overall acid catalysis disappears if $[H^+] \gg K_a$, as we find for the nitrosation of N-methylaniline. A more quantitative test of equation (3) [or (4)] can be made *via* its reciprocal form (5), when k_0^{-1} should be directly proportional to [ROH] added.

$$k_0^{-1} = \frac{K[\mathrm{ROH}]}{k[S][H^+]} + \frac{1}{k[S][H^+]} \qquad (5)$$

Such plots are shown in Figure 3 for the reaction of HN_3 in 0.1M-acid. Similar results were obtained for the same reaction in 0.5M-acid and also for the reactions of sulphamic acid, thioglycolic acid, cysteine, and N-methylaniline. These plots allow the calculation of both K and k. In Table 2 are the collected values obtained from this analysis. The experimental points for N-methylaniline were more scattered than for the other reactants because of the difficulty in obtaining reliable infinity readings in the individual experiments, and so are not sufficiently accurate to give meaningful values for K and k. However in all other cases excellent agreement is found for the derived K values with an average value of 0.68 ± 0.1 dm^3 mol^{-1}, in quite good agreement with the literature value[4] of 0.56 dm^3 mol^{-1} for K measured directly at this temperature. Similarly there is reasonable agreement between k values determined in this way and those reported for the direct nitrous acid nitrosations. The agreement is apparently not so good for the sulphamic acid reaction. We have however made the assumption that reaction occurs only *via* the anion form $NH_2SO_3^-$, whereas Hughes[12] has noted that above *ca.* 0.25M H^+ reactions also occur *via* the undissociated species HN_2SO_3H; our value probably includes a component due to this other reaction. The literature value of k for the hydrazoic acid reaction shows an acidity dependence (a salt or activity effect), so the quoted values are interpolated from the original data.[13]

Table 3. Values for k_0 for the nitrosation of sulphamic acid by Bu^{t}ONO with added Bu^{t}OH. [Bu^{t}ONO] = 1.2 × 10^{-3}M, $[H^+]$ = 0.52M

	k_0/s^{-1}	
$[NH_2SO_3H]$/M	[Bu^{t}OH] = 0.20M	[Bu^{t}OH] = 0.60M
0.02	3.51 ± 0.06	3.51 ± 0.14
0.03	5.45 ± 0.29	5.53 ± 0.13
0.04	6.94 ± 0.18	6.81 ± 0.24
0.05	8.61 ± 0.13	8.81 ± 0.36
0.06	10.5 ± 0.4	9.97 ± 0.11
0.07	11.9 ± 0.2	11.6 ± 0.5

We have examined the reaction of Pr^{i}ONO further with a very reactive substrate, thiourea,[14] over a much larger substrate concentration range. At low [thiourea], the plot of k_0 *vs.* [thiourea] is linear for two sets of experiments with different concentrations of added Pr^{i}OH. From the slopes we have calculated k values for thiourea nitrosation by nitrous acid (assuming K for Pr^{i}OH nitrosation) of 6 500 and 6 300 dm^6 mol^{-2} s^{-1}, which agree very well with the value (6 900 dm^6 mol^{-2} s^{-1}) obtained by Stedman and his co-workers from direct measurement.[14] However as [thiourea] is increased the plot becomes curved and finally, for both sets of experiments, k_0 becomes independent of [thiourea] for [thiourea] > 0.2M. An explanation of this is that at high [thiourea] the rate of nitrosation by nitrous acid is significantly greater than the rate of re-nitrosation of the alcohol Pr^{i}OH, which means that the rate of hydrolysis of Pr^{i}ONO becomes rate-limiting. Our measured limiting k_0 yields a value of 970 dm^3 mol^{-1} s^{-1} for $k_{-1}/[H^+]$ (see Scheme 2) which is somewhat larger than the average value of 570 dm^3 mol^{-1} s^{-1} obtained from the direct measurement (see Table 1). The cause of the slight discrepancy is not clear, but may be a medium effect due to the rather high [thiourea] necessary.

(c) *Nitrosation with t-Butyl Nitrite.*—We have examined the kinetics of the reactions of Bu^{t}ONO with sulphamic acid and hydrazoic acid under the same experimental conditions as used in (b) for Pr^{i}ONO. Again the reactions are rapid and yield good first-order plots. However, in marked contrast to (b), now the values of k_0 are independent of the concentration of added Bu^{t}OH at all substrate concentrations studied. The data in Table 3 give the results for the reactions of sulphamic acid (for relatively low $[NH_2SO_3H]$ at two [Bu^{t}OH]; the corresponding k_0 values are identical within the experimental error). The explanation lies in the difference in the K values for RONO formation for the two systems. For Pr^{i}ONO K values reported at 25 °C are 0.56 and 0.52 dm^3 mol^{-1}. We have been unable to obtain a K value for Bu^{t}ONO from kinetic methods because the rate constant for Bu^{t}OH is so small [see section (a)], but have estimated that at least at 0 °C K < 0.05 dm^3 mol^{-1}. Now it is likely that $1 \gg K[\mathrm{ROH}]$ [see equations (3) and (4)], so that equation (4) now becomes equation (6); thus k_0 is independent

$$k_0 = \frac{k[S][H^+]K_a}{K_a + [H^+]} \qquad (6)$$

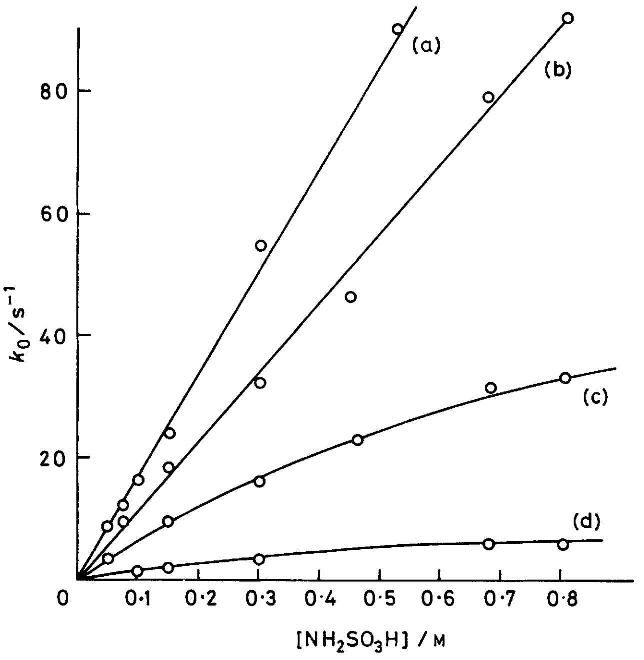


Figure 4. Substrate concentration dependence for the nitrosation of NH_2SO_3H by Bu^{t}ONO: (a) [H$^+$] = 0.50M, (b) [H$^+$] = 0.19M, (c) [H$^+$] = 0.05M, (d) [H$^+$] = 7.7 × 10^{-3}M

of [Bu^{t}OH], and first order in [S], as observed experimentally. In other words, this means that Bu^{t}ONO is virtually completely hydrolysed to nitrous acid and Bu^{t}OH before any reaction of nitrous acid with the substrate occurs, and equation (6) is identical with that expected for nitrosation by nitrous acid itself. If we assume K = 0.05 dm^3 mol^{-1} and [Bu^{t}OH] typically 0.2M, the calculated extent of hydrolysis is 95%. As expected the measured k values (for both HN_3 and NH_2SO_3H reactions) agree with the literature values given in Table 2 for the nitrous acid reactions.

However at higher [NH_3SO_3H] and [HN_3] the reactions lose their first-order dependence upon [NH_3SO_3H] and [HN_3]. This is shown graphically in Figure 4 for the reactions of sulphamic acid at several different acidities. The effect is more marked at lower acidities. This behaviour is similar to that found for the Pr^{i}ONO reactions at high [thiourea], except that it is more pronounced for Bu^{t}ONO. Again we believe that this effect arises from the fact that with high [substrate] alkyl nitrite hydrolysis becomes rate-limiting. In quantitative terms this means that $k[S][H^+]K_a/(K_a + [H^+])$ competes effectively with k_1[Bu^{t}OH]. This will happen more easily with Bu^{t}OH, for which k_1 is much smaller than it is for Pr^{i}OH and also will occur more readily at high [S] and at low [H$^+$] (since k_1 includes [H$^+$]). The limiting k_0 values at high [NH_2SO_3H] at 0.05M and 0.077M H$^+$ correspond to the situation where Bu^{t}ONO hydrolysis is fully rate-limiting. Both plots yield values of *ca.* 700 dm^3 mol^{-1} s^{-1} for $k_{-1}/[H^+]$ which are reasonably in agreement with the values of 880 and 890 dm^3 mol^{-1} s^{-1} obtained from the direct measurements (see Table 1).

A more detailed kinetic analysis of these data shows that $k_0^{-1} \propto [S]^{-1}$ and that the slopes of these plots are $\propto [H^+]^{-1}$. This is expected if [nitrous acid] is now in a steady state. The full rate equation is equation (7), and it is easy to see the double-reciprocal relationship. This enables a value of the pK_a for sulphamic acid to be determined as 1.0, which agrees well with the literature values of 0.98[12] (at 0 °C) and 1.1[13] (at 25 °C).

$$k_0 = \frac{k\,k_{-1}[S][H^+]K_a}{k_1[ROH](K_a + H^+) + k[S][H^+]K_a} \qquad (7)$$

Table 4. Effect of bromide ion on the nitrosation of (a) sulphamic acid and (b) hydrazoic acid by Bu^{t}ONO (1.2 × 10^{-3}M)

NH_2SO_3H (0.025M)^a		HN_3 (0.025M)^b	
[Br$^-$]/M	k_0/s^{-1}	[Br$^-$]/M	k_0/s^{-1}
0	0.34	0	3.26
0.05	0.33	0.025	16.9
0.10	0.28	0.050	31.2
0.15	0.28	0.075	44.5
0.20	0.25	0.125	78.9

^{a} [H$^+$] = 7.8 × 10^{-3}M. ^{b} [H$^+$] = 0.5M.

The same effect is noted for HN_3 nitrosation by Bu^{t}ONO. At low [HN_3] reaction is first-order in [HN_3], whereas as [HN_3] is increased, k_0 *vs.* [HN_3] becomes curved as the rate of Bu^{t}ONO hydrolysis becomes partly rate-limiting. We have not carried out a full kinetic analysis with this substrate.

Further confirmation of the reaction mechanism (Scheme 2) comes from the effect of added nucleophile catalysts. The nitrosation of sulphamic acid with Bu^{t}ONO is not catalysed by either Br$^-$ or Cl$^-$, whereas the reaction of Bu^{t}ONO with hydrazoic acid is markedly catalysed by both anions. The data for Br$^-$ catalysis are given in Table 4. This is exactly the pattern observed in the nitrosation of these substrates by nitrous acid itself.[12,13] Sulphamic acid behaves as do amides and ureas generally,[15] where the rate-limiting step is the proton transfer from the nitroso intermediate. For amines (and hydrazoic acid *et al.*), however, the formation of the nitroso intermediate is rate-limiting and is subject to catalysis by Br$^-$ *etc.* From the data in Table 4 for the HN_3 reaction it is possible to obtain a value for the second-order rate constant for attack by BrNO. We obtain here a value of 9.4 × 10^5 dm^3 mol^{-1} s^{-1}, which is reasonably comparable with the two published values[13] (1.3 × 10^6 and 2.0 × 10^6 dm^3 mol^{-1} s^{-1}) for the nitrous acid reaction in the presence of bromide ion.

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