Nitrosation by Alkyl Nitrites. Part 4.[1] *S*-Nitrosation in Acidic Alcohol Solvents

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Both isopropyl nitrite (IPN) and t-butyl nitrite (TBN) react rapidly with thiourea (TU) and thioglycolic acid (TGA) in isopropyl and t-butyl alcohol, respectively, containing an acid catalyst, to give the corresponding *S*-nitroso derivatives, contrasting with the behaviour of aromatic amines under the same conditions. The thiourea reaction is reversible and thiourea itself is significantly protonated under the experimental conditions. A kinetic analysis reveals that both alkyl nitrites are of comparable reactivity and also that TU is significantly more reactive than TGA. The reactive species is probably the protonated form of the alkyl nitrite. Catalysis by added Et_4NCl and Et_4NBr is interpreted in terms of ClNO and BrNO formation, but there may be a contribution due to general acid catalysis by HCl or HBr. The reaction rate is much reduced by the addition of small amounts of water.

In Part 1 of this series[2] it was shown that propyl nitrite in propanol failed to nitrosate (or diazotise) aniline derivatives in mildly acidic solution. These results showed that the protonated form of the alkyl nitrite (or something derived from it) is not a sufficiently powerful electrophile to effect nitrosation of anilines, the free-base forms of which are necessarily present in very low concentrations. However, reaction took place quite readily when halide ion or thiourea catalysts were added. The mechanistic interpretation given was that equilibrium concentrations of nitrosyl halides or of the *S*-nitroso derivative of thiourea generated *in situ* are sufficiently powerful (or are present in sufficient concentration) to react with the low concentrations of anilines present in the free-base form. It is of some interest to establish whether alkyl nitrites in alcohol solutions, again under mildly acid conditions, can bring about nitrosation of more reactive nucleophiles, which are not in effect de-activated by protonation in acid media. We chose to examine the reactions of alkyl nitrites under these conditions with thiourea (TU) and thioglycolic acid (TGA). *S*-Nitrosation is much less well-known than is *N*-nitrosation (particularly of amines), but has been more studied in recent years.[3] In aqueous solution with nitrous acid, *S*-nitrosation of TU[4] and thiols (including TGA[5]) is a rapid process which occurs at or close to the encounter-controlled limit; further, neither reaction is complicated by substrate protonation. As far as we are aware, *S*-nitrosation has not been examined mechanistically in other solvents.

From the synthetic viewpoint, alkyl nitrites are often used to effect nitrosation, particularly in alcohol solvents when there are substrate solubility problems in water. Reactions are either carried out under alkaline conditions,[6,7] where a direct reaction occurs between the alkyl nitrite and the substrate, or under acid conditions,[6] usually containing HCl when nitrosyl chloride is probably the effective reagent. In water alkyl nitrites hydrolyse in acid to give nitrous acid which produces the effective reagent,[8] whilst under mildly basic aqueous solution alkyl nitrites react directly with powerful nucleophiles such as thiolate anions.[1]

Experimental

Both alkyl nitrites were prepared by the standard method of nitrosation of the corresponding alcohol using nitrous acid.[9] Purification was by distillation. Fresh stock solutions were made up daily. Isopropyl and t-butyl alcohol were purified by distillation. Solutions of sulphuric acid in alcohol solvents were prepared by dissolving small quantities of sulphuric acid (98% analytical reagent) in the alcohol with ice cooling. All other reagents were of the highest purity grade available and were used as such.

Kinetic experiments were all carried out at 30 °C by stopped flow spectrophotometry, generally noting the increasing absorbance due to the yellow *S*-nitroso species at *ca.* 350 nm. Experiments were performed under first-order conditions with $[TU]_0$ or $[TGA]_0 \gg [RONO]_0$, and good first-order behaviour was quite general. The first-order rate constant k_0 was reproducible to within *ca.* ±5%. When the rate constants were less than *ca.* 0.01 s^{-1} the reactions were followed in a conventional spectrophotometer, again noting the appearance of the product at *ca.* 350 nm.

Results

(*a*) *Reactions of Thiourea* (*TU*).—Both alkyl nitrites in their respective alcohol solvents reacted rapidly with TU to give yellow solutions of the *S*-nitrosothiourea cation. Kinetic measurements were reproducible and were free from complication. All were carried out under first-order conditions with $[TU]_0 \gg [RONO]_0$. Results for the dependence of the first-order rate constant k_0 upon $[TU]_0$ are shown in Tables 1 and 2 for the two alkyl nitrites, at two different acidities in the case of TBN. There is no linear dependence between k_0 and $[TU]_0$, the plots are quite curved, tending towards an upper limit, and there is a significant positive intercept at $[TU]_0 = 0$. A likely explanation of the positive intercept is that the overall reaction is reversible [equation (1)]. This is certainly the case for the nitrosation of thiourea in water using nitrous acid[4] and also for the nitrosation of alcohols under the same conditions.[10] For such a situation plots of k_0 *vs.* $[TU]_0$ are expected to be linear with a positive slope and intercept from which the rate constants for the forward (k_1) amd reverse (k_{-1}) reactions can readily be obtained. However in our case such plots are distinctly curved. In principle, a number of explanations are possible, one of which depends upon the protonation of TU, which, if it takes place to a significant extent, would in effect reduce the effective acidity of the medium as the initial concentration of TU is increased. If

$$RONO + (NH_2)_2CS + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NH_2)_2CS^+NO + ROH \quad (1)$$

Table 1. Values of k_0 for the nitrosation of TU by TBN in t-butyl alcohol. [TBN] = 1×10^{-3} mol dm^{-3}.

	k_0/s^{-1}	
[TU]/mol dm^{-3}	[H_2SO_4] = 0.033 mol dm^{-3}	[H_2SO_4] = 0.066 mol dm^{-3}
0.012	0.156 ± 0.006	0.209 ± 0.005
0.024	0.203 ± 0.002	0.319 ± 0.006
0.036	0.301 ± 0.013	0.406 ± 0.003
0.048	0.296 ± 0.014	0.467 ± 0.006
0.060	0.314 ± 0.021	0.530 ± 0.009

Table 2. Values of k_0 for the nitrosation of TU by IPN in isopropyl alcohol. [IPN] = 1.2×10^{-3} mol dm^{-3}, [H_2SO_4] = 0.117 mol dm^{-3}.

[TU]/mol dm^{-3}	k_0/s^{-1}
0.0162	0.249 ± 0.007
0.0323	0.368 ± 0.006
0.0485	0.484 ± 0.012
0.0647	0.585 ± 0.012
0.0809	0.653 ± 0.026
0.0970	0.723 ± 0.011

this is the case then it should also have an effect on the acidity dependence of k_0 at constant $[TU]_0$. The results are given in Table 3 for the dependence of k_0 upon [H_2SO_4] *i.e.* the total titratable acidity, for both alkyl nitrites. Again the plots are curved with a significant positive intercept at [H_2SO_4] = 0. There is a tendency for k_0 to approach an upper limit at high acidity. This can readily be explained if TU becomes significantly protonated in these solutions, thus lowering the effective TU concentration. In water the pK_a of the protonated form of TU is -1.19 and protonation is believed to occur principally at the sulphur atom.[11] Further, the pK_a values of substituted phenyl thioureas are larger in alcohol solvents than in water,[12] typically by about 4 units. If a similar solvent effect occurs for TU itself, then this brings the pK_a value into the region where a significant amount of protonation would occur at the acidities of our experiments. If an allowance is made for TU protonation then the expression for k_0 is that given in equation (2) where k_1 is the third-order rate constant for the

$$k_0 = k_1K_a[TU]_T[H_2SO_4]/(K_a + [H_2SO_4]) + k_{-1} \quad (2)$$

$$\text{Rate of forward reaction} = k_1[RONO][TU][H_2SO_4] \quad (3)$$

$$\text{Rate of back reaction} = k_{-1}[(NH_2)_2CS^+NO] \quad (4)$$

forward reaction [equation (3)], k_{-1} the first-order rate constant for the reverse reaction [equation (4)], K_a the acid-dissociation constant of $(NH_2)_2CS^+H$, and $[TU]_T$ the total stoicheiometric concentration of TU. We can estimate k_{-1} as 0.08 s^{-1} from a plot of k_0 *vs.* [TU] (data from Table 1). Rearrangement of equation (2) shows that $(k_0 - k_{-1})^{-1}$ should be a linear function of $[H_2SO_4]^{-1}$. The results from Table 3 when treated in this way do indeed give good lines with a positive slope and intercept for both alkyl nitrites, and yield values of 1.12 and 1.38 respectively for the pK_a for $(NH_2)_2CS^+H$, respectively, in the two alcohol solvents. We have used these values to 'correct' the data in Tables 1 and 2 to allow for TU protonation. For TBN at both acidities we obtain good straight lines of different slopes (see Figure 1), but with a common intercept, as predicted. The results yield an average value of 252 dm^6 mol^{-2} s^{-1} for k_1 [equation (3)] and of 0.11 s^{-1} for k_{-1}. Similar results are also obtained from the double reciprocal plot. We can thus deduce a value of 2 290 ± 390 dm^6 mol^{-2} for K_{XNO} (= k_1/k_{-1}) the equilibrium constant for $(NH_2)_2CS^+NO$ formation from TBN in t-butyl alcohol. This appears to be a reasonable value, given that the corresponding value in aqueous solution using nitrous acid is 5 000 dm^6 mol^{-2}.[4]

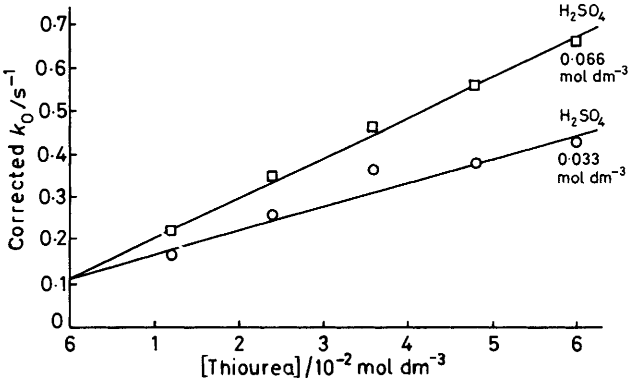


Figure 1. Plot of k_0 *vs* TU corrected for protonation for nitrosation by TBN in t-butyl alcohol.

Similar results were obtained with the reaction of IPN with thiourea in isopropyl alcohol. The kinetic analysis yielded a value 248 dm^6 mol^{-2} s^{-1} for k_1 and 0.13 s^{-1} for k_{-1} and hence a value of 1 910 ± 300 dm^6 mol^{-2} for K_{XNO}. There appears to be very little difference between the kinetic parameters for the two different alkyl nitrite–alcohol systems.

(*b*) *Reactions of Thioglycolic Acid* (*TGA*).—TGA behaved in some ways in a similar fashion to TU in that both alkyl nitrites reacted readily to give a solution of the yellow thionitrite RSNO. Kinetic measurements were carried out as for TU. However, the kinetic dependence on both [TGA] and [H_2SO_4] is now strictly first-order, contrasting with the behaviour of TU. The results for both alkyl nitrites are given in Table 4. Now plots of k_0 *vs.* both [TGA] and [H_2SO_4] are linear showing no curvature and there is no positive intercept at [TGA] = 0 and [H_2SO_4] = 0. A simple explanation is that the reaction is not now significantly reversible and also TGA is not protonated at the sulphur atom to any detectable extent. This parallels the behaviour in aqueous solution using nitrous acid as the reagent. TGA is significantly less reactive than is TU. Analysis of the data in Tables 4 and 5 yields values of k_1 [equation (3) for TGA substrate] of 7.5 ± 0.5 dm^6 mol^{-2} s^{-1} for the reaction with TBN in t-butyl alcohol and of 6.1 ± 0.3 dm^6 mol^{-2} s^{-1} for IPN in isopropyl alcohol.

The rate of reaction of IPN with TGA in isopropyl alcohol is markedly reduced by the addition of small amounts of water as shown in Figure 2. The value of k_0 decreases sharply when very small amounts of water are added, but after *ca.* 5% the effect is very much reduced.

(*c*) *Nucleophilic Catalysis*.—As expected, from the results given in Part 1 with the reaction of amines, nucleophilic

Table 3. Dependence of the rate constant upon acidity for the nitrosation of TU by TBN and by IPN. [RONO] = 1 × 10^{-3} mol dm^{-3}.

TBN[a]		IPN[b]	
$[H_2SO_4]$/mol dm^{-3}	k_0/s^{-1}	$[H_2SO_4]$/mol dm^{-3}	k_0/s^{-1}
0.0264	0.156 ± 0.003	0.0140	0.192 ± 0.017
0.0396	0.186 ± 0.007	0.0234	0.228 ± 0.019
0.0528	0.222 ± 0.015	0.0468	0.274 ± 0.006
0.1056	0.279 ± 0.005	0.0936	0.330 ± 0.005
0.1584	0.305 ± 0.005	0.1404	0.317 ± 0.003
0.2111	0.328 ± 0.005	0.1872	0.330 ± 0.005
0.2639	0.341 ± 0.006	0.2340	0.323 ± 0.012

[a] [TU] = 0.0150 mol dm^{-3}. [b] [TU] = 0.0186 mol dm^{-3}.

Table 4. Values of k_0 for the nitrosation of TGA by TBN and IPN. [RONO] = 2.5 × 10^{-4} mol dm^{-3}.

TBN			IPN[a]	
[TGA]/mol dm^{-3}	$[H_2SO_4]$/mol dm^{-3}	$10^2k_0/s^{-1}$	[TGA]/mol dm^{-3}	$10^2k_0/s^{-1}$
0.010	0.1014	0.80 ± 0.03	0.0143	2.26 ± 0.08
0.020	0.1014	1.53 ± 0.09	0.0199	3.07 ± 0.20
0.030	0.1014	2.09 ± 0.09	0.0257	4.11 ± 0.20
0.040	0.1014	2.83 ± 0.10	0.0314	5.02 ± 0.20
0.050	0.1014	3.67 ± 0.10	0.0371	5.64 ± 0.05
0.060	0.1014	4.34 ± 0.03	0.0428	6.30 ± 0.03
0.020	0.0203	0.34 ± 0.01		
0.020	0.0406	0.64 ± 0.02		
0.020	0.0608	1.00 ± 0.04		
0.020	0.0811	1.36 ± 0.01		
0.020	0.1014	1.53 ± 0.10		
0.020	0.1217	2.01 ± 0.10		

[a] $[H_2SO_4]$ = 0.234 mol dm^{-3}.

Table 5. Effect of added Et_4NCl on the rate constant for nitrosation of TGA by IPN (2.5 × 10^{-4} mol dm^{-3}). [TGA] = 1.44 × 10^{-2} mol dm^{-3}.

$[H_2SO_4]$ = 0.0811 mol dm^{-3}		$[H_2SO_4]$ = 6.6 × 10^{-4} mol dm^{-3}	
$[Et_4NCl]$/mol dm^{-3}	k_0/s^{-1}	$[Et_4NCl]$/mol dm^{-3}	$10^3k_0/s^{-1}$
0	0.0136 ± 0.0001	7.08 × 10^{-3}	5.15 ± 0.01
5.66 × 10^{-3}	0.0633 ± 0.003	9.44 × 10^{-3}	5.13 ± 0.02
1.13 × 10^{-2}	0.100 ± 0.001	1.89 × 10^{-2}	4.64 ± 0.16
1.69 × 10^{-2}	0.132 ± 0.004	2.83 × 10^{-2}	5.10 ± 0.03
2.26 × 10^{-2}	0.155 ± 0.002	4.72 × 10^{-2}	5.31 ± 0.06

Table 6. Catalysis by HCl in the nitrosation of TGA by TBN. [TGA] = 7.23 × 10^{-3} mol dm^{-3}, [TBN] = 5 × 10^{-4} mol dm^{-3}.

10^3[HCl]/mol dm^{-3}	$10^2k_0/s^{-1}$
2.18	1.35
4.35	2.74
8.70	5.23
13.1	7.78

catalysis occurs by added bromide ion, chloride ion and thiourea, in the reaction of TGA with TBN in t-butyl alcohol. Some of the results are shown in Table 5. For Et_4NCl, catalysis occurs when $[Et_4NCl] < [H_2SO_4]$ but not when $[Et_4NCl] > [H_2SO_4]$. When catalysis occurs k_0 is not a linear function of $[Et_4NCl]$; the positive intercept represents the uncatalysed reaction, but there is a marked curvature to the plot. Added Et_4NBr behaved in a similar fashion. There is also a tendency for reactions to lose the strictly first-order dependence upon $[H_2SO_4]$ and [TGA] in the presence of either Et_4NCl or Et_4NBr. Reaction using HCl is also rapid, the plot of k_0 *vs.* [HCl] (data in Table 6) is linear and passes through the origin. The catalytic effect of HCl is over a hundred times greater than that of H_2SO_4. Catalysis of TGA nitrosation by TU is also pronounced (see Table 7), again giving curved plots for k_0 *vs.* [TU]. Similar catalytic effects were observed for the nitrosation of TGA by IPN in isopropyl alcohol.

Discussion

It is clear that alkyl nitrites in alcohol solvents are efficient *S*-nitrosating agents in the absence of nucleophile catalysts. All of the reactions are acid-catalysed and therefore involve, in some way, the protonated forms of the alkyl nitrites. The results are all consistent with a direct rate-limiting transfer of the NO group from $RO^+(H)NO$ to the sulphur atom. Equally the results are consistent with a rapid breakdown of $RO^+(H)NO$ to give the free (solvated) nitrosonium ion which then reacts in a rate-limiting stage. Recently[13] evidence has been presented for the involvement of NO^+ in nitrosation reactions in mildly acidic solutions of alkyl nitrites or nitrous acid in acetonitrile solvent. Therefore, for the most reactive of substrates (including TGA), a

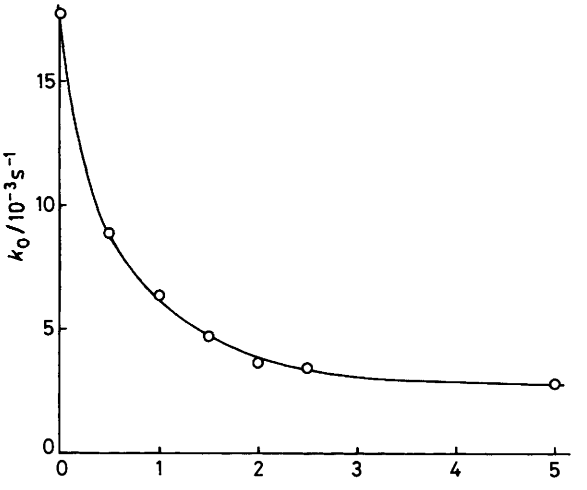


Figure 2. Effect of water on the rate constant for the nitrosation of TGA by IPN in isopropyl alcohol.

Table 7. Catalysis by TU in the nitrosation of TGA by TBN. [TBN] = 2.5×10^{-4} mol dm^{-3}, [H_2SO_4] = 0.066 mol dm^{-3}, [TGA] = 0.0144 mol dm^{-3}.

[TU]/mol dm^{-3}	k_0/s^{-1}
0	$6.4 \times 10^{-3} \pm 2 \times 10^{-4}$
0.0060	$0.0226 \pm 9 \times 10^{-4}$
0.0120	$0.0341 \pm 1.6 \times 10^{-3}$
0.0180	$0.0420 \pm 6 \times 10^{-4}$
0.0240	$0.0495 \pm 7 \times 10^{-4}$
0.0300	$0.0531 \pm 4 \times 10^{-4}$

zero-order kinetic dependence on [substrate] is observed (*cf.* the nitration of reactive aromatics). In the present system, however, there is no hint of a change to a zero-order condition, so there is no direct evidence in favour of NO^+ formation. In this case, with such a nucleophilic solvent (alcohol) the equilibrium [equation (5)] would be displaced very much to the right-hand side. For this reason and since there is no zero-order kinetic evidence we will write the nitrosating agent derived from alkyl nitrites in acid alcohol solvents as the protonated form of the alkyl nitrite.

$$\mathrm{NO^+ + ROH(solvent) \rightleftharpoons RO^+(H)NO \rightleftharpoons RONO} \quad (5)$$

The outline mechanism for the reaction with TU is given in Scheme 1. All of the kinetic results agree quantitatively with such a scheme. The same mechanism applies to the reaction of TGA, except that there is no protonation equilibrium involving TGA, and the second stage is effectively irreversible.

$$\mathrm{RONO + H_2SO_4 \rightleftharpoons RO^+(H)NO\ HSO_4^-}$$

$$\mathrm{RO^+(H)NO\ HSO_4^- + (NH_2)_2CS \rightleftharpoons}$$

$$\begin{tikzcd} \mathrm{(NH_2)_2CS^+NO + ROH + HSO_4^-} \arrow[d, shift right, "\mathrm{H_2SO_4}"'] \\ \mathrm{(NH_2)_2CS^+H\ HSO_4^-} \arrow[u, shift right] \end{tikzcd}$$

Scheme 1.

We have written the protonation of the alkyl nitrite involving undissociated sulphuric acid. Very little ionisation to give the free (solvated) proton occurs in alcohol solvents even from the conventionally (*i.e.* in water) strong acids. The dissociation constants of a number of acids are known[14] to be *ca.* 100 times smaller in t-butyl than in isopropyl alcohol, and yet overall reactivity in t-butyl alcohol is comparable to that in isopropyl alcohol from our results, so it is unlikely that the solvated proton is involved. The kinetic data throughout, analyse well if the 'acidity' is represented by the total stoicheiometric concentration of sulphuric acid. We have also written the protonation equilibria in Scheme 1 in terms of an ion-pair with the bisulphite ion. Ion-pairing is of course more extensive in some non-aqueous solvents than it is in water. In addition, a protonation to give the two separate ions $RO^+(H)NO$ and HSO_4^- should lead to non-first-order kinetic behaviour as [HSO_4^-] builds up during a kinetic run; this is contrary to the observed behaviour.

The collected data are given in Table 8. The main points to emerge are that both alkyl nitrites have comparable reactivity towards both TGA and TU, the reaction with TU is significantly reversible, and TU is more reactive than TGA by a factor of *ca.* 35. Some of these results are similar to those found for the corresponding reaction with nitrous acid in water.[3–5] Since there are no quantitative data for the protonation of alkyl nitrites, it is not possible to disseminate the third-order rate constants k_2 and hence obtain the true reactivity of the protonated alkyl nitrites. The results, however, suggest that in the present systems reaction does not occur close to the encounter limit, since the reactivity difference between TU and TGA is much greater than it is in water, where it is believed that reactions are encounter-controlled.

The solvent effect of a sharp reduction in the rate constant as small amounts of water are added, could, in principle, arise from either an effect on the equilibrium constant for protonation or on the rate constant for reaction by the intermediate, which cannot be separated from our kinetic results. Similar effects have been noted for reactions of alkyl nitrites with alcohols[15] and also for the reaction of a nitrosamine with an alcohol.[16] This has been interpreted[15] in terms of the stronger basicity of water compared with an alcohol, which thus lowers the effective acidity in the more aqueous solution.

Catalytic effects by added nucleophiles in nitrosation are commonly observed and readily interpreted in terms of intermediate formation of the corresponding nitrosyl derivative *e.g.* nitrosyl halide, whih then acts as the nitrosating reagent. It has already been assumed[1,17] that such intermediates also take part in reactions in alcohol solvents, and the present results can also be explained in this way. Normally, in aqueous solution there is a linear dependence of the rate constant on [added nucleophile] *e.g.* Cl^-. However, in alcohol solvents dissociation of halide and other salts is very small,[14] *e.g.* the dissociation constant for Et_4NBr in isopropyl alcohol is 9×10^{-4} mol dm^{-3}, so the free bromide-ion concentration in our experiments is very low indeed. In addition the dissociation constant is *ca.* 100 smaller in t-butyl alcohol than in isopropyl alcohol, so we should see the consequences of this, *i.e.* greater catalysis in isopropyl than in t-butyl alcohol if the free bromide ion is involved. This is not borne out experimentally since the two alkyl nitrite–alcohol systems behave very similarly. The probable equilibria thus involve the undissociated species as outlined for Et_4NBr in equations (6)–(8). It is possible that a

$$\mathrm{Et_4NBr + H_2SO_4 \rightleftharpoons HBr + Et_4N^+HSO_4^-} \quad (6)$$

$$\mathrm{RONO + HBr \rightleftharpoons R^+O(H)NOBr^-} \quad (7)$$

$$\mathrm{RONO + HBr \rightleftharpoons BrNO + ROH} \quad (8)$$

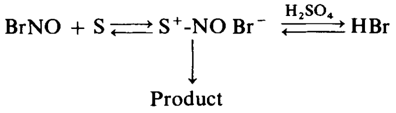
contribution to the catalytic effect arises from the action of HBr

Table 8. Rate and equilibrium constants for nitrosation of TU and TGA by TBN and IPN.

		TU		TGA
	K_{XNO}/mol^2 dm^{-6}	k_1/dm^6 mol^{-2} s^{-1}	k_{-1}/s^{-1}	k_1/dm^6 mol^{-2} s^{-1}
TBN	2 290 ± 390	252 ± 22	0.11 ± 0.02	7.5 ± 0.5
IPN	1 910 ± 300	248 ± 10	0.13 ± 0.01	6.1 ± 0.3

as a general acid [equation (7)], but we feel that the predominant effect must come from the *in situ* production of BrNO.

Previously,[17,18] curved plots have been interpreted in terms of the reversibility of the nitrosation step as outlined in Scheme 2. This can be tested quantitatively since $(k_0)^{-1}$ should be proportional to $[Et_4NBr]^{-1}$. We have obtained good double-reciprocal plots for both halides and also for both alkyl nitrites in reaction with TGA, when allowance is made for the uncatalysed component to k_0.



$$\mathrm{BrNO} + \mathrm{S} \rightleftharpoons \underset{\downarrow\ \text{Product}}{\mathrm{S^+\text{-}NO\,Br^-}} \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} \mathrm{HBr}$$

Scheme 2.

The values of k_1 for reaction of TBN with TGA is over a 100 times larger when HCl is used as the acid catalyst compared with H_2SO_4. It is difficult to see why HCl should be a more powerful acid catalyst to this extent, so it is likely that catalysis arises from equilibrium ClNO formation. The absence of catalysis when $[Et_4NCl] > [H_2SO_4]$ is readily explained by the constant [HCl] developed, which is limited by the $[H_2SO_4]$ and is consequently not affected by increasing the $[Et_4NCl]$.

Acknowledgements

We thank the SERC for a research studentship to M. J. C.

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Received 11*th October* 1988; *Paper* 8/04047H