Kinetics and Mechanism of Thionitrite Formation. Mercapto-carboxylic Acids: A New Range of Efficient Nitrous Acid Scavengers

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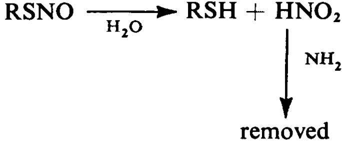
Rate constants have been measured, by stopped-flow spectrophotometry, for the nitrosation of 3-mercaptopropanoic acid (MPA), mercaptosuccinic acid (MSA), and cysteine, in aqueous acid solution at 25 °C. For each substrate the rate equation, rate = $k[HNO_2][H^+][RSH]$, was established with k values, 4 764, 1 334, and 443 $l^2\,mol^{-2}\,s^{-1}$ for MPA, MSA, and cysteine, respectively. Each reaction was catalysed by added nucleophiles (Br^- and SCN^-) and the second-order rate constants k_2 for attack by NOBr and NOSCN were deduced from the variation of the measured rate constants with $[Br^-]$ and $[SCN^-]$. For NOBr, k_2 values were in the region of $1 \times 10^5\ l\,mol^{-1}\,s^{-1}$ and for NOSCN *ca.* $1 \times 10^4\ l\,mol^{-1}\,s^{-1}$. These values are much smaller than those for aniline derivatives (which in some cases approach the diffusion-controlled limit), but since no protonation of the thiol group occurs, the overall reactivity of these mercapto-carboxylic acids generally exceeds that of *e.g.* aniline. All three are significantly more reactive than other conventional ' nitrite traps ' such as hydrazine, hydrazoic acid, sulphamic acid, sulphanilamide, *etc.* This was also established indirectly by a previously established kinetic method based on the denitrosation of a nitrosamine in the presence of ' nitrite traps ' and varying concentrations of the product secondary amine.

S-Nitrosation, although not as widely studied as *N*- and *O*-nitrosation, is now well established for a relatively small number of substrates.[1] Thiourea undergoes *S*-nitrosation particularly at higher acidities where *N*-nitrosation is suppressed by *N*-protonation.[2] The kinetics of thiourea nitrosation have been studied,[3] as have those for the rather complex decomposition of the *S*-nitroso ion first formed.[4] Thionitrites, the products of nitrosation of thiols, are generally rather unstable, although a few have been isolated and characterised:[5] of recent note the thionitrite from *N*-acetylpenicillamine.[6] Comparison with *O*-nitrosation suggests that reaction at sulphur is more rapid (as expected from its greater nucleophilicity), but is virtually irreversible,[7] contrasting markedly with the nitrosation of alcohols. Three independent investigations have demonstrated the rate law [equation (1)]

$$\text{Rate} = k[HNO_2][H^+][RSH] \qquad (1)$$

for the nitrosation of t-butyl thiol,[8] cysteine,[9] and *N*-acetylpenicillamine,[7] suggesting that the well known mechanism involving $H_2NO_2^+$ (or NO^+) is operative here, as for many *N*- and *O*-nitrosation reactions. The virtual irreversibility of thionitrite formation has been explained[7] by the much reduced expected basicity of the sulphur atom in the thionitrite, as compared with the corresponding oxygen atom in alkyl nitrites, since acid-catalysed denitrosation (or hydrolysis) is thought to involve a rapid reversible protonation. Denitrosation of thionitrites can be effected,[10] however, if reaction is carried out at relatively high acid concentration (*ca.* 3M-H_2SO_4), in the presence of a sufficient excess of a ' nitrite trap ' (*e.g.* sulphamic acid or hydrazoic acid) to ensure that the re-nitrosation of the thiol does not occur [see equation (2)].



$$\begin{tikzcd} RSNO \arrow[r, "H^+", "H_2O"'] & RSH + HNO_2 \arrow[d, "NH_2SO_3H"] \\ & \text{removed} \end{tikzcd} \qquad (2)$$

Since thiols appear to have a high reactivity towards nitrous acid and its derivatives (nitrosyl halides, *etc.*) in an effectively irreversible reaction, they might well have some application as efficient nitrite traps, particularly if substrates with a reasonably high solubility in water are chosen. We have selected three mercapto-carboxylic acids and have examined their reactivity quantitatively towards nitrosation, including the effect of bromide and thiocyanate ion catalysts. In addition we have examined two of these thiols as ' nitrite traps ' indirectly in denitrosation experiments.

Experimental

Materials.—The thiols were all commercial samples of the highest purity grade available and were used as such. *N*-Methylaniline was redistilled before use. *N*-Nitrosodiphenylamine and *N*-methyl-*N*-nitrosoaniline were prepared in the usual way from the secondary amines and nitrous acid.[11] The products from the nitrosation of 3-mercaptopropanoic acid (MPA) and mercaptosuccinic acid (MSA) were extracted into ether and the solvent was removed. Each gave a cherry-red liquid product: the one from MSA decomposed very rapidly, giving off brown fumes, and no identification was possible. The product from MPA was sufficiently stable to allow its i.r. spectrum to be measured and the characteristic thionitrite frequencies[5] were found at 1 530 (N=O stretch) and 630 cm^{-1} (S–N stretch).

Kinetics.—All the nitrosation reactions in aqueous solution at 25 °C were followed kinetically in a stopped-flow spectrophotometer by noting the appearance of the thionitrite absorption at *ca.* 330 nm, the absorbance maximum. Typical reaction concentrations were: [RSH] 5×10^{-3}M, $[HNO_2]$ 1×10^{-5}M, $[H^+]$ 4×10^{-2}M. In some reactions the effect of added bromide ion (0—0.5M) and thiocyanate (0—1M) was examined. In all cases the reactions were first-order in $[HNO_2]$ and the rate constant was unchanged on changing $[HNO_2]$. The first-order rate constants were reproducible to within ±3%. Experiments involving the denitrosation of *N*-nitrosodiphenylamine and *N*-methyl-*N*-nitrosoaniline in the presence of ' nitrite traps ' were performed as has been described,[12,13] using conventional u.v. spectrophotometry.

Results and Discussion

For the three thiols studied the typical u.v. absorption, a broad band with a maximum at *ca.* 330 nm, was observed from

Table 1. Rate constants for the nitrosation of 3-mercaptopropanoic acid (MPA)

[MPA]/M	[H$^+$]/M	[Br$^-$]/M	k_0/s^{-1}
1.0×10^{-3}	2.06×10^{-2}	0	0.093
5.0×10^{-3}	2.06×10^{-2}	0	0.480
1.0×10^{-2}	2.06×10^{-2}	0	0.959
5.0×10^{-3}	1.02×10^{-2}	0	0.258
5.0×10^{-3}	3.30×10^{-2}	0	0.777
5.0×10^{-3}	4.12×10^{-2}	0	1.015
5.0×10^{-3}	2.06×10^{-2}	0.10	0.743
5.0×10^{-3}	2.06×10^{-2}	0.25	1.112
5.0×10^{-3}	2.06×10^{-2}	0.50	1.674

[HNO_2] 1×10^{-5}M.

Table 2. Rate constants for the nitrosation of mercaptosuccinic acid (MSA)

[MSA]/M	[H$^+$]/M	[Br$^-$]/M	k_0/s^{-1}
1.0×10^{-3}	2.06×10^{-2}	0	0.032
5.0×10^{-3}	2.06×10^{-2}	0	0.145
1.0×10^{-2}	2.06×10^{-2}	0	0.308
1.0×10^{-3}	2.06×10^{-2}	0	0.030 *
5.0×10^{-3}	8.24×10^{-3}	0	0.067
5.0×10^{-3}	1.24×10^{-2}	0	0.105
5.0×10^{-3}	4.12×10^{-2}	0	0.271
5.0×10^{-3}	2.06×10^{-2}	0.25	0.171
5.0×10^{-3}	2.06×10^{-2}	0.40	0.197
5.0×10^{-3}	2.06×10^{-2}	0.50	0.215

[HNO_2] 1×10^{-5}M except * (1×10^{-4}M).

Table 3. Rate constants for the nitrosation of cysteine

[cysteine]/M	[H$^+$]/M	[Br$^-$]/M	k_0/s^{-1}
1.0×10^{-2}	1.24×10^{-2}	0	0.098
1.0×10^{-2}	4.12×10^{-2}	0	0.205
1.0×10^{-2}	6.18×10^{-2}	0	0.320
1.0×10^{-2}	2.06×10^{-2}	0	0.135
1.0×10^{-2}	2.06×10^{-2}	0.10	0.151
1.0×10^{-2}	2.06×10^{-2}	0.25	0.163
1.0×10^{-2}	2.06×10^{-2}	0.50	0.200

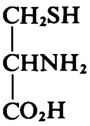
[HNO_2] 1×10^{-5}M.

Table 4. Values of k [equation (1)] at 25 °C for some nitrite traps

Substrate	k/l^2 mol^{-2} s^{-1}
$CO(NH_2)_2$ *	*ca.* 0.8
$^+NH_3OH$ *	*ca.* 4
HN_3 *	123
$NH_2NH_3^+$ †	611
MSA	1 334
MPA	4 764

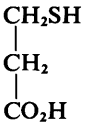
* T. A. Meyer, M. E. O'Neill, and D. L. H. Williams, in preparation. † J. R. Perrott, G. Stedman, and N. Uysal, *J. Chem. Soc., Dalton Trans.*, 1976, 2058.

the reaction solutions when reaction was complete. In the case of MPA and MSA the products were isolated as cherry-red



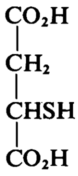
$CH_2SH-CHNH_2-CO_2H$

cysteine



$CH_2SH-CH_2-CO_2H$

3-mercapto-propanoic acid (MPA)



$CO_2H-CH_2-CHSH-CO_2H$

mercaptosuccinic acid (MSA)

liquids, and for the MPA product i.r. frequencies characteristic of thionitrites were observed. The rather unstable thionitrite from cysteine (and that from its *N*-acetyl derivative) has been isolated by earlier workers.[14] Under the conditions used for the kinetic study all reactions gave the familiar yellow colouration now associated with *S*-nitroso compounds.[2,3,5,9]

The kinetic experiments showed that all reactions studied were first-order in nitrous acid (with [RSH] $\gg$ [HNO_2]) and first-order in [RSH], and were acid catalysed. The detailed experimental results for all three substrates are given in Tables 1—3. The rate law is clearly that shown in equation (1), which is the familiar equation observed for the acid-catalysed nitrosations of a number of substrates such as amines [15] and alcohols.[7] The small positive intercept to the plot of k_0 (the observed first-order rate constant defined by $-d[HNO_2]/dt = k_0[HNO_2]$) against [H$^+$] is attributed to the contribution to the acidity of the medium by each of the acid substrates. Again, as for many other nitrosation and diazotisation reactions, these reactions were catalysed by added bromide ion and thiocyanate ion (although the extent of catalysis was not very marked). All the results are consistent with mechanisms involving rate-limiting attack by the nitrous acidium ion $H_2NO_2^+$ (or NO^+), in the absence of added Br^- or SCN^-, and by NOBr and NOSCN in the presence of the added anions.

Values of k [equation (1)] were obtained from the variation of k_0 with both [RSH] at constant acidity and [H$^+$] at constant [RSH]; good agreement was observed. For MPA, k values were 4 670 and 4 857 l^2 mol^{-2} s^{-1}, for MSA 1 460 and 1 208 l^2 mol^{-2} s^{-1} and for cysteine 448 and 438 l^2 mol^{-2} s^{-1}. These last results are in excellent agreement with an earlier reported value [9] of 456 l^2 mol^{-2} s^{-1}. It is to be expected that MPA is the most reactive of these substrates because of the position of the electron withdrawing carboxy group; the reduced reactivity of cysteine is probably due to electrostatic repulsion since at these acidities cysteine exists substantially as $CH_2SHCH(\overset{+}{N}H_3)CO_2H$. Comparison with k values of other more conventional and much used nitrite traps or scavengers (Table 4) shows that MSA and (particularly) MPA are significantly more reactive over this acidity range than are both the hydrazinium ion and hydrazoic acid, both of which are regarded as very efficient scavengers. Urea and hydroxylamine are several orders of magnitude less effective. Sulphamic acid, another widely used nitrite trap, has a different rate law over a large acid range because of the protonation equilibria involved, but in the acid range 0—0.1M [H$^+$] its reactivity is roughly similar to that of the hydrazinium ion. Some nitrosation reactions are believed to be so rapid as to approach the rate of diffusion control.[16] For a mechanism involving reaction *via* $H_2NO_2^+$, k[from equation (1)] necessarily includes the unknown equilibrium constant for nitrous acid protonation, so that it is not possible to extract the second-order rate constant. Arguments in favour of diffusion-controlled reactions are then based on the relatively small range of reactivity (as given by k values) for a range of substrates of widely differing structure. Thiourea and its alkyl-substituted derivatives have k values in the region 6 000 l^2 mol^{-2} s^{-1}, and this is thought to be close to the diffusion limit. The value for MPA is quite close to this and suggests that we are indeed close to the diffusion-controlled limit here.

Since the equilibrium constants for NOBr [17] and NOSCN [18] formation are known to be 5.1×10^{-2} and 32 l^2 mol^{-2} respectively, it is possible to evaluate the second-order rate con-

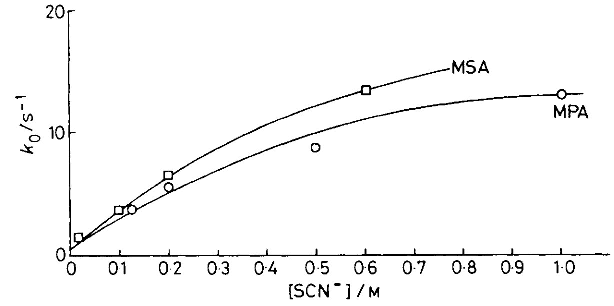
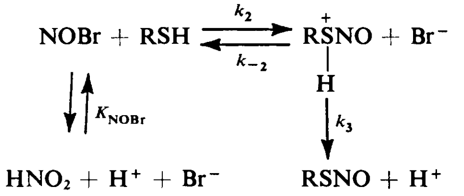


Figure 1. Thiocyanate ion catalysis in the nitrosation of MPA and MSA. Reaction conditions: $[\mathrm{H^+}]$ 0.023M; [RSH] 5.0×10^{-3}M

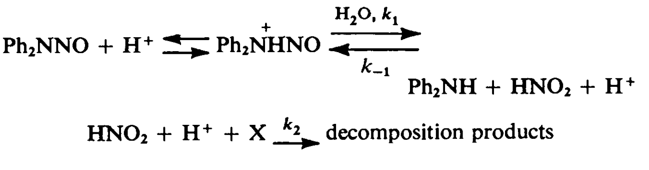
stants for the attack of NOBr and of NOSCN. The expected mechanism is outlined in equation (3). If k_{-2} is negligible compared with k_3 and if there is no substantial conversion of $\mathrm{HNO_2}$ to NOBr, then k_0 is given by equation (4), so that k_2 can readily be obtained from the variation of k_0 with $[\mathrm{Br^-}]$. The results for MPA, MSA, and cysteine are respectively 4.5×10^5, 2.6×10^4, and 1.2×10^4 l $\mathrm{mol^{-1}}$ $\mathrm{s^{-1}}$ for NOBr attack. Whilst these are quite large values they do not approach the diffusion limit shown *e.g.* by aniline [19] (k_2 1.7×10^9 l $\mathrm{mol^{-1}}$ $\mathrm{s^{-1}}$) and some aniline derivatives. However since many amines are largely protonated in acid solution, and reaction *via* NOBr occurs by reaction of the free base form, the overall reactivity of *e.g.* MPA towards nitrous acid containing bromide ion, is greater than that of aniline except at very low acidities where significant concentrations of the free amine would be present. These results confirm an existing pattern that $\mathrm{H_2NO_2^+}$ (or $\mathrm{NO^+}$) is more reactive than is NOBr; bromide ion catalysis arises because of the greater concentration of NOBr than of $\mathrm{H_2NO_2^+}$ in acid solutions of nitrous acid.


(3)

$$\begin{tikzcd} \mathrm{NOBr} + \mathrm{RSH} \arrow[r, shift left, "k_2"] \arrow[d, shift left] & \mathrm{R}\underset{\mathrm{H}}{\overset{+}{\mathrm{S}}}\mathrm{NO} + \mathrm{Br^-} \arrow[l, shift left, "k_{-2}"] \arrow[d, "k_3"] \\ \mathrm{HNO_2} + \mathrm{H^+} + \mathrm{Br^-} \arrow[u, shift left, "K_{\mathrm{NOBr}}"'] & \mathrm{RSNO} + \mathrm{H^+} \end{tikzcd} \qquad (3)$$

$$k_0 = k_2 K_{\mathrm{NOBr}}[\mathrm{H^+}][\mathrm{Br^-}][\mathrm{RSH}] \qquad (4)$$

The situation involving thiocyanate catalysis is not so straightforward. Catalysis does occur as is shown in Figure 1, but for both MPA and MSA the plots are distinctly curved. Three possibilities could account for this behaviour: (*a*) at these high $[\mathrm{SCN^-}]$ values the effective acidity of the medium is reduced by the formation of significant quantities of thiocyanic acid, (*b*) also at these high $[\mathrm{SCN^-}]$ values a significant fraction of the total nitrous acid is ' tied up ' as NOSCN, and (*c*) the reversibility of *S*-nitrosation is important *i.e.* k_{-2} $[\mathrm{SCN^-}]$ and k_3 are similar [equation (3)]. In principle it should be possible to decide whether (*a*) is important from a consideration of the $\mathrm{p}K_\mathrm{a}$ value of HSCN. However a plethora of values exists in the literature, varying from 0.97 (ref. 20) to −1.84 (ref. 21). If we assume the lowest value, then the reduction in the effective acidity in our experiments is negligible even with these quite high $[\mathrm{SCN^-}]$ values, but if the largest value is taken, then indeed the effect of the addition of 1M-KSCN does produce a substantial reduction in the acidity. Explanation (*b*) can easily be tested since K_{NOSCN} is known. At 2.0×10^{-2}M $[\mathrm{H^+}]$ and 1M-$\mathrm{SCN^-}$, total nitrite 1×10^{-4}M, a significant fraction (*ca.* 0.3) of the nitrous acid is converted into NOSCN, which accounts for the curvature of the plots in Figure 1. A further experiment was carried out to investigate possibility (*c*). The solvent isotope effect $k(\mathrm{D_2O}) : k(\mathrm{H_2O})$ was measured as 1.1 : 1 for MSA and 1.2 : 1 for MPA, for nitrosation in the presence of 1M-$\mathrm{SCN^-}$. This argues against a rate-limiting proton transfer (k_3).



$$\mathrm{Ph_2NNO} + \mathrm{H^+} \rightleftharpoons \mathrm{Ph_2\overset{+}{N}HNO} \underset{k_{-1}}{\overset{\mathrm{H_2O},\,k_1}{\rightleftharpoons}} \mathrm{Ph_2NH} + \mathrm{HNO_2} + \mathrm{H^+}$$

$$\mathrm{HNO_2} + \mathrm{H^+} + \mathrm{X} \xrightarrow{k_2} \text{decomposition products}$$

Scheme

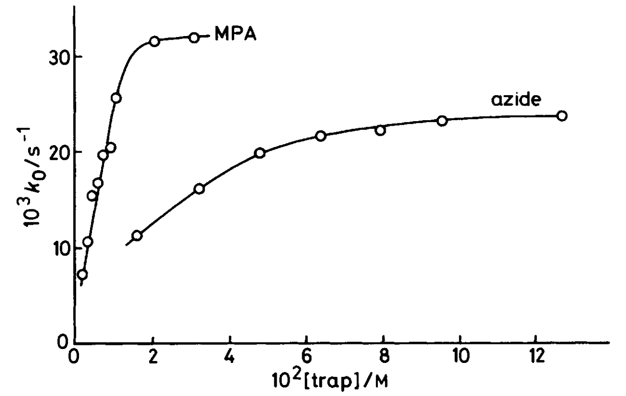


Figure 2. Plot of k_0 *vs.* [X] for the denitrosation of $\mathrm{Ph_2NNO}$ for X = MPA and $\mathrm{HN_3}$

Because of the uncertainty over the $\mathrm{p}K_\mathrm{a}$ value of HSCN it is not possible to explain with certainty and quantitatively the curvature of k_0 *vs.* $[\mathrm{SCN^-}]$ plots. However, reasonable estimates of k_2 for NOSCN attack can be obtained from the limiting slope at $[\mathrm{SCN^-}] = 0$. This leads to values of k_2 of 1.0×10^4 and 0.9×10^4 l $\mathrm{mol^{-1}}$ $\mathrm{s^{-1}}$ for MSA and MPA, respectively. It is not clear why the order of reactivity is reversed here, although the experimental error is quite high in this case, but the order of magnitude approach shows that, as expected, NOSCN is less reactive than NOBr as reflected by the k_2 values. This sequence seems to be quite general for nitrosation, having been established for the reactions of hydroxylamine,[22] morpholine,[23] aniline,[23] alcohols,[7] and now thiols.

With the high reactivity of these mercapto-carboxylic acids towards nitrosation established, it is of interest to examine their potential as nitrous acid scavengers. We have carried out the denitrosation of *N*-nitrosodiphenylamine (see Scheme) in the presence of varying concentrations of MPA and compared the results with those of earlier studies [13] using sodium azide on the scavenger X. When $k_2[\mathrm{X}] \gg k_{-1}[\mathrm{Ph_2NH}]$ applies, the reaction becomes zero-order in X and k_0 approaches a limiting value. The results are shown in Figure 2. Both plots show the tendency to a limiting value of k_0 as [X] is increased. The limit is slightly different in the two cases because the acidity is slightly higher for the MPA reaction. It is noteworthy that the limiting situation is achieved sooner for MPA, showing that k_2 is greater, as expected from the results of the direct measurements.

Similarly a quantitative measure of the relative reactivities of traps X can be made indirectly,[24] using the reaction outlined in the Scheme in general for the denitrosation of $\mathrm{R^1R^2}$-NNO, by noting the variation of k_0 with $[\mathrm{R^1R^2NH}]$ added, at constant $[\mathrm{H^+}]$ and constant excess of [X]. The relative reac-

Table 5. Rate constants for the denitrosation of *N*-methyl-*N*-nitrosoaniline (NMNA) in the presence of MSA and added *N*-methylaniline (NMA)

10^3[MSA]/M	10^2[NMA]/M	$10^4k_0/s^{-1}$
0.238		11.9
0.475		12.9
1.190		12.9
1.190	0.529	10.9
1.190	0.794	10.1
1.190	1.320	8.2

[H_2SO_4] 1.95M; [NMNA] 1 × 10^{-4}M; [NaBr] 0.1M.

Table 6. Values of k_2/k_{-1} as a function of acidity (obtained from the denitrosation of NMNA in the presence of MSA and added NMA)

[H_2SO_4]/M	k_2/k_{-1}
1.05	5.3
1.95	19.4
3.27	133

tivities of a range of X species have been deduced by the kinetic analysis from the reciprocal form of the general rate equations expected from the Scheme. This method has now been applied to MSA for R^1 = Ph, R^2 = Me in 1.95M-H_2SO_4 containing 0.1M-NaBr. As expected, k_0 is reduced by the addition of *N*-methylaniline (NMA) (see Table 5), and a plot of k_0^{-1} *vs.* [NMA] is linear (as expected from the general form of the rate equation deduced from the Scheme); thence k_2/k_{-1} can be evaluated from the slope and intercept. The value of 20 was obtained, to be compared with values [12] of 16 for HN_3, 6.4 for $NH_2NH_3^+$, 0.73 for NH_2SO_3H, and 4.9 × 10^{-2} for $^+NH_3OH$, all measured under the same conditions, again indicating the importance of MSA (and other thiols) as efficient nitrous acid scavengers.

It must be stressed that k_2/k_{-1} values obtained in this indirect way are dependent on the acidity of the reaction medium and also in some cases on the concentration of Br^- or any other nucleophile. This is because k_2 and k_{-1} are not single rate constants but include [H^+] and also [Br^-] if the initial nitrosation ($NOBr + X \longrightarrow {}^+X\text{-}NO + Br^-$) is significantly reversible. This has been discussed fully elsewhere; [12] the theory predicts that k_2/k_{-1} should increase with acidity for a situation involving a basic secondary amine R^1R^2NH and a non-basic species X such as the thiols used in this work. As expected, this is the case, as shown by the results in Table 6. It is difficult therefore to extrapolate the relative reactivities of various species X from one acidity to another, and it is not possible to predict *e.g.* that MPA is *always* a more efficient scavenger than HN_3 at all acidities, since the acid dependence of each reaction is not necessarily the same, particularly in high acid concentration. Indeed results of the indirect method for k_2/k_{-1} determination for MPA and HN_3 at 4.8M-H_2SO_4 show that at this relatively high acidity k_2/k_{-1} is 106 for MPA and 526 for HN_3, showing the reversal of the reactivity order at much lower acid concentrations.

The conclusion, however, is clear, that these mercaptocarboxylic acids (and no doubt other thiols) are very reactive towards nitrous acid and its derivatives in acid solution, and have potential use as nitrite traps, when it is necessary to remove free nitrous acid rapidly and irreversibly.

Acknowledgements

We thank the S.E.R.C. for a research studentship (to L. R. D.).

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Received 27*th April* 1983; *Paper* 3/662