A Kinetic Study of Anion Effects in the Deamination of Dodecylamine Micelles

By **Robert J. Hill** and **Geoffrey Stedman,*** University College of Swansea, Singleton Park, Swansea SA2 8PP

The thiocyanate ion catalysed deamination of dodecylamine by nitrous acid proceeds much faster when the protonated amine exists in the form of micelles than when it is a monomer. The reaction is inhibited by added chloride, bromide, nitrate, perchlorate, and tetrafluoroborate ions. At high concentrations of thiocyanate ion the rate levels off and becomes zero order. The results fit a simple Langmuir expression, with competition of the various anions for a limited number of sites at or close to the micelle surface. Relative binding constants for the various anions have been deduced.

THE deamination of long chain aliphatic amines by nitrous acid at concentrations above the critical micelle concentrations (c.m.c.) is a system of considerable interest. Such deaminations are commonly catalysed by nucleophilic anions, *via* the corresponding nitrosyl compounds[1] [equations (1)—(4)]. The conversion of the

$$RNH_3^+ \rightleftharpoons RNH_2 + H^+ \quad \text{fast } K_a \qquad (1)$$

$$H^+ + HNO_2 + X^- \rightleftharpoons ON{\cdot}X + H_2O \quad \text{fast } K_{NOX} \qquad (2)$$

$$ON{\cdot}X + RNH_2 \longrightarrow RNH{\cdot}NO + H^+ + X^- \quad \text{slow } k_a \qquad (3)$$

$$RNH{\cdot}NO \longrightarrow ROH + N_2 \quad \text{fast} \qquad (4)$$

nitrosamine to the final deamination products actually occurs in a number of stages, all of which are relatively fast. If one works at an acidity where the amine exists as the conjugate acid, and the nitrite as molecular nitrous acid the rate law may be written as (5) where $k_3 = k_aK_aK_{NOX}$.

$$-d[HNO_2]/dt = k_3[RNH_3^+][HNO_2][X^-] \qquad (5)$$

The effect of micellar additives has been investigated by Moss and Talkowski,[2] who found that for the deamination of 2-amino-octane by dinitrogen trioxide ($X = NO_2$) at pH 4, the addition of trimethyl-(1-methylheptyl)-ammonium ions produced an acceleration of 6—16 times in the rate of reaction. A somewhat different study by Hutchinson and Stedman[3] examined the deamination of a series of long chain *O*-alkylhydroxylamines (X = Cl, Br, or NCS), in which the surface active agent was the substrate, and not an additive. It was shown that there was a sharp increase in reactivity at the c.m.c., the rate law retaining the same overall form but the rate constant increasing by about an order of magnitude. It was suggested that this was due to the binding of the catalytic anions at the surface of the cationic micelle, bringing them in close proximity to the substrate amino-groups. Other explanations are possible, and the present work

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[1] J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.

[2] R. A. Moss and C. J. Talkowski, *Tetrahedron Letters*, 1971, 703.

[3] J. M. Hutchinson and G. Stedman, *J.C.S. Perkin II*, 1973, 93.

was intended to examine the competitive effect of a range of anions on the reactivity.

RESULTS

We have been concerned with a single substrate, dodecylamine, and most of the work has been done using low concentrations of nitrous acid, 10^{-3}M, at pH 2. Our preliminary experiments were made at 25°, and we ran into difficulties because we were too close to the Krafft point.[4] To avoid this we worked at 30°, although it was necessary to run blanks to allow for nitrous acid decomposition. The catalytic efficiency of an anion in deamination depends upon the equilibrium concentration of the nitrosyl compound, and its reactivity. The reactivity of nitrosyl chloride, bromide, and thiocyanate towards the alkylhydroxylamines is high, and the values of k_a (mol^{-1} dm^3 s^{-1}) vary very much less than the values [5] of $K_{\rm NOX}$ (mol^{-2} dm^6): $10^7k_a = 1{\cdot}6$ (Cl), 1·8 (Br), and 0·13 (SCN); $10^3K_{\rm NOX} = 0{\cdot}55$ (Cl), 22·5 (Br), and 46,000 (SCN). The relative catalytic efficiency is thus controlled largely by the value of $K_{\rm NOX}$ which determines the concentration of the nitrosyl compound; thus under our conditions the thiocyanate ion is the only effective catalytic species, although nitrosyl thiocyanate is intrinsically less reactive than either nitrosyl chloride or bromide. At our low concentrations of nitrous acid there was no detectable reaction by the dinitrogen trioxide mechanism ($X = NO_2$).

The kinetics were studied by following the disappearance of nitrous acid using standard colorimetric techniques. Reaction only occurred in the presence of the thiocyanate catalyst. In the presence of a large excess of amine good first-order plots were observed over 2—3 half-lives; when comparable concentrations of nitrous acid and amine were used the integrated second-order rate equation was accurately obeyed. As reaction proceeded the deamination product, dodecyl alcohol, separated out as a yellow oil. However, we did not observe this to have any effect on the kinetics. When the concentration of dodecylamine was varied it was found that the second-order rate constant $k_2 = v/[RNH_3^+][HNO_2]$ showed a sharp increase at an amine concentration close to the c.m.c. (as determined by surface tension measurements) levelling off to a constant value at higher concentrations. Thus the plot of k_2 against $[RNH_3^+]$ shows the typical sigmoid shape observed for *O*-alkylhydroxylamines, with the micelle being much more reactive than the monomeric dodecylamine.

Measurements made at amine concentrations above the c.m.c. showed that k_2 was virtually independent of $[H^+]$. These studies were made at constant anion concentration and ionic strength with varying proportions of hydronium and lithium ions. The results in Table 1 show that on increasing $[H^+]$ the value of k_2 appears to pass through a maximum. This is a small effect but we have observed it several times and believe it to be real. At the moment we have no satisfactory explanation. Other experiments showed that increasing $[SCN^-]$ caused an increase in k_2 at low concentrations but that at higher values k_2 levelled off, showing a 'saturation' effect. These results are also in Table 1.

TABLE 1

Rate constants for the thiocyanate catalysed reaction at 30°

$[H^+]$/M [a]	0·02	0·06	0·10	0·15	0·20	0·25
k_2/mol^{-1} dm^3 s^{-1}	1·67	1·90	1·80	1·85	1·75	1·63
$[SCN^-]$/M [b]	0·05	0·10	0·20	0·30	0·40	0·50
k_2/mol^{-1} dm^3 s^{-1}	0·65	0·77	1·48	1·55	1·56	1·50

$[C_{12}H_{25}NH_3^+] = 2 \times 10^{-3}$M; $[HNO_2] = 10^{-3}$M

[a] $[SCN^-] = [H^+] + [Li^+] = 0{\cdot}25$M. [b] $[H^+] = 0{\cdot}01$M.

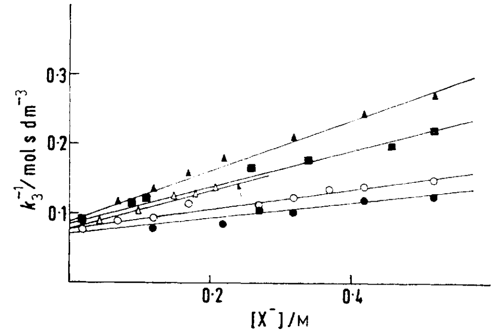
The effect of a range of other added anions, chloride, bromide, tetrafluoroborate, nitrate, and perchlorate, on the rate of the thiocyanate catalysed reaction was investigated and they were all found to act as inhibitors. This is in striking contrast to the situation in the diazotisation of monomeric amines where the first two of these ions normally act as catalysts, while the last two show no effect (apart from medium effects). The fact that a saturation effect was observed with thiocyanate ion, and that all other anions tried acted as inhibitors led us to try and fit the results to a simple Langmuir type equation (6). Writing $k_2 = k_3[SCN^-]$ this

$$k_2 = \frac{kK_{\rm SCN}[SCN^-]}{1 + K_{\rm SCN}[SCN^-] + K_{\rm X}[X^-]} \qquad (6)$$

can be re-arranged to the form (7). Plots of $1/k_3$ against

$$\frac{1}{k_3} = \frac{(1 + K_{\rm SCN}[SCN^-])}{K_{\rm SCN}k} + \frac{K_{\rm X}[X^-]}{K_{\rm SCN}k} \qquad (7)$$

$[X^-]$ give satisfactory straight lines as shown in the Figure. As a further check on equation (7) we have carried out two series of experiments at different constant thiocyanate concentrations of 0·05 and 0·20M. It can readily be shown for such experiments that if the intercepts are I' and I'' corresponding to sodium thiocyanate concentrations of $[SCN^-]'$ and $[SCN^-]''$ then $k = ([SCN^-]' - [SCN^-]'')/(I' - I'')$. Values of k obtained in this way are in the last column of Table 2, and are satisfactorily constant, giving a mean value of 1·75. Experiments in which thiocyanate was the only anion present gave a good plot of $1/k_3$ against $[SCN^-]$, and from the slope and the mean value of k a value for $K_{\rm SCN}$ was found. From the slope of plots $1/k_3$ against $[X^-]$ values of $K_{\rm X}/K_{\rm SCN}$ were found, thus yielding values of $K_{\rm X}$. The results are given in Table 2.



Plots of $1/k_3$ against X^-: NaX = ▲, $NaNO_3$; ■, $NaClO_4$; △, $NaBF_4$; ○, NaBr; ●, NaCl

In the above series of measurements all the concentrations were kept constant except that of the added inhibitor Na^+X^-. It was not therefore possible to maintain the ionic strength constant, and as our concentrations went up to *ca.* 0·5M the values of $K_{\rm X}$ may contain a contribution due to differing ionic strength effects. The mean ion activity coefficients for 0·5M solutions [6] do not vary drastically, NaNCS, 0·715; NaCl, 0·681; NaBr, 0·697; $NaClO_4$, 0·668;

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[4] A. W. Ralston and C. W. Hoerr, *J. Amer. Chem. Soc.*, 1946, **68**, 851.

[5] M. N. Hughes, T. D. B. Morgan, and G. Stedman, *J. Chem. Soc.* (*B*), 1968, 344.

[6] R. H. Stokes and R. A. Robinson, 'Electrolyte Solutions,' Butterworths, London, 1959, p. 491.

$NaNO_3$, 0·617. We do not think this is an important factor. A more serious factor may be changes in the properties of the micelle surface as the nature of the counterion changes, and we are currently looking at this point. We have also examined the fit of equation (6) to results at a constant formal ionic strength of 0·4M, *i.e.* [NaNCS] + [NaX] = 0·4M. Table 3 shows a comparison of observed values of the slope and intercept of a plot of $1/k_3$ *vs* [SCN^-] with values predicted from the data in Table 2. The internal consistency of our data seems to be quite satisfactory.

TABLE 2

Binding constants for anions at a dodecylammoniumion micelle at 30°

	K_X/ mol^{-1} dm^3 [a]	K_X/ mol^{-1} dm^3 [b]	K_X (mean)/ mol^{-1} dm^3	k_3/ mol^{-1} dm^3 s^{-1}
SCN^-			9·4	1·97
ClO_4^-	4·2	4·6	4·4	1·85
Br^-	2·25	1·75	2·0	1·5
NO_3^-	6·3	6·1	6·2	1·88
BF_4^-	5·1	4·1	4·6	1·85
Cl^-	1·6	2·0	1·8	1·56

[a] [SCN^-] = 0·05M. [b] [SCN^-] = 0·2M.

TABLE 3

Results obtained at constant formal ionic strength

	Slope		Intercept	
	Predicted	Observed	Predicted	Observed
$NaClO_4$	0·302	0·317	0·168	0·167
NaBr	0·450	0·473	0·109	0·096
$NaNO_3$	0·194	0·224	0·210	0·189
NaCl	0·449	0·426	0·105	0·[illegible]9

One disadvantage of the use of dodecylamine as a substrate is that it is scarcely possible to observe catalysis by bromide and chloride ions. Catalysis by these ions can be observed with *O*-alkylhydroxylamines. The pK_a of the *O*-methylhydroxylammonium ion is 4·7 compared with 10·6 for the methylammonium ion; clearly the concentration of the reactive free base is much greater in the former case. Similar experiments with n-$C_{12}H_{25}ONH_3^+$ gave satisfatory plots of $1/k_3$ *vs.* [X^-] and yielded binding constants at 2·1 (Br) and 2·7 (Cl), and *k* values of 155 (Br) and 16·5 (Cl).

In addition to the kinetic measurements of the effects of various anions on the rates of deamination, we have also briefly investigated the effect of the same anions on the c.m.c., under similar conditions. For 0·2M solutions of the sodium salt at 30° the c.m.c. values for the dodecylammonium ion were $1·6 \times 10^{-3}$ (Cl), $1·25 \times 10^{-3}$ (Br), $7·0 \times 10^{-3}$ (ClO_4), $5·3 \times 10^{-4}$ (BF_4), $4·3 \times 10^{-4}$ (NO_3), and $3·3 \times 10^{-4}$ (SCN). A plot of log c.m.c. against log K_X has a slope of −1·06. We have also measured the variation of c.m.c. as a function of the concentration of added salt for the two extreme members of our series, chloride and thiocyanate. The results fit the equations log c.m.c. = −0·55 log [NaCl] − 3·195 and log c.m.c. = −0·65 log [NaNCS] − 3·95 at 30°, over the range 0·05—0·2M.

DISCUSSION

The most striking features of the results are the facts that all the added anions investigated produced a marked inhibition in rate of the thiocyanate catalysed reaction, and that there is a ' saturation effect ' observed at high concentrations of thiocyanate ion. This latter effect cannot be due to a change in the molecular form of the nitrite species in the bulk of the solution. The value of K_{NOX} is known and even under the most extreme conditions only some 15% of the nitrous acid is converted to nitrosyl thiocyanate in the bulk of the solution; for the other nitrosyl halides the proportions are much smaller. It could be argued that such an effect was operative in the vicinity of the micelle surface, where the local concentrations of anions are higher than the bulk values for the solution. However, the fact that the saturation effect is also observed for chloride and bromide in the deamination of $C_{12}H_{25}ONH_3^+$ argued against this interpretation, for the values of K_{NOCl} and K_{NOBr} are very much less than K_{NONCS}.

As the substrate amino-group must surely be located at the surface of the micelle we may expect the reaction rate to be governed (among other factors) by the local concentration of thiocyanate ions. For many micellar systems it is known that some 70—90% of the charge on the micelle is neutralized by counterions in the Stern and Chapman–Gouy layers. In the presence of excess salts this percentage will increase, and tend towards 100%. The thickness of the Chapman–Gouy layer will also decrease drastically, and the counter-ions will all be found very close to the micelle surface. This provides a simple interpretation of the saturation effect observed at high thiocyanate ion concentration. On this picture, the inhibition by other anions is due to their competing for sites at or close to the micelle surface, and excluding the catalytically active thiocyanate ion from the vicinity of the micelle surface. If one supposes there to be a limited number of such sites, equal to the number of positive charges on the micelle, then the simplest treatment would lead to a Langmuir type of equation, and this does indeed describe our data.

An alternative explanation is that only anions in the Stern layer are catalytically active, and that there is only a limited number of these sites. This would also be consistent with our results. However, as the ' thickness ' of the Chapman–Gouy layer is calculated [7] to be *ca.* 1 nm at 0·1M ionic strength, and will be less at higher ionic strengths, we think it likely that these ions too are catalytically active. It seems unlikely that all the sites in the Stern and Chapman–Gouy layers are equivalent, and it is surprising that the simple Langmuir expression works as well as it does. We suspect that there is a cancellation of errors. It is also likely that our data are not good enough to detect variations from the simple expression.

The sequence of binding constants $SCN^- > NO_3^- > BF_4^- > ClO_4^- > Br^- > Cl^-$ is very close to the order that these ions appear in the lyotropic series.[7] The relative positions of neighbouring ions do vary with the method used to determine the sequence so a 1 : 1 correspondence cannot be expected. Iodide, which normally is close to the head of the series, cannot be studied in our system because of the reaction with nitrous acid that liberates iodine. The figures for chloride and bromide with $C_{12}H_{25}ONH_3^+$ micelles are similar to the data for

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[7] D. J. Shaw, ' Introduction to Colloid and Surface Chemistry,' Butterworths, London, 1968, p. 122.

dodecylammonium ion micelles. The sequence of binding constants is also identical with the order in which these anions depress the c.m.c. values. In fact a plot of log c.m.c. against log K_X had unit slope within experimental error. The most strongly bound anion produces a micelle at the lowest amine concentration. We note in passing that the k value for bromide is greater than for chloride by an order of magnitude, reflecting the usual relative catalytic efficiency of these ions in nitrosation.

Our previous work on the deamination of *O*-alkylhydroxylamines was carried out in media of formal ionic strength 0·3M, with perchlorate as the 'inert' anion. When we studied thiocyanate catalysis our thiocyanate concentrations were $<10^{-3}$M, so we were examining micelles with perchlorate as the counter-ion, and only a small proportion of thiocyanate ions. For the less reactive bromide ion we had to use greater concentrations, but these are still $<10^{-1}$M. For this concentration we would expect, on the basis of the figures in Table 1, *ca.* 10% of the anions associated with the micelle to be bromide ions. Thus in each case the fraction of sites occupied by the catalytic ion Y^- was relatively small, and hence one was in the low concentration region of the Langmuir isotherm where the fraction of sites occupied by Y^- is proportional to the concentration of Y^-, giving a simple first-order dependence of rate upon the bulk concentration of Y^-. When one is dealing with a single type of anion in solution, as in the thiocyanate catalysed reaction in the absence of added NaX described in this paper, a different situation arises. Micelles formed from ionic species M^+X^- commonly have a large degree of association and thus even at the lowest concentrations of X^- it is likely that a large fraction (θ_X) of the sites (say 70% at least), will be occupied. We shall thus be outside the low concentration region of the Langmuir isotherm for which $\theta_X \propto [X^-]$ and be approaching the saturation region for which θ_X tends to 1 for which $K_X[X^-] \gg 1$. For dodecylammonium chloride a figure of 88% is quoted.[8] As we believe the rate depends on the fraction of sites occupied by the catalytic anion this means that we do not expect to be able to observe a simple first-order dependence of rate upon the bulk concentration of catalyst. We were very fortunate to avoid this pitfall in our preliminary studies with *O*-alkylhydroxylamines.

In an attempt to check on the self-consistency of our ideas we have studied deamination in mixtures of two catalytically active anions, and attempted to predict the rate from constants determined for catalysis by each anion alone. We have studied n-$C_{12}H_{25}ONH_3^+$ and i-$C_{11}H_{23}ONH_3^+$ in mixtures of sodium chloride and sodium bromide of total ionic strength 0·2M. The predicted value of the rate constant k_2' was calculated from the expression (8). A comparison of calculated (k_2') and observed (k_2) values is given in Table 4. The agreement is satisfactory, although the similarity of chloride and bromide makes this a less sensitive test than we would like. A better combination would have been chloride and thiocyanate, being at opposite ends of our series of anions. However under conditions where chloride catalysis is measurable the thiocyanate catalysed reaction is too fast to measure; where the thiocyanate catalysed reaction is conveniently measurable we could not detect catalysis by chloride or bromide. We were thus forced to use chloride and bromide for our experiment. The alkylhydroxylamines were used rather than the alkylamines because of the very low reactivity of the latter towards chloride and bromide catalysed deamination.

$$k_2 = \frac{-\mathrm{d}[\mathrm{HNO_2}]/\mathrm{d}t}{[\mathrm{RONH_3^+}][\mathrm{HNO_2}]} = \frac{k_{\mathrm{Br}}K_{\mathrm{Br}}[\mathrm{Br^-}] + k_{\mathrm{Cl}}K_{\mathrm{Cl}}[\mathrm{Cl^-}]}{1 + K_{\mathrm{Br}}[\mathrm{Br^-}] + K_{\mathrm{Cl}}[\mathrm{Cl^-}]} \qquad (8)$$

TABLE 4

$C_{12}H_{25}ONH_3^+$

k_{Br} 155 k_{Cl} 16·5

K_{Br} 2·05 K_{Cl} 2·71

$[Br^-]$/M	$[Cl^-]$/M	k_2'/mol^{-1} dm^3 s^{-1}	k_2/mol^{-1} dm^3 s^{-1}
0·200	0·000	45	42·6
0·175	0·025	40	41·0
0·150	0·050	35	36·0
0·125	0·075	30	28·2
0·100	0·100	25	21·7
0·075	0·125	20	18·6
0·050	0·150	15	12·7
0·025	0·175	10	8·5
0·000	0·200	5·8	4·9

$C_{11}H_{23}ONH_3^+$

k_{Br} 16·8 k_{Br} 12·0

K_{Cl} 2·42 K_{Cl} 2·34

$(Br^-]$/M	$[Cl^-]$/M	k_2'/mol^{-1} dm^3 s^{-1}	k_2/mol^{-1} dm^3 s^{-1}
0·200	0·000	55	54·0
0·150	0·050	42	37·4
0·100	0·100	29	27·4
0·050	0·150	16	15·4
0·025	0·175	11	7·7
0·000	0·200	3·8	4·2

In Moss and Talkowski's study [2] the reaction conditions were 1·48M-sodium nitrite, brought to pH 4 by acidification with perchloric acid. This should correspond to *ca.* 1·2M-nitrite ion, and *ca.* 0·3M-perchlorate ion. Nitrite might be expected to come between bromide and perchlorate in the binding constant series, so one might have expected that at these high nitrite ion concentrations a saturation effect would be displayed. However, Moss and Talkowski report that they observed third-order kinetics, second order in nitrite and first order in amine. Under these conditions there is bound to be a substantial loss of nitrous acid by self-decomposition and they report deviations from third-order kinetics after 20—35% reaction which they attribute to this cause. Further kinetic evidence is clearly desirable.

In our runs with comparable concentrations of amine and nitrous acid, we observed good second-order kinetics over several half-lives. Thus the reactivity of the micelle seems to remain the same, although most of the dodecylammonium ion has been converted to dodecyl alcohol.

When a dodecyl alcohol molecule is formed it does not stay and form a mixed micelle, but is lost to the bulk of the solution (we often observe it to separate as a yellow

[8] E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, 1970, **8**, 271.

oil). Thus as reaction proceeds the type of micelle does not change, there are merely fewer of them.

Our work has been concerned with the micelle itself as a reactant. A more common type of investigation involves the addition of a surface-active agent to a reacting system. The effect of added salts has been studied in a number of these systems, *e.g.* the alkaline hydrolysis of 2,4-dinitrofluorobenzene,[9] the alkaline hydrolysis of *p*-nitrophenyl hexanoate,[10] and the acid catalysed hydrolysis of methyl orthobenzoate.[11] The first two of these are inhibited by anions, and the last by cations. If the data reported in the literature are examined, they are found to fit a simple Langmuir type equation and yields the results in Table 5.

Bunton and his co-workers have also observed systems that fit a simple Langmuir plot. Despite the fact that it is almost certainly an over-simplification, the method seems to work well.

TABLE 5

Alkaline hydrolysis of 2,4-dinitrofluorobenzene

	$NaNO_3$	NaBr	NaCl	KCl	LiCl
K_X/kK_{OH}	14·2	5·8	3·5	5·2	4·2

Alkaline hydrolysis of *p*-nitrophenyl hexanoate

	$NaNO_3$	NaBr	NaCl	NaF
K_X/kK_{OH}	260	200	72	13

Acid hydrolysis of methyl orthobenzoate

	CsCl	NH_4Cl	NaCl	$NaClO_4$	KCl	RbCl	LiQ
K_X/kK_H	47	14·5	13	12·5	11	10	10

There is a great deal of current interest in the formation of nitrosamines in foodstuffs. If reactions in micellar systems represent a simple chemical model for enzymes, then it may be that simple short-chain amines are not good models for predicting the rate of nitrosation in biological systems.

[3/1455 *Received*, 11*th July*, 1973]

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[9] C. A. Bunton and L. Robinson, *J. Org. Chem.*, 1969, **34**, 780.

[10] E. H. Cordes and L. R. Romsted, *J. Amer. Chem. Soc.*, 1968, **90**, 4404.

[11] E. H. Cordes and R. B. Dunlap, *J. Amer. Chem. Soc.*, 1968, **90**, 4395.