Cyclisation and decarboxylation in zwitterionic micelles: effects of head group structure

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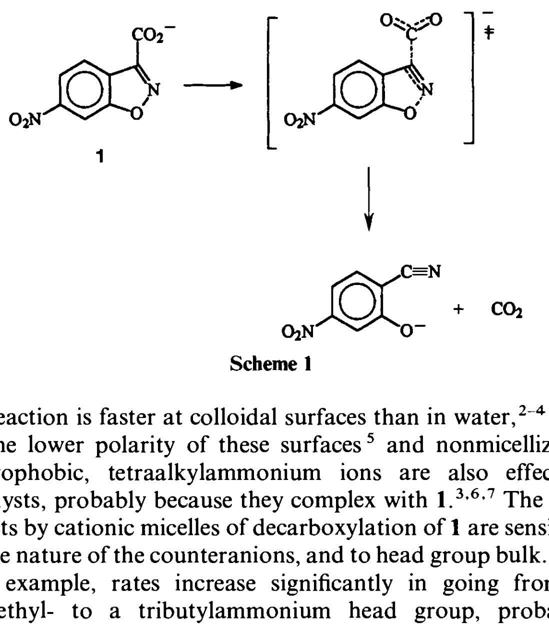
The spontaneous decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion is strongly catalysed by micelles of zwitterionic surfactants, *viz.*, sulfobetaines [$C_{14}H_{29}N^+R_2(CH_2)_3SO_3^-$, R = Me, Pr and $C_{16}H_{33}N^+Me_2(CH_2)_3SO_3^-$] and amine oxides ($C_{14}H_{29}N^+R_2O^-$, R = Me, Pr), with rates enhanced by factors of up to 1800. These micelles and those of the corresponding carboxybetaines are more effective catalysts than those of the corresponding cationic surfactants. In all cases a change from Me to Pr at the head group speeds reaction by factors of *ca.* 5–8 for the sulfobetaines and amine oxides and *ca.* 14 for the cationic surfactants. Cyclizations of the *o*-3-halopropyloxyphenoxide ions (halogen = Br, I), which are intramolecular S_N2 reactions, are modestly micellar catalysed, but structural effects on the micellar catalysis by cationic and betaine surfactants are in the same sequence, as for decarboxylation.

Introduction

The rate of decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion **1** increases sharply with decreasing solvent polarity and water content due to dispersion of charge in going from a carboxylate ion in the initial state to the charge-delocalised transition state (Scheme 1).[1]



Scheme 1

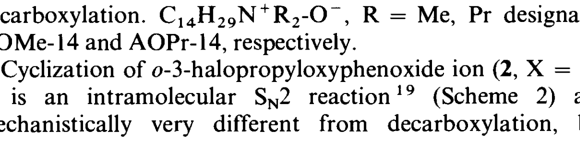
Reaction is faster at colloidal surfaces than in water,[2–4] due to the lower polarity of these surfaces[5] and nonmicellizing, hydrophobic, tetraalkylammonium ions are also effective catalysts, probably because they complex with **1**.[3,6,7] The rate effects by cationic micelles of decarboxylation of **1** are sensitive to the nature of the counteranions, and to head group bulk.[2,7,8] For example, rates increase significantly in going from a trimethyl- to a tributylammonium head group, probably because water is partially excluded from the micellar surface. However, zwitterionic are catalytically more effective than similar cationic micelles,[7,9] so charge effects are also important.

The sensitivity of rates of decarboxylation to medium effects makes this an attractive system for studying the kinetic roles of solvents and interfaces.[1–4] A multi-parameter solvation free energy relationship has been used to identify factors that control medium effects. Grate *et al.* concluded that pairing with hydrogen bonding donors strongly inhibited the reaction.[10] This conclusion was consistent with existing evidence, in particular on the ability of quaternary ammonium ions to reduce inhibition of decarboxylation of **1** by protonated amines in dichloromethane.[11] However, Ferris and Drago show that the kinetic solvent effects can be explained equally well in terms of a simpler donor–acceptor scale.[12]

A solvation free energy relationship has recently been applied to solubilisation by ionic and nonionic micelles.[13,14] Micellar solubilisation sites were shown to be less effective as hydrogen bond donors than bulk water. This generalisation probably also applies to zwitterionic micelles, although, so far as we know, the relationship has not been applied to them.

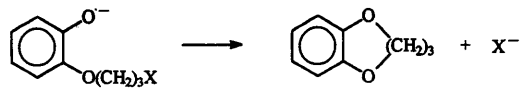
We make the generalisation that for reaction in water **1** interacts with a hydrophobic ammonium ion or micelle and the decrease of local water content or polarity in that region speeds reaction, but micelles of betaine surfactants are more effective than those of trialkylammonium surfactants,[7,9] even though the carboxylate group should be strongly hydrated.

The betaine surfactants studied to date are:[9] $C_nH_{2n+1}N^+Me_2CH_2CO_2^-$, n = 12, 14, 16 designated as CB1-12, CB1-14 and CB1-16, respectively and we planned to compare their behaviour with that of the sulfobetaines: $RN^+Me_2(CH_2)_3SO_3^-$, R = $C_{14}H_{29}$, $C_{16}H_{33}$, SB3-14 and SB3-16 respectively; and $C_{14}H_{29}N^+Pr_2(CH_2)_3SO_3^-$, SBPr3-14. Sulfobetaine surfactants catalyse the spontaneous hydrolysis of 2,4-dinitrophenylphosphate dianion,[15] which is similar to decarboxylation of **1** in its sensitivity to solvent and to normal and reverse micelles.[1,15–17]



Amine oxide surfactants form micelles which are formally neutral,[18] except at low pH, but the head group is zwitterionic and we examined the effect of head group bulk on catalysis of decarboxylation. $C_{14}H_{29}N^+R_2$-O^-, R = Me, Pr designated AOMe-14 and AOPr-14, respectively.

Cyclization of *o*-3-halopropyloxyphenoxide ion (**2**, X = Br, I) is an intramolecular S_N2 reaction[19] (Scheme 2) and mechanistically very different from decarboxylation, but medium effects are qualitatively similar. For example, micellar rate enhancements are smaller than for decarboxylation of **1**,



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2a, X = Br; 2b, X = I

Scheme 2

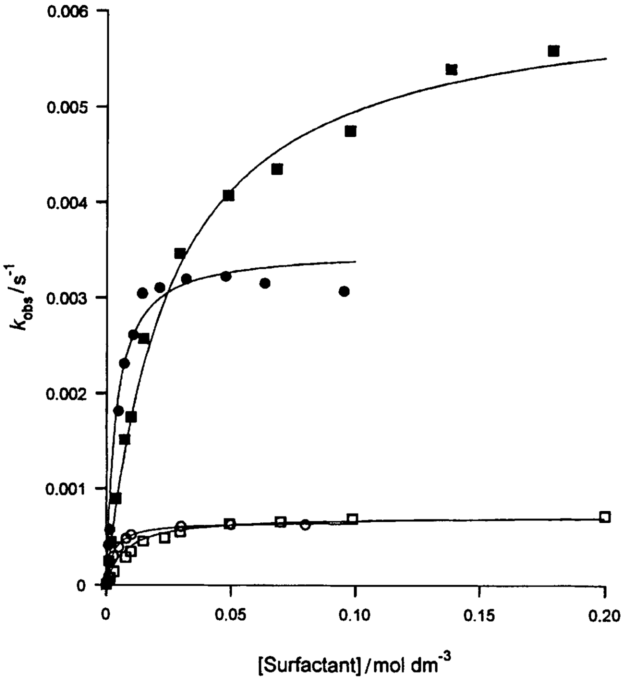

Fig. 1 Decarboxylation of **1** in sulfobetaine and amine oxide and cationic surfactants. □ = AOMe-14; ■ = AOPr-14; ○ = SB3-14; ● = SBPr3-14. Lines are theoretical.

but increase with increasing head group bulk.[20] However for a variety of cationic surfactants there are linear relations between activation free energies of decarboxylation and cyclization at micellar surfaces.[21]

We therefore also examined cyclisation of **2** in aqueous sulfobetaine surfactants. We did not examine the effect of amine oxides on this reaction because they might react nucleophilically.

We compare the behaviour of micellized zwitterionic with that of cationic surfactants,[7] the cetyltrialkylammonium bromides ($C_{16}H_{33}NR_3Br$, R = Me, Pr, CTABr, CTPABr, respectively). Our aim was to use decarboxylation and cyclisation rates as indicators of the way in which changes in surfactant head groups control properties of micelle–water interfaces. Comparison of decarboxylation with cyclisation provides evidence on the way in which head groups can affect rates of S_N2 reactions without complications due to transfer equilibria of reactants between water and micelles.[22]

Results

First-order rate constants, k_{obs}, of decarboxylation typically increase with increasing concentration of cationic or zwitterionic surfactant and reach constant values, k'_M when all the substrate is micellar incorporated.[2,22] We see this pattern of behaviour for reactions in solutions of both sulfobetaine and carboxybetaine surfactants (Fig. 1 and refs. 7, 9). These limiting values, k'_M, are reached in moderately dilute surfactant, *ca.* 0.04 mol dm^{-3}. Cationic micelles bind **1** and also **2** quantitatively at much lower concentrations[2,3,20] because of the coulombic attraction of the ammonium centre for anions.

Micellar effects upon spontaneous reactions can be treated quantitatively in terms of an equilibrium distribution of substrate, (S), between water and micelles which are treated as distinct reaction regions (Scheme 3).[5c,22,23] In this pseudophase model K_S is an association constant with respect to micellised surfactant (detergent) Dn, and k'_W and k'_M are first-order rate constants in aqueous and micellar pseudophases respectively which gives:

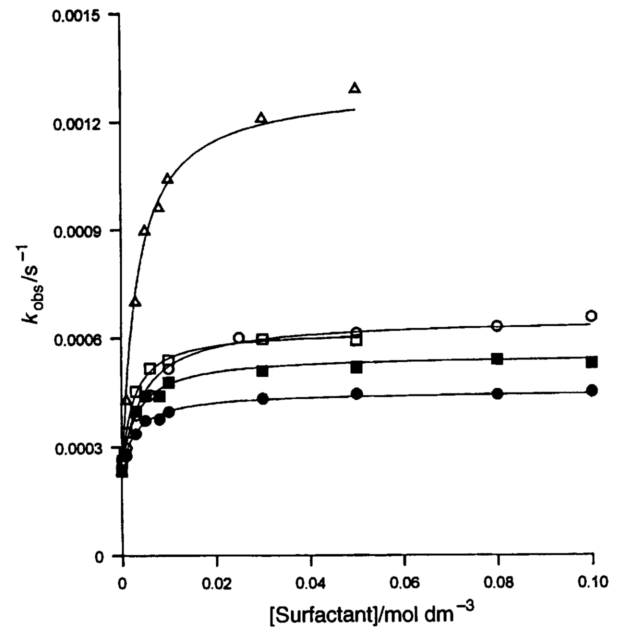

Fig. 2 Cyclisation of **2a** in carboxy- and sulfo-betaine micelles. □ = SB3-16; ■ = SB3-14; ○ = CB1-16; ● = CB1-14; △ = SBPr3-14. Lines are theoretical.

$$\begin{tikzcd}
S_W + Dn \arrow[r, shift left, "K_S"] \arrow[d, "k'_W"'] & SDn \arrow[l, shift left] \arrow[d, "k'_M"] \\
\text{products} & \arrow[l]
\end{tikzcd}$$

Scheme 3

$$k_{obs} = \frac{k'_W + k'_M K_S[Dn]}{1 + K_S[Dn]} \qquad (1)$$

The concentration of micellised surfactant is the total concentration less that of monomeric surfactant, which is often taken as the critical micelle concentration, cmc.[18] Eqn. (1) was derived for reactions of very dilute nonionic substrates and is only qualitatively applicable with ionic or very hydrophobic nonionic substrates which may interact with monomeric or premicellar surfactant, and in these cases eqn. (1) breaks down with [surfactant] ≈ cmc.[7,20c,22] These complications do not affect estimation of k'_M for reaction of micellar-bound substrate.

Rate–surfactant profiles for decarboxylation of **1** fit the pseudophase model for reactions in solutions of cationic and betaine micelles and of micellised AOMe-14 (Fig. 1 and refs. 2,7). However, AOPr-14 behaves differently from other surfactants in that k_{obs} does not increase very sharply in dilute surfactant nor become constant at higher [surfactant] (Fig. 1). We could not use higher concentrations than 0.18 mol dm^{-3} because solutions become very viscous.

The cyclisation of **2** is not strongly catalysed by either cationic or zwitterionic surfactants which have small head groups[20] (Figs. 2 and 3). This result is understandable because micelles do not markedly increase rate constants of bimolecular nucleophilic displacements in micellar pseudophases,[22] rather they increase overall rates of reaction by concentrating both

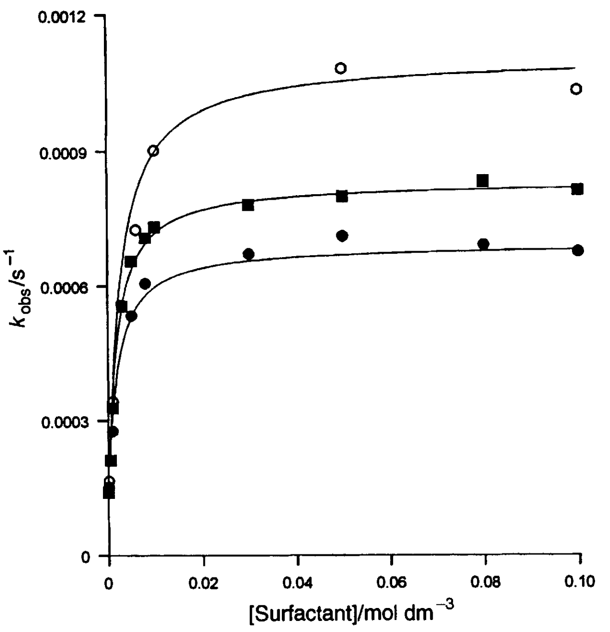

Fig. 3 Cyclisation of **2b** in carboxy- and sulfo-betaine micelles. Symbols as in Fig. 2. Lines are theoretical.

Table 1 First-order rate constants of decarboxylation at surfaces of cationic and zwitterionic micelles[a]

Surfactant	$k'_M/10^{-4}$ s^{-1}
CTABr[b]	3.0 (10^2)
CTPABr[c]	41 (1400)
CB1-14[d]	11 (370)
CB1-16[d]	12 (400)
SB3-14	6.6 (220)
SB3-16	9.2 (307)
SBPr3-14	32 (1100)
AOMe-14	7.1 (240)
AOPr-14	> 55 (1800)

[a] At 25.0 °C, values in parentheses are relative to $k'_W = 3 \times 10^{-6}$ s^{-1} in water. [b] Ref. 2. [c] Ref. 8 [d] Ref. 9.

Table 2 First-order rate constants of cyclisations at surfaces of cationic and zwitterionic micelles[a]

	$k'_M/10^{-4}$ s^{-1}	
Surfactant	X = Br	X = I
DTABr[b]	3.0 (1.3)	3.8 (2.7)
CTABr[c]	4.1 (1.8)	5.5 (3.3)
CTPABr[c]	13.0 (5.6)	26.3 (18.8)
CB1-14	4.6 (2.0)	7.3 (5.2)
CB1-16	6.5 (2.8)	11.0 (7.9)
SB3-14	5.5 (2.4)	8.4 (6.0)
SB3-16	6.2 (2.7)	
SBPr3-14	13.0 (5.6)	

[a] At 25.0 °C, values in parentheses are relative to water, k'_W = 2.33 and 1.40×10^{-4} s^{-1} for reactions of **2a** and **2b**, respectively. [b] Ref. 20*b*. [c] Ref. 20*a*.

Table 3 Binding constants to zwitterionic micelles[a]

	Substrate		
Surfactant	**2**; X = Br	**2**; X = I	**1**
SB3-14	300	450	350
SB3-16	350		400
SBPr3-14	400		
CB1-14	250	350	300
CB1-16	300	400	350

[a] Values of K_S dm^3 mol^{-1}, calculated from rate constants at 25.0 °C.

reactants at the micelle–water interface and for S_N2 reactions second-order rate constants in this region are generally similar to, or lower than those in water. Consistently values of k_{obs} for cyclisations of **2** in solutions of CTABr are not much higher than those in water.[20] However, an increase in head group bulk speeds cyclisation, especially for the iodo derivative, regardless of the charge on the head group (ref. 20*a* and Table 2). Replacement of a trimethylamino by a betaine headgroup gives small rate increases as does an increase in the length of the long tail alkyl group (Table 2).

The rate-surfactant profiles can be fitted to eqn. (1) with the values of K_S given in Table 3 and values of k'_M given in Tables 1 and 2. Binding is larger for the iodo (**2b**) than for the bromo (**2a**) derivative and increases modestly with increasing length of the surfactant alkyl group. Despite the charge on the substrates values of K_S (Table 3) are similar to those found for micellar binding of moderately hydrophobic molecules.[7,19] Cationic are much more effective than zwitterionic micelles in binding the anionic substrates, based on rate-surfactant profiles (Figs. 2 and 3 and refs. 2, 7 and 20) but it is difficult to extract realistic values of K_S because of large coulombic interactions and substrate binding to monomeric and premicellised surfactant. There is strong kinetic evidence that premicellar assemblies of quaternary ammonium salts increase rates of decarboxylation of **1** and formation of large rings from haloalkyloxyphenoxide ions.[3,6,7,20c]

Discussion

Polarities of micelle–water interfaces are lower than that of bulk water, based on spectral data,[5] and ionic hydration also appears to be slightly lower.[22,23] Consistently spontaneous reactions whose rates increase with a decrease in solvent polarity, *e.g.* decarboxylations and dianionic dephosphorylations, are faster at micellar surfaces than in water and spontaneous S_N reactions are generally slower.[22,24] Bulky head groups in cationic micelles should make the surface less polar and water-like.

Replacement of a cationic by a zwitterionic head group does not inhibit spontaneous decarboxylation,[7,9] and dephosphorylation[15] at micellar surfaces although under some conditions it may slow the overall reaction by decreasing micellar incorporation of the anionic substrates.[22] A carboxylate ion, *e.g.* **1**, will interact unfavourably with sulfonate or carboxylate centres in a betaine micelle and the interaction will decrease as charge moves out of the carboxylate ion in the transition state (Scheme 1). The situation is similar for spontaneous dephosphorylations[15] and for reactions in micellised amine oxides.

The high reaction rate in solutions of AOPr-14 (Fig. 1) may be due to a combination of two effects, a decrease in local polarity due to replacement of methyl groups in AOMe-14 by propyl groups, and unfavourable charge–dipole interactions in the initial state. However, viscosity increases markedly with increasing [AOPr-14] which indicates that extended structures, rather than spherical or spheroidal micelles, form under these conditions. Such structures should behave like sub-microscopic solvent-like regions and exclusion of water from these regions would markedly speed decarboxylation. We note that rates of decarboxylation of **1** in micellised CTABr increase on addition of sodium tosylate which gives very high viscosity probably due to formation of extended structures.[2,7]

Micellar catalysis of decarboxylation in solutions of cationic surfactants is increased by an increase in bulk of the head group (Table 1) and for *N*-methyl surfactants by a change from cations to zwitterions. The situation is more complicated when the two effects are combined, for example, a change from CTABr to SB3-14 or SB3-16 increases k'_M by factors of *ca.* 2–3, but $k'_M = 32 \times 10^{-4}$ s^{-1} for reaction of **1** in SBPr3-14 and is 41×10^{-4} s^{-1} for reaction in CTPABr (Table 1). Therefore, with bulky head groups cationic are more effective catalysts than otherwise similar sulfobetaines. It appears that the presence of the large propyl groups assists the reaction by making the micellar surface less polar but the effect is more evident in cationic than in sulfobetaine micelles. This generalisation does not apply to decarboxylation in amine oxides (Table 1).

Rates of cyclisation of **2** at micellar surfaces are not very sensitive to changes in head group structures (Table 2 and ref. 20). In these intramolecular S_N2 reactions charge is transferred from aryl oxide ion in the initial state to an incipient halide ion in the transition state.[19] Head group interactions with the halide ion are important and micellar rate enhancements are consistently larger with the iodo than with the bromo substrate (ref. 20*a* and Table 2), but in these reactions the bulk of the head group seems to be more important than its charge.

The in-line conformation of the transition state of cyclisation is very different from that of decarboxylation where charge moves from a carboxylate moiety into a heterocyclic group.[1] Despite these mechanistic differences plots of log k'_M for cyclisation *vs.* log k'_M for decarboxylation are linear for a number of cationic surfactants, with slopes of 0.46 and 0.64 for the bromide and iodide substrates, respectively.[21] The new rate data for reactions in the zwitterionic micelles (Tables 1 and 2) fit reasonably well in the original plots. This result fits the widely used pseudophase model of rate effects in association colloids in which the surface of the colloid, *e.g.* of a micelle, is regarded as a sub-microscopic reaction region distinct from bulk solvent, and the generalisations that relate rate effects to solvent polarity[25] seem to be applicable, at least qualitatively, to micellar-mediated reactions, with allowance for the asymmetric charge distributions at surfaces of ionic and zwitterionic micelles.[22c,26]

Cyclisation (and S_N2 reactions with anionic nucleophiles) are less sensitive than decarboxylation to solvent effects,[1,10,19] and also to changes in structures of micellar interfaces.[15,16] Hydration of carboxylate and aryl oxide groups inhibits both reactions, but hydration of the incipient halide ion in the transition state partially offsets this effect, especially for the bromide, **2a**, with a consequent difference in the slopes of free energy plots of k'_M for reactions of **2a**,**b** as compared with decarboxylation of **1**. Based on recent evidence[13,14] these generalisations should apply to rate effects of both solvents[1,19] and submicroscopic interfaces.[3,4,21]

Experimental

Materials

The preparation and purification of the substrates and surfactants has been described.[1,9,15,19,20] Solutions were made up in redistilled, deionised water. The critical micelle concentrations of the surfactants in water are:[27] DTABr = 1.4×10^{-2} mol dm^{-3}; CTABr = 8.3×10^{-4} mol dm^{-3}; CTPABr = 5.5×10^{-4} mol dm^{-3}; CBl-14 = 1.5×10^{-4} mol dm^{-3}; CBl-16 = 2.2×10^{-5} mol dm^{-3}; SB3-14 = 2.8×10^{-4} mol dm^{-3}; SB3-16 = 3.5×10^{-5} mol dm^{-3}; SBPr3-14 = 1.8×10^{-4} mol dm^{-3}; AOMe-14 = 1.4×10^{-4} mol dm^{-3}; AOPr-14 = 5.4×10^{-5} mol dm^{-3}.

Kinetics

Decarboxylation was followed spectrophotometrically at 410 nm, with freshly prepared solutions of 6-nitrobenzisoxazole-3-carboxylic acid, 10^{-4} and 10^{-3} mol dm^{-3} NaOH, at 25.0 °C. Cyclisations were followed spectrophotometrically at 290 nm. Substrate was added as the phenol in EtOH or MeCN so that the final solution contained 0.1 vol% organic solvent and 10^{-4} mol dm^{-3} substrate and generally 10^{-3} or 10^{-2} mol dm^{-3} NaOH. Added NaOH has little effect on the rates of these reactions, for example in 0.05 mol dm^{-3} SB3-14 a change of [NaOH] from 10^{-3} to 0.5 mol dm^{-3} increases k_{obs} of decarboxylation of **1** by *ca.* 5% and similar small effects were seen for cyclisation.

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