Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate Ion in Surfactant Self Assemblies

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Decarboxylation of the 6-nitrobenzisoxazole-3-carboxylate ion is speeded more by small assemblies of didodecyl(dimethyl)ammonium chloride (DDDACl) than by fully formed assemblies or by normal cationic micelles. The first-order rate constants, $k'_{\rm M}$, of reaction of fully micelle-bound substrate increase with decreasing surface charge density of normal cationic micelles with a change from hydrophilic to less hydrophilic counter-ions, *e.g.*, in going from CTAOH to CTAOTos (CTA = $C_{16}H_{33}NMe_3$ and Tos = toluene-*p*-sulphonate), or from cationic to zwitterionic micelles. These changes are ascribed to changes in transfer free energies of the initial-state carboxylate ion and the charge-delocalized transition state so that small assemblies of cationic amphiphiles, *e.g.*, of DDDA or $(C_8H_{17})_3N^+R$, are better catalysts than cationic micelles because of less initial-state stabilization. A similar explanation can be applied to catalysis of decarboxylation by synthetic cationic vesicles.

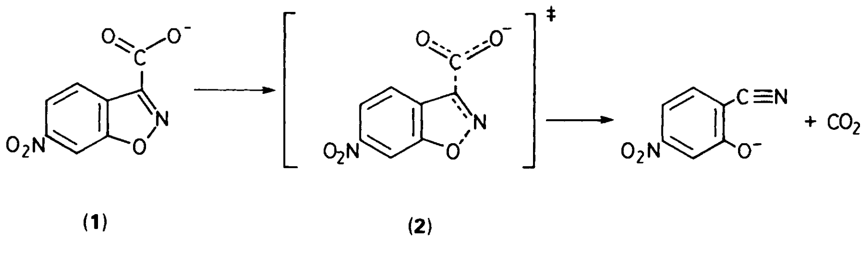
The rates of many chemical reactions are affected by colloidal self assemblies.[1,2] Aqueous micelles are the most widely studied systems, but synthetic vesicles and assemblies of hydrophobic quaternary ammonium ions can also change reaction rates. These rate effects, and changes in position of equilibrium, are generally explained in terms of a pseudophase model in which reactants are partitioned between water and the colloidal pseudophase. The overall rate is the sum of rates in each pseudophase and for many reactions rate constant surfactant profiles can be fitted to relatively simple distribution models based on the concentration of micellized surfactant, *i.e.*, the total concentration less that of monomeric surfactant.[1,2] An alternative model, based on transition-state theory does not require consideration of reactant distribution between water and micelles.[3]

The critical micelle concentration, cmc, is generally assumed to be the concentration of monomeric surfactant, so that there should be no rate effect at surfactant concentrations below the cmc. There are, however, many examples of rate effects at surfactant concentration below the cmc,[1,4] but their interpretation is uncertain. For example, electrolytes and hydrophobic solutes decrease the cmc, so reactant-induced micellization could explain the rate increase. It is difficult to distinguish between this situation and that in which the reactants interact with monomeric surfactant or submicelles because reaction rates generally increase monotonically with surfactant concentration even at concentrations below the cmc.

Rate constants of many bimolecular reactions go through maxima with increasing surfactant concentration and these maxima can be treated quantitatively in terms of the distribution of both reactants between water and micelles. However, with some nucleophilic aromatic substitutions there are rate extrema in very dilute cationic surfactant (1–4 mmol dm^{-3}) which may be due to the interaction of the reactants with monomeric or submicellar surfactant.[5] Nucleophilic aromatic substitution is mechanistically complex,[6] and we chose a simpler reaction for study. Rates of anionic decarboxylations increase sharply with a decrease in medium polarity.[7] Decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion (**1**) is well studied.[7a,8–10], and first-order rate constants in micelles increase with increasing substrate binding and become constant when substrate is fully bound.

Micellar surfaces are less polar than water[1,11] and, like apolar solvents, they stabilize the charge-delocalized transition state (**2**) relative to (**1**). It is easy to analyse quantitatively the effects of micelles, or similar colloids, upon rates of spontaneous reactions. Only monotonic rate increases have been observed with increase in concentrations of surfactant or hydrophobic ammonium ion,[1,2b] and we re-examined decarboxylation of (**1**) in dilute single-chain surfactants and in a twin-tailed surfactant.

The single chain surfactants were cetyltrimethyl ammonium hydroxide, chloride, toluene-*p*-sulphonate and sulphate, CTAOH, CTACl, CTAOTos, and $CTA(SO_4)_{0.5}$, *N*-*N*-dimethyl-



(**1**) (**2**)

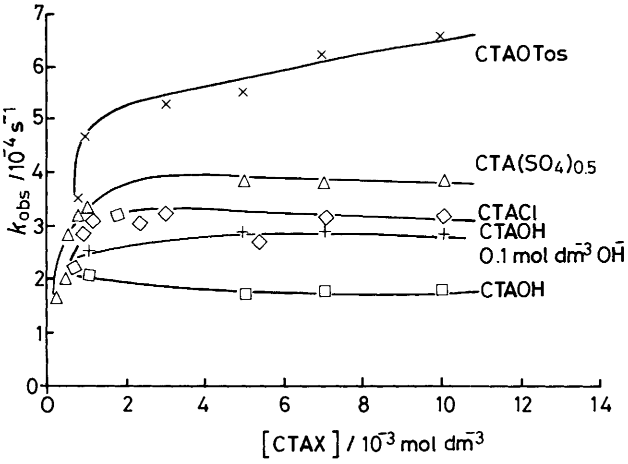


Figure 1. Dependence of rate constant of decarboxylation on the surfactant counter-ion.

Table 1. Decarboxylation in CTACl + NaCl.[a]

[CTACl]/10^{-3} mol dm^{-3}	k_{obs}/10^{-4} s^{-1}
3.0	4.05 (3.83)
4.0	3.98
5.0	3.95

[a] With 0.1 mol dm^{-3} NaCl, value in parentheses is with 0.5 mol dm^{-3} NaCl; in the absence of salt k'_M *ca.* 3.2 × 10^{-4} s^{-1} (Figure 1).

N-tetradecylglycine, C_{14} betaine, (**3b**), and *N*-*N*-dimethyl-*N*-hexadecylglycine, C_{16} betaine, (**3a**),

$$RN^+Me_2CH_2COO^-$$

(**3**) **a**; R = $C_{16}H_{33}$
b; R = $C_{14}H_{29}$
c; R = $C_{12}H_{25}$

The twin-tailed surfactant was didodecyl(dimethyl)ammonium chloride, DDDACl [$(C_{12}H_{25})_2NMe_2Cl$]. Decarboxylation of (**1**) has been followed in *N*,*N*-dimethyl-*N*-dodecylglycine [C_{12} betaine, (*3c*),[8b]], in synthetic vesicles,[9] in tri(n-octyl)alkyl ammonium ions, [9,10] and in a hydroxyethyl functionalized micelle.[8b]

Decarboxylation of (**1**) is a good indicator of polarity of solvents[7a] and of interiors of cyclodextrins,[12] and is a potentially useful probe of the surface structures of colloidal assemblies of amphiphiles.

Results

Reaction in Cetyltrimethylammonium Surfactants.— The monotonic increase of the first-order rate constant, k_{obs}, with increasing [surfactant] and with fully bound substrate (Figure 1) is similar to that for the reaction with CTABr, where at high [CTABr]: k_{obs} *ca.* 3 × 10^{-4} s^{-1} at 25 °C.[8a]

In the earlier work added salts with hydrophilic anions were found to increase or decrease reaction rate, depending, in part, upon the salt concentration. Interpretation of these results was complicated by the mixture of anions in the solution, and we now avoid this problem (Table 1). In the earlier work toluene-*p*-sulphonate ion initially speeded and then sharply slowed the reaction in CTABr, because it displaced substrate from the micelles,[8a] but CTAOTos speeds reaction at all concentrations. The competition between substrate and $OTos^-$ is very important because we did not reach the limiting value, k'_M, for fully bound substrate even at high [CTAOTos] (Figure 1).

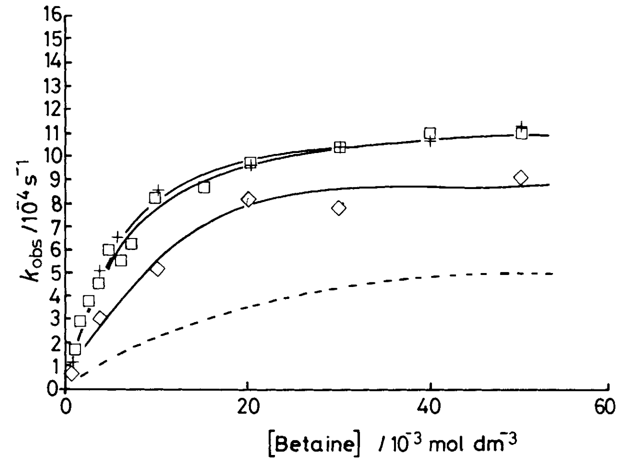


Figure 2. Decarboxylation in betaine surfactants: +, C_{16} betaine; ■, C_{14} betaine; ◇, C_{16} betaine + 0.1 mol dm^{-3} NaBr; ---- C_{12} betaine.[8b]

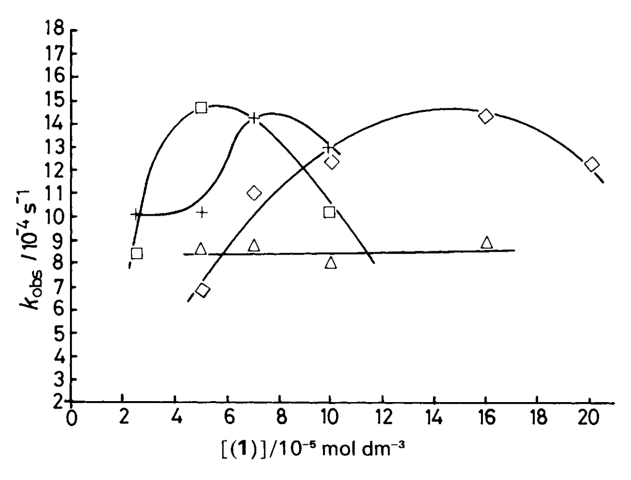


Figure 3. Decarboxylation in DDDACl and 0.01 mol dm^{-3} NaOH: □, 4 × 10^{-4} mol dm^{-3}; +, 6 × 10^{-4} mol dm^{-3}; ◇, 8 × 10^{-4} mol dm^{-3}; △, 6 × 10^{-3} mol dm^{-3} DDDACl, respectively.

Reaction in Betaine Surfactants.—Micellized C_{12} betaine gave higher values of k'_M than did CTABr, but higher surfactant concentrations were needed to fully bind the substrate.[8b] The behaviour is similar with the C_{14} and C_{16} betaines, but k'_M is higher. Added NaBr slightly slows reaction, probably by excluding substrate from the micelle (Figure 2).

Reaction in Didodecyl(dimethyl)ammonium Chloride.—The variation of k_{obs} with [DDDACl] is complex and depends upon the concentrations of the added substrate and NaOH. Values of k_{obs} go through maxima in very dilute DDDACl, and then through shallow minima (Figure 3). The positions of these extrema shift to lower [DDDACl] as [OH^-] is increased (Table 2) and depend upon [(**1**)]. We could not use other added electrolytes because DDDACl and the corresponding salts are sparingly soluble in water.

Discussion

Extrema such as those in Figure 3 had not been seen in any surfactant-mediated spontaneous reaction, regardless of mechanism or substrate charge.[1,2] Decarboxylation of (**1**) is

Table 2. Effect of NaOH upon decarboxylation in DDDACl.[a]

$[DDDACl]/10^{-3}$ mol dm^{-3}	$[NaOH]$/mol dm^{-3}		
	0.001	0.01	0.1
0.1	—	4.32	8.63
0.2	12.9	—	—
0.4	15.5	10.3	6.37
0.6	11.5	12.9	6.17
0.8	10.3	12.4	6.49
1.0	9.34	11.2	6.52
1.5	6.85	10.8	6.90
2.0	7.39	7.08	7.43
4.0	7.29	8.00	7.41
6.0	8.72	8.04	7.79
8.0	10.5	8.34	7.66
10.0	11.1	8.43	7.66
15.0	12.5	9.87	
20.0	13.7	10.0	

[a] Values of k_{obs} 10^{-4} s^{-1} at 25.0 °C with 10^{-4} mol dm^{-3} (**1**).

Table 3. First-order rate constants of decarboxylation in cationic and zwitterionic assemblies.[a]

Amphiphile	$k_M/10^{-4}$ s^{-1}
CTACl	3.2 (110)
CTABr	*ca.* 3.0 (100)
$CTA(SO_4)_{0.5}$	3.9 (130)
CTAOTos	>6.6 (220)
CTAOH	1.8 (60)
C_{12} betaine[b]	6 (200)
C_{14} betaine	11 (370)
C_{16} betaine	11 (370)
$C_{16}H_{33}NMe_2CH_2CH_2OH$	3.3 (110)
$C_{16}H_{33}NMe_2CH_2CH_2O^-$[b]	>6 (200)
$(C_8H_{17})_3NEtOMs$[c]	270 (9×10^3)
DDDACl	*ca.* 16 (5×10^2)[d]
DDDACl	>14 (5×10^2)[e]

[a] At 25.0 °C, values in parentheses are relative to $k_{obs} = 3.0 \times 10^{-6}$ s^{-1} ref. 8(*a*). [b] Ref. 8(*b*). [c] Ref. 10. [d] At first rate maximum in dilute DDDACl (Figure 3). [e] At high [DDDACl] (Table 2).

mechanistically simple, so extrema should be related to some structural features of the DDDACl assemblies. The rate maxima are at values of [DDDACl]/[(**1**)] of 6–8, and disappear when DDDACl (6×10^{-3} mol dm^{-3}) is in large excess over (**1**). The simplest explanation of these results is that small clusters form in dilute surfactant and contain, on average 6–8 surfactants per substrate, but in more concentrated surfactant the assemblies are large and not perturbed by substrate. This conclusion is consistent with the effect of NaOH upon the position of the extrema (Table 2). Added electrolytes decrease the values of the cmc for normal surfactants, by screening head-group repulsion, and stabilize micelles, relative to monomeric surfactant.[1,2,13] They should also stabilize micelles relative to small clusters and clusters relative to monomer. We do not know the structures of assemblies of DDDACl, but consideration of monomer packing suggests that twin-tailed surfactants could form bilayers rather than spherical micelles.[14] Vesicle formation has been postulated for very dilute surfactant with hydrophilic counter-ions,[14b,c] but small clusters would not have been detected by methods used to study the didodecyl surfactants. Twin-tailed surfactants have a higher hydrophobic–hydrophilic balance than similar single-chain surfactants so they could form small clusters, especially if a polarizable anionic solute interacts with them. For example tri(n-octyl)alkylammonium ions are surface active, but do not micellize.[15] However, they appear to form small clusters, especially in the presence of hydrophobic solutes.[9,10] Cluster growth should be assisted by the presence of NaOH, and rate extrema change to lower [surfactant] and almost disappear in 0.1 mol dm^{-3} NaOH, probably because the larger assemblies are catalytically less effective (Table 2 and Figure 3). It is difficult to obtain physical evidence for clusters if they are too small to give much light or neutron scattering, and experiments with fluorescent probes are probably not feasible because the probes are typically large conjugated molecules like substrate (**1**) and could greatly perturb small amphiphile clusters.

The rate extrema (Figure 3) show that small clusters of DDDACl are catalytically more effective than normal micelles or assemblies (Figures 1 and 2), as are small clusters of tri-(n-octyl)alkylammonium ions.[9,10] However, the catalytic effectiveness cannot be explained solely in terms of the size of the colloidal assembly, because Kunitake and co-workers found that synthetic vesicles of sonicated ditetradecyl(dialkyl)-ammonium ions are better catalysts than normal micelles in decarboxylation of (**1**).[9]

Rate enhancements of spontaneous, unimolecular reactions by micelles or similar aqueous colloids depend upon the substrate distribution and relative first-order rate constants in water and the colloids, which are treated as distinct reaction media, *i.e.*, as pseudophases. The relation between the rate constants in water and micelles (k'_W and k'_M) depend upon the transfer free energies of initial and transition states in going from water to micelles, *i.e.*, upon coulombic and specific dispersive interactions. The initial state is a high charge density carboxylate ion. Coulombic attractions depend upon charge density at the colloidal surface,[16] and should be larger for a micelle, with an aggregation number of 50–100, than for a small assembly. Therefore, cationic micelles should be more effective than small cationic clusters in stabilizing an ion such as (**1**). Small clusters of tri(n-octyl)alkylammonium ions seem to be relatively ineffective at binding hydrophilic anions, although they interact strongly with polarizable, low charge density, anions.[9,10,17]

Charge is extensively delocalized in transition state (**2**), and dispersive attractions between it and the cationic head groups will be important. Polarizable solutes interact readily with cationic head groups, and there are strong interactions between quaternary ammonium ions and aromatic solutes, especially those that have strongly electron-releasing substituents.[8a,18,9] The net result of these coulombic and dispersive interactions should be greater initial-state stabilization by cationic micelles than by submicellar assemblies. Dispersive attractions are more important in the transition than in the initial state. Therefore, for fully bound substrate, the relative free energy of activation, should be lower for reaction in a small cationic submicelle than in a fully formed micelle.

This explanation is consistent with a considerable amount of kinetic evidence on reactions involving cationic and zwitterionic amphiphiles,[8] (Table 3). In solutions of cetyltrimethylammonium surfactants with univalent counter-ions k'_M increases with decreasing fractional micellar charge, α. Values of α from light scattering[19] are: CTAOH, *ca.* 0.5; CTACl, 0.27; CTABr, 0.22; $CTA(SO_4)_{0.5}$, 0.07 and other methods give similar values.[1,2b] The value of α for CTAOTos is probably low, because toluene-*p*-sulphonate ion binds very strongly to cationic micelles.[8a,20,21] Micelles that have high fractional ionization, *i.e.*, high surface charge, should interact most strongly with (**1**) provided that it is present in low concentrations and does not perturb the micellar structure. The variation of k_{obs} with $[CTA(SO_4)_{0.5}]$ (Figure 1) deviates from our postulated dependence of k'_M upon α. For univalent counter-ions α is related to the ability of the counter-ion to occupy sites at the micellar surface[1c,d,2b,c] but a divalent ion, *e.g.* SO_4^{2-}, gives a low value of α because of its strong coulombic interaction with the micelle rather than its ability to bind specifically at the micellar surface.[16b,19,22]

Zwitterionic micelles, *e.g.*, the betaines and $C_{16}H_{33}N^+$-$Me_2CH_2CH_2O^-$, should not interact strongly with the initial state by a coulombic attraction, and they give relatively high values of k'_M (Figure 2 and Table 3).

The twin-tailed surfactants, *e.g.*, DDDACl at relatively high concentration, and the corresponding C_{14} and C_{16} derivatives as sonicated vesicles,[9] are also better catalysts than the CTA^+ surfactants. So far as we are aware, fractional ionizations are not known for assemblies of the twin-tailed surfactants, but packing of two hydrophobic alkyl groups should give greater head-group spacing than that in simple spherical micelles of CTAX, for example (see ref. 14). Decarboxylation should be speeded by this low surface charge density.

Values of binding constants of substrate to collcidal assemblies provide a measure of initial-state stabilization by them. Binding constants of non-ionic solutes can be determined kinetically while allowing for the concentration of monomeric surfactant.[1,2] We cannot use this treatment because of the increase in rate below the cmc. Approximate binding constants of (**1**) to micelles or similar assemblies are given by the reciprocal of the surfactant concentration that gives half the maximum rate enhancement.[23] (This estimate neglects the cmc value and the effects of solute).

Estimated binding constants for CTA^+ surfactants are 10^3 dm^3 mol^{-1} or larger for CTACl, CTABr, and $CTA(SO_4)_{0.5}$ [Figure 1 and ref. 8(*a*)], but they are *ca.* 200 dm^3 mol^{-1} for the C_{14} and C_{16} betaines (Figure 2), and even lower for the C_{12} betaine.[8b] Despite uncertainties in these values the differences between them support our hypothesis that the lesser catalysis by CTA^+, as compared with betaine micelles, is due in part to initial-state stabilization because of strong coulombic attractions. These considerations apply only when (**1**) is fully bound. We could not apply these arguments to reactions in the twin-tailed surfactants because their concentrations were not high enough to give complete substrate binding and the high reaction rates in very dilute DDDACl (Figure 3) prevented our estimating even an approximate binding constant.

Spontaneous formation of micelles or other assemblies from ionic amphiphiles involves a balance between hydrophobic attractive forces, coulombic head-group repulsions and attractions of counter-ions. The presence of two or more hydrophobic groups increases hydrophobic attractions and permits formation of small assemblies, probably of varying composition, with little attraction for hydrophilic counter-ions. These assemblies should be stabilized by polarizable solutes that interact strongly with quaternary ammonium ions. These interactions could occur with single-chain cationic surfactants, and submicellar complexes could be involved in reactions in dilute surfactants.[4] However, if rate constants increase monotonically with [surfactant] we cannot distinguish between formation of submicellar assemblies and reactant induced micellization as in bimolecular reactions in DDDACl, for example.[24] The rate extrema for decarboxylation in DDDACl cannot be explained in terms of substrate—induced formation of large assemblies, although the dependence of k_{obs} upon [substrate] in dilute DDDACl (Figure 3) suggests that (**1**) interacts with, and stabilizes, small clusters of $DDDA^+$.

Experimental

Materials.—The preparation and purification of the reagents and surfactants has been described.[24]

Kinetics.—Reactions were followed spectrophotometrically at 410 nm.[8] Solutions were made up in CO_2-free redistilled H_2O. Freshly prepared solutions of 6-nitrobenzisoxazole-3-carboxylic acid were used and all reactions were followed in aqueous NaOH (1–5 mmol dm^{-3} unless specified). Buffered solutions have been used in some earlier experiments, but the rate constants were similar to those in 0.002 mol dm^{-3} NaOH. The substrate concentration was 10^4 mol dm^{-3} and all experiments were carried out at 25.0 °C. For reactions in solutions of $(CTA)_2SO_4$ the specified molarity is written in terms of moles of CTA^+. Duplicate values of k_{obs} agreed within 5%.

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