Micellar Effects upon the Reaction of Azide Ion with *N*-Alkyl-2-chloropyridinium Ions

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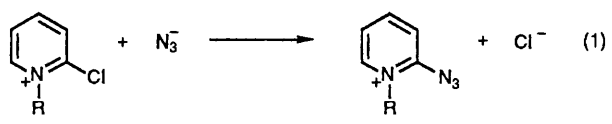
The reaction of *N*-alkyl-2-chloropyridinium ions (**1a–f**; alkyl = Me, n-hexyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl) with N_3^- is affected by cationic micelles of cetyltrimethylammonium ion (CTAX, X = Cl^-, Br^-, N_3^-), which inhibit the reaction of ion (**1a**) at low [surfactant] but catalyse it at high [surfactant]. First-order rate constants, k_ψ, for the reaction of ion (**1b**) continue to increase with increasing [surfactant] but, for reaction of the hydrophobic substrates (**1c–f**) at a given [NaN_3], k_ψ goes through maxima with increasing [surfactant]. Reaction in CTABr is always faster than in CTACl, but the difference decreases with increasing substrate hydrophobicity so the rate–surfactant profiles do not fit the pseudophase, ion-exchange model. For reactions of substrates (**1c–f**) with N_3^-, k_ψ increases with [substrate] in the absence of surfactant and it also increases with [$CTAN_3$]. The rate enhancement for reaction of ion (**1f**) in water is greater than that of ion (**1a**) by a factor of *ca.* 1.2 $\times 10^4$, and this is probably due to self-micellization of 2-chloro-*N*-hexadecylpyridinium ion. Second-order rate constants for reactions of ions (**1a–f**) with N_3^- in MeCN–water (1 : 1 w/w) are very similar.

Ionic colloidal self-assemblies, *e.g.* micelles,[1–4] vesicles,[5] and microemulsion droplets,[6,7] assist bimolecular reactions of counterions with substrates bound to the assemblies. The variation of the observed first-order rate constant, k_ψ, with concentration of surfactant, counterion, and added inert electrolyte can be explained in terms of a pseudophase model which treats the micelles as a distinct reaction medium.[1,3,8] The distribution of reactants between micelles and water can often be measured directly[9] or estimated, provided that it is assumed that the two reactants bind independently, and a second-order rate constant can be calculated for the micellar pseudophase.[9–13] Generally, second-order rate constants in the micelle are not very different from those in water. These observations suggest that micellar catalysis of bimolecular reactions is due largely to concentration of both reactants in the small volume of the micelles. But there are some exceptions to this generalization; for example, estimated second-order rate constants in the micelle for aromatic substitution by azide ion are much larger than those in water.[12] Apparently the discrepancy is not due to abnormal micellar binding of azide ion because the second-order rate constants for deacylation or attack on alkyl benzenesulphonate by azide ion are very similar in water and in the micellar pseudophase.[11–13]

Our approach in this work involved a search for other reactions of azide ion which might give larger second-order rate constants in micelles than those found for its reactions in water.

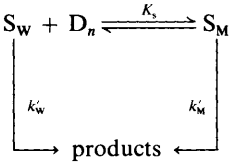
We used a series of *N*-alkyl-2-chloropyridinium ions (**1**) the hydrophobicity of which could be varied without affecting the reaction mechanism [equation (1)].



(1)

a; R = Me
b; R = n-C_6H_{13}
c; R = n-$C_{10}H_{21}$
d; R = n-$C_{12}H_{25}$
e; R = n-$C_{14}H_{29}$
f; R = n-$C_{16}H_{33}$

The reaction of OH^- with ions (**1**) has been studied in the absence of added surfactant, but it is speeded by cationic micelles when the substrate is hydrophobic enough to be micellar bound.[14,15] This kinetic behaviour can be explained in terms of a pseudophase model on the assumption that OH^- and inert anions compete for the micelle. The second-order rate constants are smaller in the micelle than in water by a factor of *ca.* 3–5 and this difference can be rationalized on the basis of a negative salt effect due to micellar counterions.[14,15] When the alkyl group in *N*-alkyl-2-chloropyridinium ions (**1**) was very hydrophobic, *e.g.* R = n-$C_{14}H_{29}$ or n-$C_{16}H_{33}$, its self-association gave rate enhancements in the absence of added surfactant. A quantitative treatment of our reactions is generally based on Scheme 1.[1,10,15]



Scheme 1.

The distribution of substrate S between water (S_W) and micelle (S_M) is given by equation (2)[16] where [D_n] = [D] −

$$\frac{[S_M]}{[S_T]} = \frac{K_s[D_n]}{1 + K_s[D_n]} \quad (2)$$

cmc, where D_n is micellized surfactant and cmc is the critical micelle concentration, k'_W and k'_M are first-order rate constants, and K_s is a binding constant, while T denotes the total concentration. The observed rate constant is given by equation (3).[16]

$$k_\psi = \frac{k'_W + k'_M K_s([D] - \text{cmc})}{1 + K_s([D] - \text{cmc})} \quad (3)$$

The first-order rate constants are given by equation (4) and (5) where [N_{3W}^-] is a molarity in terms of total solution volume,

$$k'_W = k_W[N_{3W}^-] \quad (4)$$

Table 1. Effect of substrate concentration on reactivity.[a]

10^6[Substrate]/mol dm^{-3}	Me	C_6H_{13}	$C_{10}H_{21}$	$C_{12}H_{25}$[b]	$C_{14}H_{29}$[c]	$C_{16}H_{33}$
3					28.7 (50.2)[d]	3 000[d]
5					32.8 (53)[d]	4 900[d]
7					33 (60)[d]	7 600[d]
10	4.80		7.65	8.5	35 (73)[d]	9 100
20	4.82		7.7	8.6	47 (84)[d]	13 400
40	4.85		7.8	8.8	51.4 (114)[d]	18 600
50	4.9	6.58	7.96	9.7	59 (139)[d]	38 200
80	4.77	6.55	8.3	10.3	(193)[d]	57 300
100	4.80	6.64	8.5	125	74 (207)[d]	
150		6.75	8.9	32		
200		6.66	10.9	66	82 (243)[d]	

[a] Values of 10^4 k_ψ/s^{-1} at 25.0 °C with 0.1 mol dm^{-3} NaN_3 unless specified otherwise. [b] 0.01 mol dm^{-3} NaN_3. [c] 0.001 mol dm^{-3} NaN_3. [d] 0.002 mol dm^{-3} dm^{-3} NaN_3.

Table 2. Reactions in aqueous acetonitrile.[a]

	Alkyl group					
	Me	C_6H_{13}	$C_{10}H_{21}$	$C_{12}H_{25}$	$C_{14}H_{29}$	$C_{16}H_{33}$
10^3 k_ψ/s^{-1}	4.7	4.4	4.5	4.6	4.62	4.65

[a] Initial rate constants at 25.0 °C with 5 × 10^{-5} mol dm^{-3} substrate in water–MeCN (1:1 w/w) and 0.01 mol dm^{-3} NaN_3.

$$k'_M = k_M m^S_{N_3} = k_M[N^-_{3M}]/[D_n] \quad (5)$$

and the second-order rate constant, k_M is written in terms of the mole ratio of micellar-bound N_3^- to micellar head groups,[14,17] where equation (6) holds.

$$m^S_{N_3} = [N^-_{3M}]/([D] - \text{cmc}) \quad (6)$$

For reaction of azide ion in a micelle with an inert counterion (X) the ionic distribution is assumed to follow equation (7),[2,18] shown for azide ion, with concentrations written in terms of molarity in the total solution.

$$K_x^{N_3} = [N^-_{3W}][X^-_M]/[X^-_W][N^-_{3M}] \quad (7)$$

Provided that β, the extent of charge neutralization of micellar head groups by counterion is constant, equations 2–7 can be combined and the variation of k_ψ with [surfactant] can be predicted in terms of the various kinetic and equilibrium constants.[10–19]

The treatment gives satisfactory fits for many ionic reactions such as those of OH^- with *N*-alkyl-2-halogenopyridinium ion,[14,16] and carbonate and carboxylic esters,[20,21] and we attempted to apply it to reactions of N_3^- with *N*-alkyl-2-chloropyridinium ion.

The second-order rate constants, k_W and k_M, in equations (4) and (5) have different dimensions, but they can be compared provided that the volume element in the micelles is estimated and [reagent] is written as molarities in the micellar pseudophase.[14–21] In general, second-order rate constants are often similar in aqueous and micellar psuedophases except for reaction of azide ion with 2-bromo-3,5-dinitropyridine[22] and with 2,4-dinitrochloro-benzene and -naphthalene (DNCB) and (DNCN).[12] However, reactions of N_3^- with hydrophobic *N*-alkyl-2-chloropyridinium ions have much larger second-order rate constants in cationic micelles than in water.

Experimental

Materials.—The preparation or purification of surfactants and *N*-alkyl-2-chloropyridinium salts (**1**) has been described,[14,15] but cetyltrimethylammonium azide, $CTAN_3$, was synthesized from $(CTA)_2SO_4$ and $Ba(N_3)_2$ in a manner similar to that for CTAOH.[21,23] The products of the reactions of NaN_3 with substrates (**1a–f**) in MeCN were identified by IR and NMR spectroscopy and the experimental procedure has been described.[11]

Kinetics.—The reactions of NaN_3 with substrates (**1**) was followed spectrophotometrically in water at 25 °C with a Perkin-Elmer spectrophotometer for the slow reactions. The substrates have λ_{max} 275 nm and the products absorb at λ_{max} 293–300 nm. Repetitive scanning of the spectrum of the reaction mixture showed that no intermediate built up during the reaction. Except where noted otherwise substrate (5 × 10^{-5} mol dm^{-3}) and NaN_3 (2 × 10^{-3} to 10^{-1} mol dm^{-3}) were used. The reactions were generally cleanly first order and the rate constants k_ψ-values are in reciprocal seconds. Reactions were followed in solutions of cetyltrimethylammonium ion (CTAX, X = Br, Cl, N_3).

Results

Reaction in Water.—The reactions of methyl, n-hexyl, and n-decyl derivatives (**1a–c**) are independent of [substrate] in the range of (1–10) × 10^{-5} mol dm^3 in 0.1 mol dm^{-3} NaN_3 (Table 1). The second-order rate constants k_W are 0.05, 0.065, and 0.08 dm^3 mol^{-1} s^{-1} at 25 °C. The slightly increased reactivities of (**1b**) and compounds (**1c**) are probably due to the formation of a dimer. Although for reactions of the dodecyl and tetradecyl derivatives (**1d**) and (**1e**) the rate constants increased with increasing [substrate] (Table 1), we found that the reaction rate of the hexadecyl derivative (**1f**) increased *sharply* with increasing [substrate] (Table 1), almost certainly because of substrate aggregation which attracts N_3^- to the cationic aggregate. The rate enhancements for the hydrophobic substrates are observed for values of [substrate] much lower than the critical micelle concentration (cmc) of the *N*-alkyl-2-chloropyridinium salts, because, for *N*-hexadecylpyridinium chloride, cmc = 8 × 10^{-4} mol dm^{-3}.[11] The high reactivities of substrates (**1e–f**) disappear if the reaction is carried out in aqueous MeCN (Table 2). However, substrate aggregation of

Table 3. Reaction of 2-chloro-*N*-methylpyridinium ion in CTABr.[a]

10^3[CTABr]/mol dm^{-3}	$10^5 k_\psi$/s^{-1}
0.0	8.1 (7.5)[b]
0.4	6.2 (7.4)
0.7	5.5 (7.4)
1	5.2 (7.3)
3	6 (7.0)
4	6.7 (7.2)
5	7.6 (7.4)
6	8.12 (7.8)
10	10.5 (8.2)
13	12.5 (8.5)

[a] Values of k_ψ/s^{-1} at 25.0 °C with 5×10^{-5} mol dm^{-3} substrate and 0.01 mol dm^{-3} NaN_3. [b] Values in parentheses are for the effect of 0.02 mol dm^{-3} NaBr upon the reaction.

Table 4. Reaction of 2-chloro-*N*-hexylpyridinium ion in surfactant.[a]

	$10^3 k_\psi$/s^{-1}	
10^3[Surfactant]/mol dm^{-3}	CTABr	CTACl
1	0.29	0.26
2	0.49	0.48
4	0.86	0.80
7	1.31	1.3
10	1.6	1.48
30	3.03	2.3
60	4.1	3.0
100	5.7	3.6
130	7.6	
150		4.3
200		6.2

[a] At 25.0 °C with 5×10^{-5} mol dm^{-3} substrate and 0.01 mol dm^{-3} NaN_3.

Table 5. Salt effects upon reaction of 2-chloro-*N*-hexadecylpyridinium ion in water.[a]

10^6[Substrate]/ mol dm^{-3}	No salt	0.01 mol dm^{-3} NaCl	0.01 mol dm^{-3} NaBr
2	0.15	0.072	0.084
3	0.30	0.10	0.12
5	0.49	0.15	0.165
7	0.76	0.25	0.25
10	0.91	0.39	0.41
20	1.34	0.55	0.6
40	1.86	0.6	0.64
50	3.82	1.26	1.34
80	5.73	2.3	2.5

[a] Values of k_ψ/s^{-1} at 25.0 °C with 0.01 mol dm^{-3} NaN_3.

compounds (**1c–f**) is clearly important in water (Table 1), and aggregation should be broken up by MeCN which disrupts the macrostructure of water.

Added NaCl and NaBr slowed reaction of the hexadecyl derivative (**1f**) with NaN_3 (Table 5), probably because of competition between inert halide ion and N_3^- for micellized substrate.

Micellar Effects.—*2-Chloro-*N*-methylpyridinium chloride* (**1a**). Reaction was inhibited by micelles of CTABr at low concentration and there was little catalysis at high [CTABr], but addition of NaBr decreased both inhibition and catalysis (Table 3).

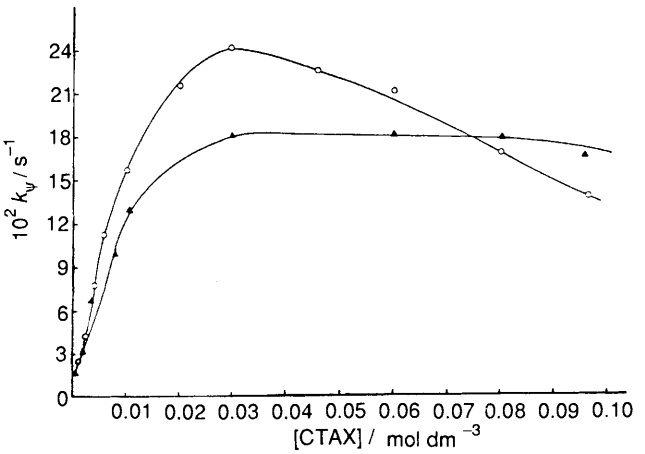


Figure 1. Variation of the first-order rate constant k_ψ for the reactions of 2-chloro-*N*-decylpyridinium ion (**1c**) with 0.01 mol dm^{-3} NaN_3; ○ in CTBr, ▲ in CTACl.

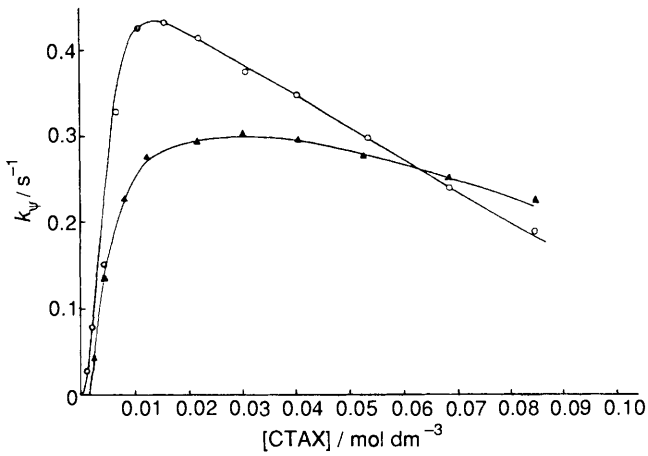


Figure 2. Variation of first-order rate constant k_ψ for the reaction of 2-chloro-*N*-dodecylpyridinium ion (**1d**) with 0.01 mol dm^{-3} NaN_3; ○ in CTABr, ▲ in CTACl.

*2-Chloro-*N*-hexylpyridinium chloride* (**1b**). Reaction was catalysed by cationic micelles of CTABr or CTACl and the first-order rate constants did not go through maxima with increasing [CTABr] or [CTACl] but continued to increase; the reaction was always faster in CTABr (Tables 4 and 5).

Decyl, dodecyl, and tetradecyl derivatives. For reactions of these substrates (**1c–e**) with N_3^- in the presence of CTABr or CTACl, first-order rate constants went through maxima with increasing [surfactant] (Figures 1, 2, and 3). The rate enhancement was unexpectedly larger in CTABr than in CTACl and increased with substrate hydrophobicity, which decreased the [surfactant] needed for maximum rate enhancement. The maximum rate enhancements, relative to the reactivity of the methyl substrate (**1a**) in water, were very much larger than those generally found in micellar-catalysed reactions (Table 6). For reaction of substitute (**1f**) with 0.01 mol dm^{-3} NaOH in CTACl the maximum rate enhancement was by a factor of *ca.* 10,[15] whereas for reactions with N_3^- it was *ca.* 1.2×10^4. Generally, micellar rate enhancements of bimolecular reactions of hydrophilic ions are by factors of 10–10^2.[1–5,15,24]

The pseudophase ion-exchange model fits were satisfactory for reactions of OH^- with substrate (**1d–f**),[14,15] but for reactions of N_3^- it is difficult to account for micellar effects upon these reactions in view of the observation that under some conditions reactions were faster in CTABr than in CTACl

Table 6. Relative maximum micellar rate enhancement.

Substrate	Alkyl group	Surfactant	10^3[D]/mol dm^{-3}	[NaN_3]/mol dm^{-3}	k_{max}[a]/s^{-1}	k_{rel}[b]
(**1b**)	C_6H_{13}	CTABr	130	10^{-2}	0.0076	95
(**1b**)	C_6H_{13}	CTACl	200	10^{-2}	0.0062	78
(**1c**)	$C_{10}H_{21}$	CTACl	30	10^{-2}	0.18	2.5×10^3
(**1c**)	$C_{10}H_{21}$	CTABr	30	10^{-2}	0.24	3×10^3
(**1d**)	$C_{12}H_{25}$	CTACl	20	10^{-2}	0.30	3.8×10^3
(**1d**)	$C_{12}H_{25}$	CTABr	14	10^{-2}	0.43	5.4×10^3
(**1e**)	$C_{14}H_{29}$	CTACl	3.5	2×10^{-3}	0.44	5.5×10^3
(**1e**)	$C_{14}H_{29}$	CTABr	2	2×10^{-3}	0.56	7×10^3
(**1f**)	$C_{16}H_{33}$	CTACl	0.9	10^{-3}	0.94	1.2×10^4
(**1f**)	$C_{16}H_{33}$	CTABr	1	10^{-3}	1.2	1.5×10^4

[a] At the rate maximum. [b] Relative to rate constant for reaction of the 2-chloro-*N*-methylpyridinium salt (**1a**) in water with 0.01 mol dm^{-3} NaN_3 (no added surfactant).

Table 7. The effect of CTACl upon the reaction of substrate (**1f**).[a]

	[**1f**]/10^{-6} mol dm^{-3}	
10^4[CTACl]/mol dm^{-3}	2	4
1	0.3	0.33
2	0.33	0.36
2.5	0.36	0.39
3	0.45	0.48
4	0.62	0.67
5	0.68 (0.73)[b]	0.75 (0.81)[b]
7	0.72 (0.75)[b]	0.88 (0.98)[b]
9	0.83 (0.95)[b]	0.94 (1.2)[b]
10	0.73	0.75
20	0.43	0.42
30	0.19	0.21

[a] Values of k_ψ/s^{-1} at 25.0 °C with 0.001 mol dm^{-3} NaN_3. [b] Values in parentheses are for reaction in CTABr.

Table 8. Reaction of 2-bromo-*N*-hexadecylpyridinium ion in $CTAN_3$.[a]

[$CTAN_3$]/ 10^{-4} mol dm^{-3}	[**1f**]/10^{-6} mol dm^{-3}		
	2	4	8
8	0.028	0.04	0.093
10	0.04	0.09	0.12
15	0.08	0.14	
20	0.18	0.19	0.29
30	0.22	0.23	
40	0.25	0.27	
50	0.28	0.31	0.4
60	0.33	0.35	0.52

[a] Values of k_ψ/s^{-1} at 25.0 °C.

(Figures 1–3), which is contrary to the predictions of the model.[2,17,18]

The observed first-order rate constants k_ψ increased steadily with increasing [$CTAN_3$] even under conditions for which compound (**1f**) should be fully micellar bound. When we used constant [$CTAN_3$] and varied the [substrate], k_ψ increased slightly. Similar substrate effects were observed for reaction of compounds (**1f**) in CTACl (Tables 7 and 8).

Discussion

Reaction of Methyl Derivative (**1a**).—The reaction of the methyl derivative (**1a**) with N_3^- was slightly inhibited by cationic micelles at low [surfactant], but with increasing [surfactant] the observed first-order rate constant k_ψ increased

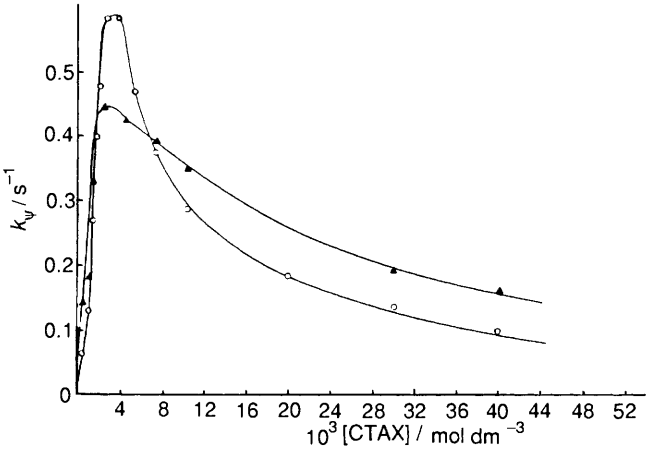


Figure 3. Variation of the first-order rate constant k_ψ for the reaction of 2-chloro-*N*-tetradecylpyridinium ion (**1e**) with 0.002 mol dm^{-3} NaN_3; ○ in CTABr, ▲ in CTACl.

(Table 3). We ascribe the inhibition to weak binding of the substrate and attraction of N_3^- toward the micellar surface; therefore reaction occurred largely in the aqueous pseudophase. At high [surfactant] the binding of substrate became large, and co-operative binding between N_3^- and substrate will have increased the binding to the micellar pseudophase; as a result we observed slight catalysis, and addition of 0.02 mol dm^{-3} NaBr decreased both the inhibition and the catalysis (Table 3).

Reaction of Hexyl Derivative (**1b**).—The reaction of substrate (**1b**) with N_3^- was catalysed by cationic micelles of CTACl or CTABr. The rate–surfactant profiles do not go through maxima but continue to increase with increasing [surfactant] and the reaction was always faster in CTABr than in CTACl (Table 4). This could be ascribed to co-operative binding of N_3^- with substrate, followed by binding of this ion pair to the micellar surface.

Reactions of Hydrophobic Substrates (**1c–f**).—The large rate enhancements for the reactions of hydrophobic substrates (**1c–f**) with increasing [substrate] (Table 1) are clear evidence for reaction of aggregated rather than free substrate. The enhancement was much larger than that found for reaction of OH^- with substrates (**1e–d**),[15] which suggests that aggregation is a co-operative phenomenon involving hydrophobic substrate and azide ions. Azide ion is much more hydrophobic and more polarized than hydroxide ion and is therefore more able to interact with and stabilize a cluster of *N*-alkyl-2-chloropyridinium ions as in the case of binding to cationic micelles.[2,12]

These rate enhancements (Table 1) were probably not due to hydrophobic substrate micellization because they were observed at [substrate] much lower than the expected cmc.[25] Salt inhibition did not follow the usual anion order because NaBr inhibited the reactions of substrate (**1f**) less than did NaCl and this suggests that the halide ions are competing with N_3^- for substrate aggregates, but that Br^- in particular can also stabilize substrate aggregates which would assist reaction (Table 5). The methyl, hexyl, decyl, dodecyl, tetradecyl, and hexadecyl derivatives (**1a–f**) reacted normally in aqueous MeCN (Table 2), which confirms that substrate aggregation of the more hydrophobic substrates in water is very important for these compounds.

The changes in rate maxima with increasing [CTABr] or [CTACl], Figures 1–3, and the increasing rate enhancement (k_{rel}) with increasing substrate hydrophobicity are qualitatively as predicted by a pseudophase model [equations (2)–(7)]. The rate enhancement in very dilute surfactant could be ascribed to induced micellization. As mentioned previously, treatments based on equations (2)–(7) do not fit the rate–surfactant profiles.

Bimolecular ionic reactions are generally faster in CTACl than in CTABr,[1–3,14] but this anion order was not followed here (Figures 1–3 and Table 6). Most micellar effects upon bimolecular reactions in water have been treated quantitatively by assuming that the two reactants bind independently to the micelle and that their effects upon micellar structure are relatively unimportant.[9–18] For instance, micellar catalysis of reaction of OH^- with compounds (**1d**) and (**1e**) was analysed by assuming that *N*-alkyl-2-chloropyridinium[15] ion was partitioned between micelle and water according to the equation developed for the binding of neutral molecules [equation (2)]. It was assumed that the hydrophobic interaction was much more important than the unfavourable coulombic interaction.

These assumptions are not acceptable if there are interactions between reactants and this is probably the situation for a mixture of N_3^- and *N*-alkyl-2-chloropyridinium ion. If these ions form pairs or large clusters, each will increase the binding of the other and in addition they may bind to monomeric surfactant or to its submicellar aggregates.

There is some evidence (*e.g.*, salt effects) for co-operative binding of counterions caused by inert salts upon micellar reactions of carbocations,[17,26] also, based on kinetic evidence,[27] inert salts in high concentration will force even such a hydrophilic anion as OH^- to bind to anionic micelles and thus to induce micellization.[28] Reaction of inorganic substrates provided kinetic evidence for interaction of reactants with submicellar species.[29,30] There is also physical evidence for these interactions or induced micellization[29] and rate effects below the cmc are also common in reactions of hydrophobic organic substrates.[2,28]

Quantitatively the rate–surfactant profiles for reactions of compounds (**1c**) and (**1d**) with N_3^- in CTACl or CTABr (Figures 1–3) generally show maxima but the [surfactant] needed to reach the maximum decreases with increasing substrate hydrophobicity. For reaction of substrate (**1c**) rate maxima occur at *ca.* 0.03 mol dm^{-3} in CTABr or CTACl, for reaction of (**1d**) the rate maxima occur at *ca.* 0.02 mol dm^{-3} in CTABr, and those for (**1e**) occur at 2.5×10^{-3} mol dm^{-3} in CTACl and 2×10^{-3} mol dm^{-3} in CTABr. After the maxima the rate decreases slowly with increasing [surfactant] and more slowly than predicted by an ion-exchange model. This behaviour has been observed in the reaction of *N*-alkyl-2-bromopyridinium ions with N_3^-.[11] This indicates another failure of the widely used ion-exchange treatment. On the other hand, the reaction of constant [(**1f**)] in $CTAN_3$ gave a first-order rate constant, k_ψ, which continued to increase with increasing [$CTAN_3$], and the rate enhancement also increased with increasing [(**1f**)] at constant [$CTAN_3$] (Table 8).

So we conclude that reaction of hydrophobic substrate is speeded by cationic surfactant but only with dilute substrates, *ca.* 2×10^{-6} mol dm^{-3}, on the other hand, at high [substrate] cationic micelles inhibit the reaction because the added surfactant in effect 'dilutes' the substrate in the aggregate. This behaviour has been observed in the reaction of *N*-hexadecyl-*N*,*N*-dimethylglycinate with OH^- in the presence of CTACl.[31]

For reactions in the absence of added surfactant the rate enhancements due to substrate aggregation were usually large, up to a factor of *ca.* 1.5×10^4 [for reaction of (**1f**) with 10^{-3} mol dm^{-3} NaN_3] relative to reaction of compound (**1a**) (Table 6). This proximity effect promotes reaction more effectively than in a mixture of substrate (**1f**) and micelles of CTACl, CTABr, or $CTAN_3$, where the added surfactant in effects 'dilutes' the substrate in the aggregate.

Generally, rate enhancements due to substrate aggregation are smaller than those observed here and for acid hydrolysis of monoalkylsulphates,[32] deacylation by OH^-, and reaction of OH^- with *N*-alkyl-2-chloropyridinium ion or *N*-alkyl-2-bromopyridinium ion the enhancements[1,14,16,33] are within a factor of 10 to 10^2.

The rate enhancement by factors of almost 10^5 for reaction of substrate (**1f**) with N_3^- in the presence (or absence) of surfactant (Tables 1, 4) was similar in magnitude to the rate enhancements in intramolecular as compared with intermolecular reactions.[34–37]

We cannot estimate the second-order rate constant in the micellar psuedophase by an ion-exchange model because this model does not explain our rate–surfactant profiles quantitatively. However, we can estimate minimum values of k_M by assuming that the hydrophobic substrate (**1f**) and N_3^- are fully micellar bound at high [surfactant] such as 9×10^{-4} mol dm^{-3} CTACl or CTABr when using 10^{-3} mol dm^{-3} NaN_3. The binding constant K_s 850 dm^3 mol^{-1} in CTACl was estimated by ultrafiltration.[14] Substrate binding should therefore be extensive. Under these conditions $k_M = 0.94$ and 1.2 s^{-1} in CTACl and CTABr (Table 7). When the substrate was fully micellar bound and the micelle was saturated with N_3^-, and if we assume that equation (5A) holds, then $\beta = 0.75$, and k_M will be

$$k_\psi = k_M m^s_{N_3} = k_M[N^-_{3M}]/[D_n] = k_M\beta \qquad (5A)$$

ca. 1.25 and 1.6 s^{-1} in CTACl and CTABr respectively; k_M should be higher because the micelle is not saturated with N_3^- and substrate is probably not fully micellar bound. The calculated values of k_M do not change markedly on using data at higher [surfactant]. The second-order rate constant k_M is based on the concentration written as a molar ratio, but if the molar volume element of the reaction in the micelle is 0.14 dm^3,[2,3,17] the second-order rate constant is given by equation (8), so k_2^m

$$k_2^m = 0.14\ k_M \qquad (8)$$

based on molarity of N_3^- in the micellar pseudophase is *ca.* 0.22 dm^3 mol^{-1} s^{-1} as a minimum. The actual value will almost certainly be higher. Excess of Br^- will displace N_3^- from the micellar pseudophase unless co-operative binding of N_3^- with substrate is important.[11,12]

Now we can see that the minimum value of k_2^m, 0.22 dm^3 mol^{-1} s^{-1}, for the hydrophobic substrate (**1f**) is much larger than that of k_W 5×10^{-4} dm^3 mol^{-1} s^{-1} for reaction of compound (**1a**) in water (Table 1). This very large difference between the reactivity of N_3^- in water and in cationic micelles is similar to, but larger than, that observed for reaction of N_3^- with 2,4-dinitrochlorobenzene.[12]

We should note that the calculation of the second-order rate

constants in the micellar pseudophase k_M is based on the assumption that both reactants are distributed uniformly at the micellar surface and that they do not bind co-operatively.

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