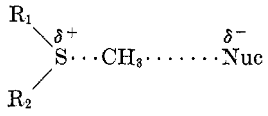

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assume that a similar transition state is involved in methyl transfer from any methylsulfonium compound. In order to test this hypothesis, we are continuing the study of nonenzymic transmethylation on molecules which are more closely related to SAM in structure, but which are not so readily decomposed in basic media.

Registry No.—**2a**, 29898-80-4; **2b**, 29843-53-6; **2c**, 29898-81-5; **2d**, 29898-82-6; **2e**, 5556-64-9; **2f**, 5556-65-0; **2g**, 29913-34-6; **2h**, 29913-35-7; **2i**, 29913-36-8; **2j**, 29913-37-9; **2k**, 29913-38-0; **2l**, 29890-17-3; **3a**, 10504-64-0; **3b**, 706-63-8.

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Catalysis of Nucleophilic Substitutions by Micelles of Dicationic Detergents[1]

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Dicationic detergents (I), $\mathrm{RN^+Me_2(CH_2)_nN^+Me_2R\ 2Br^-}$ (where R = cetyl and $n = 4$ and 6), readily micellize, and the micelles are effective catalysts of the reactions of hydroxide ions with chloro- and fluoro-2,4-dinitrobenzene and hydroxide and fluoride ions with *p*-nitrophenyl diphenyl phosphate. With $n = 4$ and 6, those detergents are two- to fivefold better catalysts than cetyltrimethylammonium bromide, CTABr. The dicationic detergent $\mathrm{RN^+Me_2CH_2C{\equiv}CCH_2N^+Me_2RBr_2^-}$ also micellizes, but it and I ($n = 2$) are not markedly better catalysts than CTABr.

Catalysis by ionic micelles and polyelectrolytes is well established and has been extensively reviewed.[3-6] The catalysis can be explained qualitatively in terms of the ionic and hydrophobic interactions of the reactants and transition state with the micelle, and, although strong binding is observed between substrate and many micelles,[7,8] micellar catalysis is generally relatively small *e.g.*, in the 10–100 range. Micellar catalysis can be increased by introducing the reagent into the micelle,[9] either by chemical binding or by comicellization,[10] and modification of the micellar structure is another approach.[8c] Polyelectrolyte catalysis is often much larger than micellar catalysis.[3] Micelles have very mobile structures,[11] whereas the charged groups in a polyelectrolyte are linked by alkyl or other chains, and we have therefore prepared a series of dicationic detergents (I and II), which combine some features of polyelectrolytes and detergents and compared their effectiveness as catalysts with that of cetyltrimethylammonium bromide (CTABr) for anionic nucleophilic attack upon uncharged substrates in the hope of increasing the effectiveness of micellar catalysis and the ease of micellization. The reactions used were those of hydroxide ion with chloro- and fluoro-2,4-dinitrobenzene (2,4-DNCB and DNFB),[8a,12] and hydroxide and fluoride ion with *p*-nitrophenyl diphenyl phosphate.[8b,c] There was also a possibility that some of these dicationic detergents might not form micelles because of constraints imposed by the bridging methylene chains, or the butyne group, and therefore the critical micelle concentrations (cmc) were also measured. We found that these dicationic detergents were sometimes catalytically active at very low concentrations and more effective than CTABr.

$$\underset{\mathrm{I}}{\mathrm{RMe_2\overset{+}{N}(CH_2)_n\overset{+}{N}Me_2R\ 2Br^-}}\qquad \underset{\mathrm{II}}{\mathrm{RMe_2\overset{+}{N}CH_2C{\equiv}CCH_2\overset{+}{N}Me_2R\ 2Br^-}}$$

R = cetyl; $n = 2$, 4, 6 for Ia, b, c, respectively

Experimental Section

Materials.—The *N,N'*-tetramethyldiamines were commercial products (Aldrich) and were redistilled before use. They were quaternized with a 10% excess of cetyl bromide in refluxing ethanol under nitrogen for 2–3 days (12 days for the ethane derivative, Ia). The detergents were precipitated with ether after evaporation of the bulk of ethanol, washed well with ether, and recrystallized from aqueous ethanol. The values of the cmc and the elemental analyses are given in Table I.

In order to make certain that both amino groups were quaternized, we showed spectrophotometrically that the reaction of hydroxide ion with the fluoro- or chloro-2,4-dinitrobenzene gave 2,4-dinitrophenol rather than the dinitroaniline which would have been formed had the solution contained free amine.

Kinetics.—The reactions were followed spectrophotometrically using a Gilford spectrophotometer with a water-jacketed cell compartment at 25.0° following methods already described.[8,12] *p*-Nitrophenyl diphenyl phosphate was added as a solution in purified dioxane, so that the final solution contained 0.5%

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[1] Support of this work by the National Science Foundation and the Arthritis and Metabolic Diseases Institute of the U. S. Public Health Service is gratefully acknowledged.

[2] Recipient of an award under Project Catalyst of the American Chemical Society.

[3] H. Morawetz, *Advan. Catal. Relat. Subj.*, **20**, 341 (1969); *Accounts Chem. Res.*, **3**, 354 (1970).

[4] E. H. Cordes and R. B. Dunlap, *ibid.*, **2**, 329 (1969).

[5] E. J. Fendler and J. H. Fendler, *Advan. Phys. Org. Chem.*, **8**, 271 (1970).

[6] T. C. Bruice, in "The Enzymes," Vol. 2, 3rd ed, Academic Press, New York, N. Y., 1970, p 217.

[7] (a) F. M. Menger and C. E. Portnoy, *J. Amer. Chem. Soc.*, **89**, 4698 (1967); (b) D. G. Herries, W. Bishop, and F. M. Richards, *J. Phys. Chem.*, **68**, 1842 (1964).

[8] (a) C. A. Bunton and L. Robinson, *J. Amer. Chem. Soc.*, **90**, 5972 (1968); (b) *J. Org. Chem.*, **34**, 773 (1969); (c) C. A. Bunton, L. Sepulveda, and L. Robinson, *ibid.*, **35**, 108 (1970).

[9] (a) C. E. Wagner, C.-J. Hsu, and C. S. Pratt, *J. Amer. Chem. Soc.*, **89**, 6366 (1967); (b) T. C. Bruice, J. Katzhendler, and L. R. Fedor, *ibid.*, **90**, 1333 (1968); (c) C. A. Bunton, M. Stam, and L. Robinson, *ibid.*, **92**, 7393 (1970).

[10] C. Gitler and A. Ochoa Solano, *ibid.*, **90**, 5004 (1968).

[11] K. Shinoda, T. Nakagawa, B.-I. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York, N. Y., 1963, Chapter 1; P. H. Elworthy, A. T. Florence, and C. B. Macfarlane, "Solubilization by Surface Active Agents," Chapman and Hall, London, 1968, Chapter 1.

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

TABLE I

PROPERTIES OF THE DICATIONIC DETERGENTS

Bridging group	10^5 cmc, M^a	Formula	Calcd, % C	H	N	Br	Found, % C	H	N	Br
Ia ethane	1	$C_{38}H_{82}N_2Br_2H_2O$	61.3	11.4	3.8	21.4	61.5	11.5	3.8	21.9
	1.4^b									
	1.0^c									
Ib butane	3	$C_{40}H_{86}N_2Br_2H_2O$	62.2	11.5	3.6	20.7	61.9	11.7	3.5	20.9
	3.2^b									
	3.5^c									
Ic hexane	7	$C_{42}H_{90}N_2Br_2$	64.4	11.5	3.6	20.6	64.5	11.8	3.7	20.7
	6.5^b									
	7.0^c									
	6.5^d									
II butyne	1	$C_{40}H_{82}N_2Br_2$	64.0	11.1	3.7	21.3	63.9	11.1	3.7	21.0

[a] Measured using the dye method unless specified; addition of 10^{-5} M p-nitrophenyl diphenyl phosphate and 0.5 vol % dioxane did not change the cmc of Ia. [b] Measured by surface tension. [c] In the presence of 0.01 M NaOH. [d] In the presence of 0.01 M NaF.

dioxane, and for the reaction in which fluoride ion was the nucleophile the solution was maintained at pH 9.0 using 0.01 M sodium borate. The concentrations of the substrates were $<10^{-5}$ M. The first-order rate constants, k_ψ, sec^{-1}, were calculated graphically, and the second-order rate constants, k_2, are in l. mol^{-1} sec^{-1}.

Critical Micelle Concentrations.—The values of the cmc were determined by the dye method,[11,13,14] using bromophenol blue (Table I). We also attempted to determine the cmc conductometrically[11,15] but were unable to observe breaks in plots of equivalent conductance against concentration characteristic of micellization, probably because the free detergent is a weak electrolyte. Because of the low cmc's we were unable to use viscosity measurements for determining them, but in favorable cases the cmc can be determined by surface tension measurements.[11] Plots of the surface tension against log C_D (where C_D is the detergent concentration) decreased with increasing C_D to a sharp break at the cmc, and then remained constant up to concentrations several fold greater than the cmc. The surface tension was measured conventionally by De Nouy's method.

Results

The rate constants are shown as a function of detergent concentration in Figures 1 and 2 and Tables II–VI.

TABLE II

REACTION OF HYDROXIDE ION WITH p-NITROPHENYL DIPHENYL PHOSPHATE[a]

10^4C_D, M	Detergent Ib	Ic
5.00	9.58	13.2
7.50		10.5
8.00	7.67	
10.0	7.39	9.16
20.0	5.84	6.86

[a] Values of k_2, l. mol^{-1} sec^{-1}, at 25.0° with 0.01 M NaOH and high concentrations of Ib,c.

(Note the break in the scale of Figure 2 which allows the plot to cover a wide range of detergent concentration.) The results for reactions of p-nitrophenyl diphenyl phosphate are given in Figures 1 and 2, Table II includes rate constants at higher concentrations of Ib,c, and Table III gives rate constants in the presence of II. These results show that very low concentrations of detergent have little kinetic effect. Tables IV–VI give rate constants for reactions of the halobenzenes.

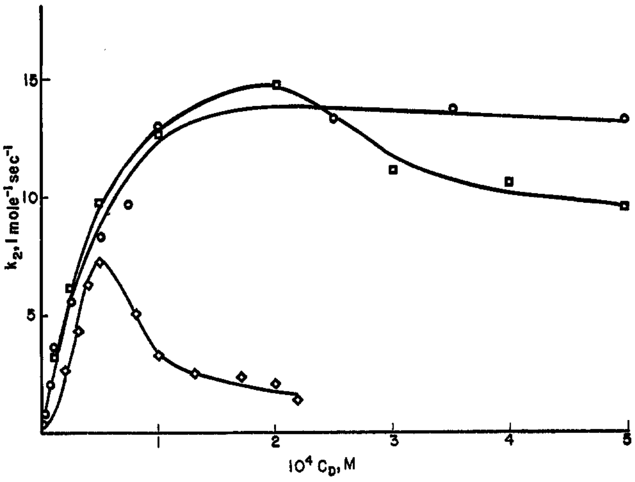

Figure 1.—Catalysis by dicationic detergents of the reaction of 0.01 M sodium hydroxide with p-nitrophenyl diphenyl phosphate at 25.0°: ◇, Ia; □, Ib; ○, Ic.

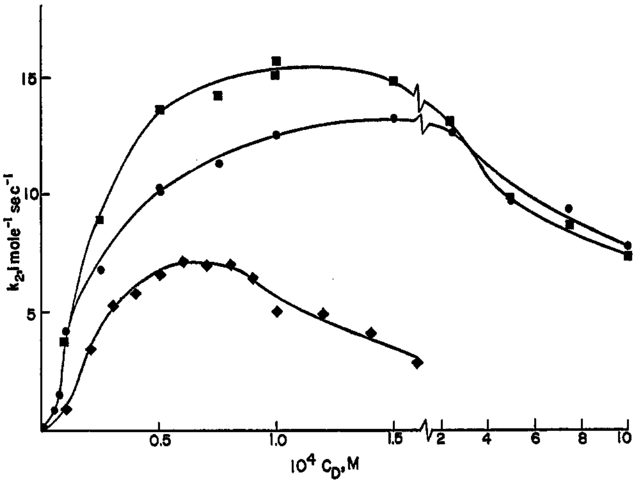

Figure 2.—Catalysis by cationic detergents of the reaction of 0.01 M sodium fluoride with p-nitrophenyl diphenyl phosphate at 25.0° and pH 9.0: ◆, Ia; ■, Ib; ●, Ic.

Neither of the detergents Ia or II derived from the ethane- and butyneamines were effective catalysts of the reaction of hydroxide ion with chloro- and fluoro-2,4-dinitrobenzene (Tables IV and VI). Both of these detergents are less soluble than CTABr and the detergents (Ib,c) derived from the butane- and hexanediamines, and little catalysis was observed within the concentration limits imposed by solubility; this factor pre-

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(13) M. L. Corrin, H. B. Klevens, and W. D. Harkins, *J. Chem. Phys.*, **14**, 480 (1946).

(14) P. Mukerjee and K. J. Myseis, *J. Amer. Chem. Soc.*, **77**, 2937 (1955).

(15) R. J. Williams, J. N. Phillips, and K. J. Mysels, *Trans. Faraday Soc.*, **51**, 728 (1955).

TABLE III

REACTIONS OF *p*-NITROPHENYL DIPHENYL PHOSPHATE WITH HYDROXIDE AND FLUORIDE IONS[a]

	Reagent			Reagent	
10^4C_D, *M*	OH^-	F^-	10^4C_D, *M*	OH^-	F^-
0	4.83	1.05	1.50	31.6	64.9, 68.1
0.01		0.99	2.00	47.8	70.9
0.02		1.00	2.50		89.1
0.05		1.40	3.00	56.8	94.8
0.25		32.0	3.50	45.5	97.2
0.50	5.60	40.6	4.00	61.5	92.4
1.00	13.2	60.9	4.50	58.0, 61.7	88.1

[a] Values of $10k_2$ l. mol^{-1} sec^{-1}, with 0.01 *M* nucelophile at 25.0°, with II.

TABLE IV

REACTION OF HYDROXIDE ION WITH FLUORO-2,4-DINITROBENZENE[a]

	Detergent		
10^4C_D, *M*	Ia	Ib	Ic
	0.12	0.12	0.12
0.20	0.21	0.47	
0.30	0.24		0.52
0.40	0.37		
0.50	0.41	1.17	0.87
0.60	0.41		
0.75	0.39		1.43
0.90	0.34		
1.00	0.34	2.03	2.09
1.40	0.27		
1.60	0.24		
2.00		2.84	
3.00			4.78
3.00		3.84	
5.00		7.28	6.87
7.50			9.24
10.0		9.98	12.0
20.0		13.3	
30.0		16.0	14.3
36.0		16.9	14.2
50.0		17.2	
70.0		17.9	14.2

[a] Values of k_2, l. mol^{-1} sec^{-1} at 25.0° and 0.01 *M* NaOH.

vented our studying some of these reactions in detail over a range of detergent concentrations.

Critical Micelle Concentrations.—For all these dicationic detergents the values of the cmc are much lower (Table I) than those found for a cationic detergent such as CTABr for which cmc ≈ 10^{-3} *M*[11] (the actual value depends upon the medium and the method of measurement).

The cmc values were first obtained using a dye which could affect micellization,[11,14] particularly because the cmc is sometimes not much larger than the dye concentration of 1–10 × 10^{-5} *M*. (Lower dye concentrations were used with those detergents which had the lowest cmc.) Although the dye method is not particularly reliable, the cmc values using this method and that of surface tension are in reasonable agreement.

We generally observed catalysis at detergent concentrations considerably below the cmc. We therefore measured the cmc under conditions corresponding more closely to those used in the kinetic runs and found little change in the cmc (Table I).

Quantitative Treatment of the Rate Data.—It is generally assumed that micellar catalysis and inhibition of the substrate, S, with X^- can be interpreted in terms of the following scheme[5,7a,8]

$$\begin{tikzcd} D_n + S \arrow[rr, shift left, "K"] \arrow[dr, "k_2^{w}", "X^-"'] & & SD_n \arrow[ll, shift left] \arrow[dl, "k_2^{m}"', "X^-"] \\ & \text{products} & \end{tikzcd}$$

leading to the rate equation

$$k_2 = \frac{k_2^{w} + k_2^{m}(K/N)(C_D - \text{cmc})}{1 + (K/N)(C_D - \text{cmc})} \tag{1}$$

where C_D is the detergent concentration and N the aggregation number. Equation 1 can be written as[7a]

$$\frac{1}{k_2 - k_2^{w}} = \frac{1}{k_2^{m} - k_2^{w}} + \frac{N}{(k_2^{m} - k_2^{w})K(C_D - \text{cmc})} \tag{1a}$$

This treatment assumes that only one substrate molecule is incorporated into each micelle, D_n, an assumption which is reasonable when the micelles are in a large excess over the substrate. It has been used successfully for a number of spontaneous reactions but cannot be applied in any simple way for many reactions which involve an external ionic reagent, because these reactions generally lead to rate maxima in plots of rate constant against detergent concentration,[4,5,8,16] whereas eq 1 predicts a rate plateau. These rate maxima have

TABLE V

REACTION OF HYDROXIDE ION WITH CHLORO-2,4-DINITROBENZENE[a]

	Detergent		
10^4C_D, *M*	Ia	Ib	Ic
0	1.4	1.4	1.4
0.10	1.6	6.36	
0.25	3.4	13.8	7.4
0.40	4.0[b]		
0.50		28.4	14.9
0.75		40.0	24.0
1.00		70.6	34.6
1.50			54.4
2.50		152	76.4
5.00		169	137
7.50		198	168
10.0		212	207
20.0		255	220
36.0		244	
50.0		238	208
60.0		205	206

[a] Values of 10^4k_2, l. mol^{-1} sec^{-1}, at 25.0° and 0.05 *M* NaOH; with 1 × 10^{-5} *M* II, 10^4k_2 = 1.5 l. mol^{-1} sec^{-1}. Higher detergent concentrations could not be used because of the low solubility of II in 0.05 *M* NaOH. [b] Precipitation occurred at higher concentrations of Ia.

TABLE VI

REACTION OF FLUORO-2,4-DINITROFLUOROBENZENE WITH HYDROXIDE ION[a]

10^4C_D, *M*	$10k_2$, l. mol^{-1} sec^{-1}
0	1.20
0.05	0.90
0.10	1.20
0.15	1.00
0.20[b]	1.14

[a] With II and 0.01 *M* NaOH at 25.0°. [b] Precipitation occurred at this and higher concentrations.

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[16] R. B. Dunlap and E. H. Cordes, *J. Amer. Chem. Soc.*, **90**, 4395 (1968); L. R. Romsted and E. H. Cordes, *ibid.*, **90**, 4404 (1968).

TABLE VII

RATE ENHANCEMENTS[a]

	Detergent									
	CTABr		Ia		Ib		Ic		II	
Reaction[b]	k_r	C_D (max)	k_r	C_D (max)	k_r	C_D (max)	k_r	C_D (max)	k_r	C_D (max)
$ArOPO(OPh)_2 + OH^-$	11	4×10^{-3}	15	5×10^{-5}	30	2×10^{-4}	28	3×10^{-4}	12	4×0^{-4}
$ArOPO(OPh)_2 + F^-$	33	2×10^{-3}	72	7×10^{-5}	155	1×10^{-4}	182	1.5×10^{-4}	93	3.5×10^{-4}
2,4-DNFB + OH^- [c]	60	2×10^{-2}	36	6×10^{-5}	150	7×10^{-3}	120	4×10^{-3}		
2,4-DNCB + OH^- [c]	61	1.4×10^{-2}			182	2×10^{-3}	157	2×10^{-3}		

[a] In water at 25.0° k_r is the maximum relative to that in water. [b] Ar = *p*-nitrophenyl. [c] The rate maxima could not be reached for these reactions with some of the detergents.

been explained in terms of ionic deactivation by the micelle[8,17] (for an alternative explanation, see ref 4 and 16).

In favorable cases the binding constant, K, can be determined directly,[4,5,7b,8] but this procudure is not feasible for a number of substrates such as fluoro-2,4-dinitrobenzene where there is a slow reaction even at low pH in the presence of cationic detergents.[12]

For the reaction of hydroxide ion with fluoro-2,4-dinitrobenzene in the presence of the detergents derived from the butane- and hexanediamines (Ib,c), we unexpectedly observed plateaus rather than rate maxima in plots of rate constant against detergent concentration (Table IV). We therefore attempted to apply eq 1a to these two reactions. A major problem is that, in using eq 1a, it is necessary to assume that the cmc in the kinetic solution is that determined in the absence of substrate. This assumption is clearly unsatisfactory because in all these reactions there is extensive catalysis at detergent concentrations below the cmc (Table I). This behavior appears to be general with substrates which are strongly incorporated into the micelle, suggesting that submicellar aggregates are catalytically active or that the substrate promotes micellization.[8b,9b,15] (There is considerable evidence for promotion of micellization by added solutes.[11])

Because eq 1a cannot be used, we rewrite it as[8b]

$$\frac{k_2 - k_2^{w}}{k_2^{m} - k_2} = \frac{K}{N}(C_D - \text{cmc}) \tag{2}$$

which can be used without making any assumptions about the cmc, except that it is constant under the reaction conditions, although it is necessary to assume that k_2^m is given by the values of k_2 in the plateau region at the high detergent concentrations, and use of eq 2 places a great deal of weight on the values of k_2 at intermediate detergent concentrations. Figure 3 illustrates the treatment for the reaction of fluoro-2,4-dinitrobenzene with 0.01 *M* sodium hydroxide in solutions of the dicationic detergents (Ib,c) derived from the butane and hexane diamines and gives values of $K/N \approx 1300$ and 2000, respectively.

We could not calculate K/N for fluoro-2,4-dinitrobenzene in CTABr using either kinetic or distribution methods,[12] but for chloro-2,4-dinitrobenzene in CTABr $K/N \approx 75$.[8a] (For the anionic detergent sodium lauryl sulfate, K/N is approximately the same for chloro- and fluoro-2,4-dinitrobenzene,[8a,12] and this is therefore probably true also for CTABr.) Also we do not know the value of the aggregation number, N, for micelles of these dicationic detergents, although because of methylene bridging they could well be smaller than for CTABr, but our kinetic results suggest that these micellized dicationic detergents (Ib,c) derived from the butane- and hexanediamines are much better than CTABr at binding nonpolar solutes. Even though the treatments based on eq 1 depend on a variety of assumptions and approximation, the indications of strong substrate–micelle binding are supported by the steepness of plots of rate constant against detergent concentration for all these dicationic detergents.

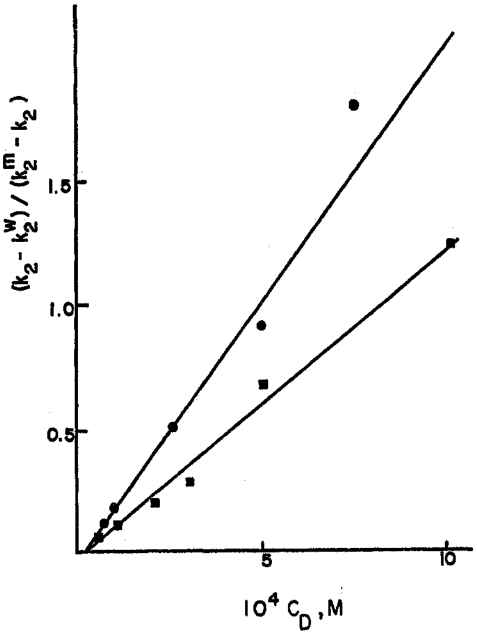

Figure 3.—Quantitative treatment of the micellar catalyzed reaction of 0.01 *M* sodium hydroxide with 2,4-dinitrofluorobenzene at 25.0°: ■, Ib; ●, Ic.

Discussion

In Table VII we compare the maximum rate enhancements (relative to rates in the absence of detergent) and the corresponding detergent concentrations for these dicationic detergents with those observed earlier using CTABr.[8,12] These results illustrate the greater catalytic efficiency of most of these detergents over CTABr. For most of these reactions the rate maxima are observed at lower detergent concentrations with these dicationic detergents than with CTABr.[8,12]

The critical micelle concentrations are also considerably lower with micelles derived from these dicationic detergents as compared with CTABr. Micellization occurs when hydrophobic binding overcomes the electrostatic repulsions, and bridging the quaternary ammonium residues should therefore stabilize the micelles provided that the bridging group is not so rigid as to

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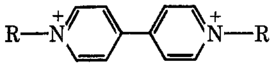
[17] G. J. Buist, C. A. Bunton, L. Robinson, L. Sepulveda, and M. F. Stam, *J. Amer. Chem. Soc.*, **92**, 4072 (1970).

make it difficult for the long alkyl chains to bind together. Ethane and butyne bridging groups should impose a considerable degree of rigidity upon the detergents and make it difficult for them to form approximately spherical micelles, but even here micellization is observed and the cmc's are low. Micelles of monocationic detergents are approximately spherical,[5,11] but this may not be true with micelles of Ia and II, and evidence on the size and shape of these micelles is needed.

The fact that rate maxima or plateaus are observed at low concentrations of these dicationic detergents, relative to CTABr, indicates strong interactions between substrate and micelle. (The low cmc is also a factor, because micelles then form at low detergent concentration.) The concentrations for rate maxima are smaller by a factor of 10–100 for these dicationic detergents than for CTABr[8,12] (Table VII). This rate enhancement at low catalyst concentration is one measure of effectiveness; another is the extent of the rate enhancement. On this score also, these dicationic detergents are better micellar catalysts for some reactions than CTABr, although the relative effectiveness depends very much upon the reaction under consideration (Table VII). The dicationic detergents (Ib,c) derived from the butane- and hexanediamines are better catalysts than CTABr for all the reactions considered, but their superiority is most marked for the reaction of fluoride ion with *p*-nitrophenyl diphenyl phosphate. The bridging methylene chain which increases micellar stability could also sterically hinder approach of the anionic nucleophile to a phosphate ester at or near the micellar surface, and this hindrance could be less for an attacking fluoride than for the more strongly hydrated hydroxide ion.

The detergents Ia and II derived from the ethane- and butynediamines are no better catalysts than CTABr for the attack of hydroxide ion upon the substrates (Table VII). They are, however, very effective catalysts when fluoride is the attacking anion, as appears to be general for micelles of these dicationic detergents.

Some studies on the bipyridylium ions (III) have



III

some bearing on the properties of our dicationic detergents I and II. The dications III are very readily reduced to radical cations,[18] whose stabilization requires coplanarity of the rings, but, if R = cetyl, the radical cation does not form,[19] probably because bonding of the alkyl groups in a micelle forces the rings into a nonplanar skew conformation.

Catalysis by Submicellar Aggregates.—In some reactions, *e.g.*, those catalyzed by Ia, the maximum rate is observed at detergent concentrations below the cmc, *i.e.*, in a region where the detergent is apparently not micellized, and where it is not in a large excess over the substrate.

The simple treatment of micellar catalysis, eq 1, assumes that only a fully formed micelle is catalytically active, and that incorporation of the substrate does not markedly perturb the structure of the micelle.[5,7a] This treatment is rarely completely satisfactory because catalysis is often observed at detergent concentrations below the cmc, and there is evidence for the promotion of micellization by added solutes.[11,14] It seems that these effects are more than usually important for reactions catalyzed by these dicationic detergents, especially Ia.

One additional aspect of micellar catalysis by Ia is the very sharp decrease of the rate constant with increasing detergent concentration past that for the rate maximum. Although we cannot interpret the rate profiles quantitatively, this steep fall suggests that this detergent (relative to the others) interacts very strongly with the nucleophilic anion so that there is considerable deactivation of it at high detergent concentrations.

Comparison between the catalytic effectiveness of these dicationic detergents with that of CTABr brings out the way in which structural changes can affect micellar catalysis, and at present we have no explanation for the large differences in the rate enhancements of reactions which are at first sight very similar (Table VII).

Registry No.—Ia, 21948-95-8; Ib, 29908-17-6; Ic, 15590-96-2; II, 29843-46-7; *p*-nitrophenyldiphenyl phosphate, 10359-36-1; 2,4-DNFB, 70-34-8; 2,4-DNCB, 97-00-7.

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[18] L. Michaelis, *Biochem. Z.*, **250**, 564 (1932).

[19] M. F. Stam, Thesis, University of Liverpool, England, 1969.