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Micellar Effects upon Spontaneous Hydrolyses and Their Relation to Mechanism

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Abstract: Cationic micelles of cetyltrimethylammonium surfactants (CTAX; X = Cl, Br, OMes, $0.5SO_4$) and anionic micelles of sodium lauryl sulfate (NaLS) typically inhibit spontaneous hydrolyses. The substrates were $(4\text{-}YC_6H_4CO)_2O$ (Y = *t*-Bu, H, NO_2, CN), $(4\text{-}YC_6H_4O)_2CO$ and $4\text{-}YC_6H_4OCOCl$ (Y = H, NO_2), PhCOCl, $PhCH_2Br$, $PhSO_3Me$, and $o\text{-}C_6H_4(CO)_2O$. Hydrolysis of $4\text{-}O_2NC_6H_4OCOCl$ is slightly speeded by CTABr, but the other hydrolyses are inhibited by both anionic and cationic micelles. Micellar inhibition of anhydride hydrolysis increases with increasing hydrophobicity of the substrate, which will cause it to reside more deeply in the micelle, away from the water-micelle interface. There is also a mechanistic effect, because hydrolyses of acyclic anhydrides, carbonates, and chloroformates are faster in cationic than in anionic micelles, which is consistent with the transition state having anionic character. The S_N2 hydrolysis of $PhSO_3Me$ is also faster in CTAOMes than in NaLS. Hydrolyses of $PhCH_2Br$, PhCHMeCl, Ph_2CHCl, Ph_2CHBr, and PhCOCl are faster in NaLS than in cationic micelles, and the effect of micellar charge is largest for reactions of Ph_2CHCl and Ph_2CHBr, where the transition state has the greatest carbocationic character. Halide micellar counterions do not react with the acyl or alkyl halides, but they attack $PhSO_3Me$. Carbocations generated by heterolysis of Ph_2CHCl or Ph_2CHBr are not trapped by halide counterions. Relative rates in cationic and anionic micelles are insensitive to substrate hydrophobicity but appear to be indicative of reaction mechanism.

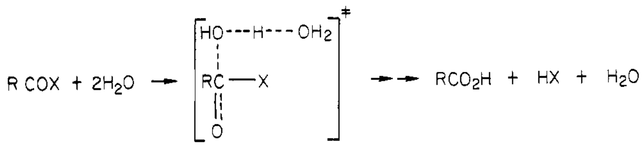
Micellar effects upon bimolecular reactions in aqueous systems have been extensively studied, but there has been less work on spontaneous unimolecular or bimolecular water-catalyzed reactions.[1] These reactions are important because micellar effects on unimolecular reactions provide direct evidence on the role of the micelle as a reaction medium,[5,6] and those on water-catalyzed reactions should give evidence on the reactivity of water in the micellar pseudophase.[7-9]

The polarity of the micellar surface appears to be lower than that of water,[10,11] and S_N1 reactions are slower in micelles than in water,[9,12-14] but spontaneous anionic decarboxylations and decompositions of anionic aryl phosphates and sulfates are faster.[5,6]

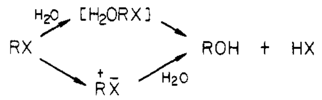
Spontaneous water-catalyzed hydrolysis of bis(4-nitrophenyl) carbonate is slightly slower in micelles of cetyltrimethylammonium bromide (CTABr) than in water,[9b] and micelles have little effect on rates of water addition to preformed carbocations[7] or on the equilibrium constant for aldehyde hydration,[8] suggesting that these reactions are occurring in a water-rich environment.[9]

Micellar effects upon bimolecular ionic reactions are clearly dependent upon the charge type of the reaction,[2,16] and the extent to which the micelle brings reactants together or keeps them apart. For many nonsolvolytic bimolecular reactions, second-order rate constants in the micellar pseudophase are similar to, or smaller than, those in water.[3,4,17] The situation is less obvious for unimolecular or water-catalyzed reactions where water is omnipresent. The micellar pseudophase can be considered akin to a solvent, except that reactions in ionic micelles are not occurring in an electrically neutral medium.[18]

Scheme I



Scheme II



Our approach was to investigate the effect of micellar charge upon a series of spontaneous reactions. The initial, and often the rate limiting, step in deacylation is carbonyl addition, which is often concerted with proton loss to a general base,[20] which in our system is a water molecule (Scheme I).[20,21]

Substitution at a saturated carbon atom is often described in terms of a duality of mechanism, with an S_N1 reaction going by spontaneous bond breaking to give a reactive carbocation, or ion pair, and an S_N2 mechanism involving concerted bond making

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(1) For general references on micellar rate effects, see ref 2-4.

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(18) For most ionic micelles, counterions are associated on the average with ca. 70% of the head groups, so that there is ca. 30% unit charge per micellized surfactant.[19]

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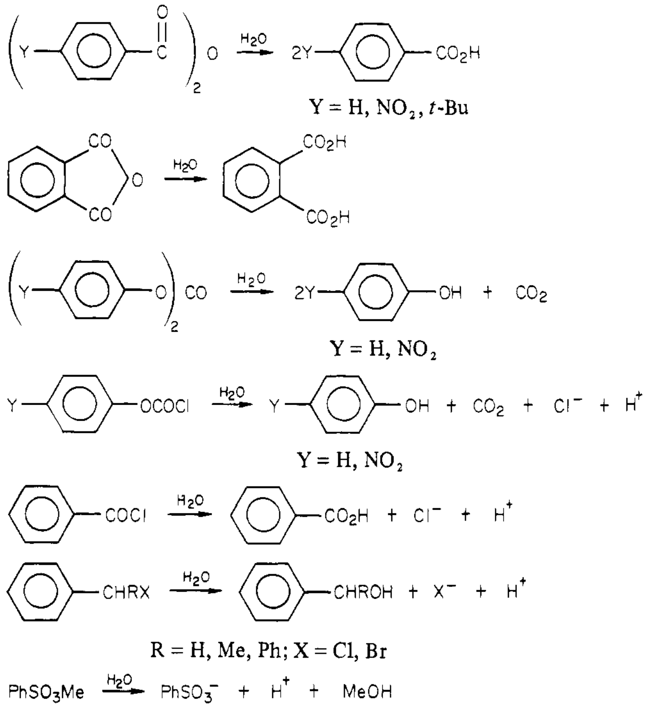
Scheme III

$$Ar_2CHX \rightleftarrows X^- + Ar_2C^+H \rightarrow Ar_2CHOH$$

Scheme IV



and breaking.[22] One can also describe those processes in terms of a mechanistic continuum (Scheme II), and most recent discussions follow this approach.[23]

As acyl substrates, we used carboxylic anhydrides and carbonate esters, for which the rate-limiting step is almost certainly nucleophilic addition,[21,24] and chlorides, where the mechanism could involve carbonyl addition or be S_N-like with extensive C–Cl bond breaking in the transition state. In studying substitution at saturated carbon, we used alkyl halides or methanesulfonates and varied the alkyl group.

The common ion effect is observed in S_N1 reactions when a relatively long-lived carbocation can be recaptured by the leaving anion. For example, solvolysis of diarylmethyl halides is often inhibited by the common halide ion (Scheme III).[22]

This process could occur in a cationic micelle having a halide counterion, e.g., in cetyltrimethylammonium halide, because of the high concentration of halide counterion at the micellar surface.[19]

As an anionic surfactant we used sodium lauryl sulfate (NaLS), and as cationic surfactants, cetyltrimethylammonium chloride, bromide, mesylate, and sulfate (CTACl, CTABr, CTAOMes, and $(CTA)_2SO_4$, respectively).

There is no net change of charge in these spontaneous uni- and bimolecular reactions, but in deacylation the positive charge upon the attacking water molecule is dispersed into other solvent water molecules (Scheme I) so that an anionoid organic moiety could interact favorably with a cationic micellar head group. The situation is more complicated in an S_N reaction where the transition state may be akin to an ion pair or to an intermediate with partial positive and negative charges on the incoming water and the leaving anion (Scheme II).

Table I. Substrate Reactivities in Water and Effects of Micellar Charge on Reactivity[a]

		surfactant[b]			
substrate	$10^3k_W'$, s^{-1}	CTABr	CTACl	CTA_2-SO_4	CTAOMes
$(PhO)_2CO$	0.0035	large			
$(4\text{-}O_2NC_6H_4O)_2CO$	0.45	5			
$(4\text{-}t\text{-}BuC_6H_4CO)_2O$	0.21	1.6			
$(PhCO)_2O$	0.33	2			
$(4\text{-}NCC_6H_4CO)_2O$	3.40	1.9		1.7	
$(4\text{-}O_2NC_6H_4CO)_2O$	26.6	2.6			
$o\text{-}C_6H_4(CO)_2O$	12.6	0.9			
PhOCOCl	13.6	1.8		1.7	
$4\text{-}O_2NC_6H_4OCOCl$	76.0	5	5	5.5	
PhCOCl	86.0	0.7			
$PhSO_3Me$	0.011				1.8
$PhCH_2Br$	0.156	0.7			≈0.7
PhCHMeCl	51.0	<0.5	0.15	0.15	
Ph_2CHCl	990[c]	≈0.02	≈0.01	≈0.02	
Ph_2CHBr	7760[c]	v s[d]	v s	v s	

[a] In water at 25.0 °C. [b] Values of k^+/k^-, relative to reaction in NaLS. [c] Calculated from data in ref 28. [d] Very small.

Therefore micellar effects should depend upon reaction mechanism and micellar charge. For example, in an S_N1 reaction in a micelle, water nucleophilicity should not be important, as compared with solvation of the leaving anion,[25] but charge interactions with the carbocationic center may be. On the other hand, water reactivity and micellar medium effects should be important in deacylations. We hoped to see relations between micellar effects and the mechanisms of spontaneous reactions. Water reactivity should not depend markedly on micellar charge, but interactions between ionic micelles and polar transition states could depend on mechanism, and relative rate effects of cationic and anionic micelles should provide mechanistic information on the reactions shown in Scheme IV.

The nonmicellar solvolyses have been extensively studied, although often in organic or mixed solvents,[20-24,26,27] and we therefore measured the rate constants of solvolysis in water or estimated them from data in mixed solvents by using the Grunwald–Winstein equation.[28]

Experimental Section

Materials. The preparation and purification of most of the surfactants followed standard methods.[2,5] In particular, sodium lauryl sulfate (BDH) was recrystallized several times (H_2O) and was then washed with Et_2O and dried under vacuum until there was no minimum in a plot of surface tension against concentration.

The substrates were commercial samples, recrystallized or redistilled as necessary, or were prepared by standard methods.

Kinetics. Reactions were followed spectrophotometrically with Gilford or Beckman spectrophotometers with standard procedures.[9b,21d,24c] The substrates were added to the reaction solutions in 1-cm cuvettes as relatively concentrated solutions in MeCN, so that the final reaction mixture contained 0.1% of MeCN and the substrate concentrations were in the range 10^{-5}–10^{-4} M. These concentrations were chosen so as to give absorbance changes of 0.1–0.5 in the course of reaction; some of the substrates react readily with OH^-, and these reactions were suppressed by addition of strong acid (10^{-3}–10^{-2} M), corresponding to the counteranion of the surfactant (variation of $[H^+]$ did not affect the rate constants).

All the reactions were followed at 25.0 °C in distilled deionized water, and the first-order rate constants (k_ψ) are in reciprocal seconds.

We were able to follow most of the reactions to completion, but where they were too slow, e.g., with diphenyl carbonate in surfactant, we completed the reaction by adding NaOH (equivalent to 10^{-2} M) and then

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(25) The lower polarity of the micelle, as compared with water,[10,11] should result in an inhibiting medium effect on S_N1 reactions that occur most readily in solvents of high polarity.[22]

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Table II. Hydrolysis of Benzoic Anhydrides[a]

	substrate								
	4,4'-(t-Bu)$_2$		4,4'-H$_2$		4,4'-(CN)$_2$			4,4'-(NO$_2$)$_2$	
[D], M	CTABr	NaLS	CTABr	NaLS	CTABr	CTA$_2$SO$_4$	NaLS	CTABr	NaLS
0.001			0.86						
0.002			0.64						
0.0025								0.31	0.90
0.003	0.042								
0.005	0.024	0.033	0.25	0.70				0.29	0.89
0.0075									0.48
0.01	0.018	0.018	0.14	0.34		0.78		0.27	0.34
0.02	0.017	0.015	0.12	0.083	0.77		0.45	0.23	0.10
0.04	0.017	0.011	0.078	0.053	0.74	0.62	0.37	0.22	0.094
0.05			0.061						
0.06	0.017	0.011		0.036	0.68	0.59	0.036	0.21	0.089
0.08				0.030	0.65		0.34	0.21	0.083
0.10				0.030	0.62	0.55		0.21	0.079
0.12							0.32		
0.16							0.32		

[a] Values of k_{rel}. D = surfactant.

Table III. Hydrolysis of Phthalic Anhydride[a]

[D], M	CTABr	NaLS
0.005	0.77	0.72
0.01	0.69	0.67
0.02	0.63	0.60
0.04	0.52	0.51
0.06	0.44	0.47
0.08	0.36	0.38
0.1	0.34	0.34

[a] Values of k_{rel}.

Table IV. Hydrolysis of Diaryl Carbonates[a]

	substrate		
	(PhO)$_2$CO	(4-O$_2$NC$_6$H$_4$O)$_2$CO	
[D], M	CTABr	CTABr	NaLS
0.002		0.86	
0.005	0.17	0.79	0.64
0.01	0.11	0.71	0.27
0.02	0.063	0.62	0.18
0.04	0.060	0.58	0.16
0.06	0.051	0.56	0.12
0.08		0.54	0.11
0.09		0.54	
0.10	0.053	0.54	
0.12		0.54	

[a] Values of k_{rel}.

after a time adding an equivalent amount of HCl and measuring the absorbance corresponding to complete reaction, allowing for dilution. The wavelengths used are the following: formation of phenol and 4-nitrophenol, 270 and 346 nm, respectively; reactions of benzoic, 4-nitrobenzoic, 4-*tert*-butylbenzoic, 4-cyanobenzoic, and phthalic anhydride, 245, 270 260, 260, and 235 nm, respectively; reaction of PhCOCl, 245 nm; reactions of PhCH$_2$Br, PhCHMeCl, Ph$_2$CHCl, Ph$_2$CHBr, and PhSO$_3$Me, 225, 235, 235, 240, and 262 nm, respectively.

In a few experiments the relatively low solubility of CTABr prevented our determining the rate constant for fully micellar bound substrate; here, we quote an upper limit for it.

Results

Reactions in the Absence of Surfactant. The first-order rate contants (k_w') for the spontaneous hydrolyses in water at 25.0 °C are listed in Table I. For some of the sparingly soluble substrates, the reaction medium contained small amounts of MeCN and the rate constants in water were obtained by extrapolation.

Deacylations. The structural effects are as expected, with electron-withdrawing groups generally speeding up hydrolysis.[26,29] Reactions are faster in water than in aqueous organic solvents.

Alkyl Halides and Benzenesulfonate. Reaction is speeded up by α-methyl and phenyl groups[22] (Table I). Rate constants for hydrolysis of Ph$_2$CHCl and Ph$_2$CHBr were obtained by extrapolation.[28]

Reactions in Micellar Solutions. The variations of rate constants with the nature and concentration of the surfactant (designated as D) are illustrated by values of k_{rel}, which is the ratio of the rate constant in the micellar solution to that in water and is <1 for almost all the hydrolyses (Tables II–VIII). The effect of micellar charge is given by k^+/k^-, where k^+ is the rate constant in a cationic micelle and k^- is that in an anionic micelle of NaLS, for fully micellar bound substrate (Table I).

The surfactant concentrations, including those of cetyltrimethylammonium sulfate (CTA$_2$SO$_4$), are given in molarity, so that a solution of CTA$_2$SO$_4$ contains twice the concentration of ammonium ions as equimolar solutions of the other cationic surfactants. As a result, values of k_{rel} decrease more sharply with CTA$_2$SO$_4$ than with the other cationic surfactants, but the limiting values are similar.

The variations of rate constants with [surfactant] are very dependent upon substrate hydrophobicity, which governs the distribution of the substrate between the aqueous and micellar pseudophases. For example, a hydrophobic *p-tert*-butyl substituent should not affect the mechanism of hydrolysis of an anhydride, but it will favor micellar binding of the substrate and therefore sharpen the falloff of rate constant with [surfactant]. For a spontaneous reaction, the variation of rate constant with [surfactant] depends upon the distribution of substrate between the two pseudophases and the rate constant in each.[2,4,9b] In favorable cases these factors can be separated, provided that the concentration of micellized surfactant can be estimated, which generally involves the assumption that the critical micelle concentration (cmc) gives the concentration of monomeric surfactant. This approach fails when reactants are very hydrophobic and promote micellization or when reaction occurs in submicellar aggregates. These situations are not unusual,[5b,30] and we see them here with the more hydrophobic substrates. Therefore we concentrate our attention on the rate constants k^+ and k^- at high [surfactant] where all the reaction occurs in the micelles. In addition, the binding constants of the substrates do not, of themselves, provide mechanistic information, and they are typically insensitive to micellar charge.

Anhydride Hydrolysis. Micelles of CTABr and NaLS inhibit anhydride hydrolysis (Tables II and III), and the rate constants

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Table V. Hydrolyses of Acid Chlorides[a]

	substrate								
	PhOCOCl[b]			4-$O_2NC_6H_4OCOCl$				PhCOCl[c]	
	CTABr	CTA_2SO_4	NaLS	CTABr[c]	CTACl[d]	CTA_2SO_4[d]	NaLS	CTABr	NaLS
0.001					1.08				
0.004					1.20				
0.005	0.85		0.97	1.17 (1.16)			0.95		
0.0075			0.85						
0.01	0.73	0.55	0.68	1.30	1.70	1.38	0.79	0.48	
0.02	0.54		0.50	1.45 (1.46)	1.64	1.46	0.62	0.26	0.53
0.04	0.43	0.45	0.35	1.46 (1.47)		1.91	0.36	0.15	0.31
0.06	0.39	0.35	0.24	1.51	1.67	1.72	0.33		
0.07								0.093	0.19
0.08				1.53 (1.51)			0.32		
0.09	0.35		0.19						
0.10		0.31		1.58		1.77	0.32	0.081	0.15
0.12	0.33		0.18						
0.15			0.19					0.050	0.092
0.20								0.041	0.067
0.25									0.063

[a] Values of k_{rel}. [b] In 10^{-3} M HBr. [c] In 3×10^{-3} M HBr, values in parentheses are in 10^{-2} M HBr. [d] In 10^{-2} M HCl or H_2SO_4.

Table VI. Hydrolysis of Primary Alkyl Substrates[a]

	substrate				
	MeOBs		PhCH$_2$Br		
[D], M	CTAOMes	NaLS	CTABr	CTAOMes	NaLS
0.01	0.95	0.83	0.30		0.75
0.02	0.90	0.71	0.24	0.28	0.42
0.04	0.81	0.60	0.17		0.21
0.06			0.11	0.13	0.15
0.07	0.74	0.41			
0.08			0.094		0.14
0.10	0.71	0.40	0.091	0.097	0.13
0.12		0.39			
0.15					0.13

[a] Values of k_{rel}.

Table VII. Hydrolysis of 1-Phenethyl Chloride[a]

[D], M	CTABr	CTACl	CTA_2SO_4	NaLS
0.01			0.13	0.41
0.02	0.14	0.14	0.072	
0.03			0.047	
0.04	0.067	0.065	0.035	0.18
0.05			0.031	
0.06	0.045	0.047		
0.07			0.020	0.14
0.08	0.032	0.031		
0.10	0.026	0.026	0.017	0.076
0.15		0.015		0.058
0.20		0.0084	0.0085	0.054
0.25			0.0083	
0.40		0.0080		0.054

[a] Values of k_{rel}.

Table VIII. Hydrolysis of Diphenylmethyl Halides[a]

	substrate					
	Ph$_2$CHCl[b]			Ph$_2$CHBr		
[D], M	CTABr	CTACl	CTA_2-SO_3	CTABr	CTACl	CTA_2-SO_4
0.01			0.090			
0.02	0.066	0.078				0.062
0.03			0.045			
0.04	0.037	0.041	0.033	0.049	0.061	0.026
0.05			0.024			0.023
0.07	0.0242	0.026	0.015	0.027	0.026	0.015
0.10	0.015	0.016	0.011	0.018	0.022	0.013
0.12			0.010			
0.15	0.0121	0.011		0.013	0.016	
0.30		0.0076			0.0093	
0.40		0.0074			0.0086	
0.45					0.0082	

[a] Values of k_{rel}. [b] In 0.2 M NaLS, $k_{rel} = 0.52$.

tend toward limiting values with increasing [surfactant]. With the benzoic anhydrides, NaLS is a better inhibitor than CTABr, but for phthalic anhydride both surfactants have similar effects (Tables II and III).

Carbonate Hydrolysis. Both cationic and anionic micelles inhibit hydrolysis of bis(4-nitrophenyl) carbonate (Table IV), and the rate constants reach limiting values with increasing [surfactant]. The inhibition of hydrolysis of bis(4-nitrophenyl) carbonate by CTABr at 25 °C is very similar to that found at 50 °C by Menger and co-workers.[9b]

The hydrolysis of diphenyl carbonate in NaLS is too slow to be followed at 25 °C, and we did not determine this rate constant. However, with both carbonates, NaLS is a better inhibitor than CTABr.

Hydrolysis of Acid Chlorides. Two chloroformates and benzoyl chloride were examined (Table V).

Hydrolysis of phenyl chloroformate follows the usual pattern for carbonyl addition reactions, with micellized NaLS being a better inhibitor than CTABr, but 4-nitrophenyl chloroformate behaves differently from the other substrates in that micellized CTABr, CTACl, and CTA_2SO_4 weakly catalyzed its hydrolysis (Table V).

Benzoyl chloride behaves differently from the chloroformates in that micellized CTABr is a better inhibitor of the hydrolysis than is NaLS (Table V).

We attempted to follow the hydrolysis of cinnamoyl chloride (at 235 nm), but it was too fast to follow in either water or 0.2 M NaLS. However, $k_\psi \approx 0.8$ s^{-1} in 0.2 M CTACl, showing that a cationic micelle inhibits hydrolysis, relative to reactions in water or in anionic micelles.

Reaction rates in cationic micelles are relatively insensitive to the nature of the counteranion (Table V), and for hydrolysis of 4-nitrophenyl chloroformate, CTACl and CTA_2SO_4 are slightly better catalysts than CTABr, showing that halide exchange, giving a more reactive substrate, is unimportant, e.g.:

$$\mathrm{RCOCl} + \mathrm{Br}^- \nrightarrow \mathrm{RCOBr} + \mathrm{Cl}^-$$

Micellar Reactions at Saturated Carbon. Methyl Benzenesulfonate. Halide ions are effective nucleophiles toward MeOBs in the presence of cationic micelles, so the effects on the spontaneous hydrolysis were estimated from experiments in CTAOMes and NaLS (Table VI). Both these surfactants slightly inhibit hydrolysis, with NaLS having the larger effect.

Alkyl Halides. Both anionic and cationic micelles inhibit spontaneous hydrolyses of alkyl halides, but there are striking effects due to micellar charge.

Table IX. Salt Effects upon Hydrolyses in Cationic Micelles[a]

	substrate		
[NaCl], M	PhCHMeCl	Ph_2CHCl[b]	Ph_2CHBr
0.00	1.33	16.0	170
0.05		13.0	
0.10	1.15		140
0.15		11.4	
0.20	1.00		115
0.30	0.84	9.0	
0.40			100
0.60		7.7	

[a] Values of 10^3k_ψ, s^{-1} in 0.1 MCTACl. [b] In 0.07 M CTABr, $10^3k_\psi = 23.9$ and 20.3 s^{-1} with no added salt and with 0.04 M NaBr, respectively.

Reaction of benzyl bromide is inhibited slightly more by cationic than by anionic micelles (Table VI), and this charge effect is more marked for hydrolysis of 1-phenylethyl chloride (Table VII).

The effect of micellar charge is most striking for hydrolysis of diphenylmethyl halides. The reactions are sharply inhibited by cationic micelles regardless of the nature of the counteranion (Table VIII), but anionic micelles of NaLS have much smaller effects. The reaction of Ph_2CHBr is too fast to be followed in either water or 0.2 M NaLS, and we could only just follow hydrolysis of Ph_2CHCl in 0.2 M NaLS, where $k_\psi \approx 0.5$ s^{-1}, i.e.; reaction is only slightly slower than in water where our extrapolated $k_\psi \approx 1$ s^{-1} (cf., ref 28) is subject to a large uncertainty.

Under conditions in which the secondary alkyl halides should be extensively micellar bound, there is a slight inhibition by NaCl or NaBr (Table IX). This appears to be a medium effect, because NaCl gives similar rate decreases with Ph_2CHCl and Ph_2CHBr. If Cl^- captured a carbocation formed from Ph_2CHBr, hydrolysis of this substrate would be sharply inhibited. Hydrolysis of $PhMe_2CCl$ was too fast to be followed by conventional methods in our aqueous solutions.

Discussion

The striking features of the micellar effects upon these spontaneous reactions are the spread of the rate effects, which range from a small acceleration of hydrolysis of 4-nitrophenyl chloroformate by CTAX (Table V) to large retardations, e.g., by factors of ca. 10^2 in hydrolyses of anhydrides by NaLS (Table II) and of secondary alkyl halides by cationic micelles (Tables VII and VIII). The rate effects evidently depend on micellar charge as well as on substrate hydrophobicity. Therefore, considering first the bimolecular, water-catalyzed reactions, we conclude that reactivity of water in the micelle is not the only factor controlling reaction rate, and it is necessary to compare rate constants for fully bound substrate in cationic and anionic micelles rather than rate constants relative to those in water.

The relation of rate constant to [surfactant] depends upon the extent of substrate incorporation in the micelles and the rate constants in the aqueous and micellar pseudophases. In several cases, e.g., deacylations, where reactions of micellar-bound substrates are slower in NaLS than in cationic surfactants, the micellar effects are reversed in dilute surfactant (Table II). This result is due to the relatively high cmc of NaLS (e.g., 8×10^{-3} M) as compared to those of the cationic C_{16} surfactants (cmc $\approx 10^{-3}$ M), which means that substrate incorporation is low in dilute NaLS.[31]

It is difficult to quantify the effects of substrate hydrophobicity, because electronic effects of subbstituents may influence mechanism and therefore micellar effects. However, 4,4′-di-*tert*-butyl benzoic anhydride and benzoic anhydride have similar reactivities in water (Table I), but rate constants fall more steeply with increasing [surfactant] and reach lower limiting values with the more hydrophobic substrate (Table II). These results suggest that the di-*tert*-butyl derivative is, on the average, located in a more apolar region of the micelles (cf., ref 2, 10, and 32). Conversely, values of k_{rel} are increased by polar substituents, e.g., nitro or cyano groups, that will favor substrate location in the more aqueous regions of the micelle.

Reactions of Carbonyl Derivatives. Both cationic and anionic micelles inhibit most of these reactions, but generally reaction in a cationic micelle is faster than in an anionic micelle of NaLS. Water should be somewhat less available in a micelle than in bulk solvent, which should of itself inhibit hydrolysis,[9] regardless of micellar charge, but for cationic micelles there is apparently a compensatory factor that offsets the lowered reactivity of water but is absent, or relatively small, in anionic micelles. The transition state for these carbonyl reactions generally includes a base, e.g., water, that abstracts a proton from the attacking water molecule,[21] leaving the organic moiety with a net negative charge that should interact beneficially with the cationic head groups of a micelle.[33]

Although hydrolyses of acyclic anhydrides and carbonates are faster in cationic micelles than in NaLS (Tables I, II, and IV), hydrolysis of phthalic anhydride is slightly faster in NaLS than in CTABr (Table I and III). The proton inventory method suggests that there are differences in bond making and breaking steps in hydrolyses of acyclic and cyclic anhydrides,[24d] which may be reflected in the micellar effects.

Acid Chlorides. Benzoyl chloride behaves differently from the chloroformates, despite the formal similarities in structure, because reaction is faster in an anionic than in a cationic micelle (Table V). Solvolyses of benzoyl chloride and related acyl halides have been discussed in terms of carbonyl addition, or S_N mechanisms, with the key difference being the extent to which the C–Cl band is broken in the transition state.[26,27b] Breaking of this bond will decrease the anionoid character of the organic moiety in the transition state, and the difference in the micellar effects on hydrolyses of chloroformates and benzoyl chloride suggests that departure of chloride has made considerable progress in the latter reaction. The mechanistic implications of these micellar effects upon the hydrolysis of benzoyl chloride will be considered further after discussion of reactions of alkyl halides and related substrates.

Substitution at Saturated Carbon. The variation of substrate structure was such that we span the S_N2–S_N1 spectrum of mechanism.

Diphenylmethyl chloride and bromide represent one mechanistic extreme, because in some solvents the carbocation is sufficiently dissociated from the halide ion to discriminate between it and other nucleophilic anions and solvent molecules. This common ion effect can cause the kinetics to deviate from first order during reaction.[22,34]

The relatively high concentration of halide ion in the Stern layer of micelles of CTACl or CTABr[19] might cause capture of the diphenylmethyl carbocation by halide at high [surfactant], but this reaction is unimportant. There is no deviation from first-order kinetics when the alkyl chloride is hydrolyzed in CTABr, or the alkyl bromide in CTACl. Interconversion of the alkyl halides during reaction would give such a deviation; as confirmation of these conclusions, we find similar rate constants for reaction in the various cationic micelles (Tables VII and VIII), and the behavior is similar for sulfate and halide micellar counterions.

This evidence suggests that diphenylmethyl halides react in a region of the micelle in which there is sufficient water to capture the cation (or the related ion pair), and Menger's porous cluster model of a micelle explains these results.[9,35–37]

Both cationic and anionic micelles inhibit all these S_N reactions

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[32] Eriksson, J. D.; Gillberg, G. *Acta Chem. Scand.* **1966**, *20*, 2019. Griffith, O. H.; Waggoner, A. S. *Acc. Chem. Res.* **1969**, *2*, 17.

(33) This observation is consistent with rate enhancement by electron withdrawing groups.[29]

(34) A common ion retardation would in any event not be observable in nonmicellar experiments with the very dilute substrate (ca. 10^{-4} M) that we used.

(35) A key feature of Menger's porous cluster micellar model is that parts of the alkyl groups of the surfactant are exposed to water. Other models explain this exposure.[36]

(36) Dill, K.; Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 676. Fromherz, P. *Chem. Phys. Lett.* **1981**, *77*, 460.

(37) It is noteworthy that chloride and bromide ion react with micellar-bound methyl benzenesulfonate but not the carbocationic intermediate generated in hydrolysis of a diphenylmethyl halide.

of alkyl substrates, but there is a relation between the micellar effect on rate and the structure of the alkyl group. The ability of the substrate to generate a carbocation, or the related ion pair, follows the sequence Me $\ll$ PhCH$_2$ < PhMeCH < Ph$_2$CH.[22] Inhibition by a cationic micelle increases sharply as we follow this structural sequence, as do the ratios k^+/k^- (Tables I, VI, and VII). The relative rates in cationic and anionic micelles are most useful mechanistically, because they should not be particularly dependent on hydrophobicity of the substrate or its location.

As we go from a methyl to a diphenylmethyl substrate, the inhibition by an anionic micelle of NaLS does not increase strongly but there is a striking increase in the inhibition by a cationic micelle, regardless of the nature of the micelle counterion.

The decreased availability of waaer in the micelle, and its lower polarity than bulk water, will slow water addition reactions in the S_N1–S_N2 mechanistic spectrum.[9b,12,13,15] The increased inhibition by cationic micelles shown in Tables VI and VII suggests that Coulombic repulsions between the micelle and the forming carbocation center are very important.

There has been considerable discussion as to the merging of the so-called S_N2 and S_N1 mechanisms,[22,23,38] and the most economical explanation is shown in Scheme II. The reaction of diphenylmethyl halides should follow the lower path, possibly with an ion pair intermediate, en route to the carbocation.[39] Reactions of methyl substrates probably follow a reaction path close to that which includes the hypothetical pentacovalent intermediate, but with only a single transition state between reactants and products.[42] (The energetics of formation of a methyl cation are so unfavorable that it is safe to assume nucleophilic involvement in the hydrolysis of methyl benzenesulfonate.[23b,44]) The substitution of electron releasing groups at the reaction center causes the reaction coordinate to move toward that for a classical S_N1 reaction. With increasing development of positive charge at the reaction center, there will be a relatively more favorable interaction with an anionic as compared with a cationic head group, because the leaving anion will interact preferentially with water molecules by hydrogen bonding.[23,45,46]

The S_N2 mechanism can encompass situations in which there is concerted bond making and breaking with a single transition state and others in which the transition state has considerable carbocationic character, or in which a short-lived intermediate is involved.[23,38,41a] Similar descriptions can be applied to reactions of reactive carbonyl compounds, e.g., acyl halides.

Comparison of Mechanisms of Hydrolyses of Chloroformates and Acid Chlorides. The key observation is that the effect of micellar charge upon rates of hydrolysis is different for reactions of chloroformates and acyl chlorides (Table V).

The hydrolyses of both benzoyl and cinnamoyl chloride are faster in anionic micelles of NaLS than in cationic micelles, whereas we find the opposite behavior with chloroformates. These observations suggest that C–Cl bond breaking has made more progress in the transition states for hydrolysis of benzoyl or cinnamoyl chloride than for hydrolysis of the chloroformates. In other words, hydrolyses of the acyl chlorides seem to be similar to the S_N reactions of alkyl halides, whereas hydrolyses of the chloroformates are more akin to carbonyl addition reactions of carbonate esters or acid anhydrides.[48]

These mechanistic differences are probably related to the electronic effects of the phenyl or styryl as compared with aryloxy groups. Inductive electron attraction by the aryloxy groups assists nucleophilic attack and inhibits loss of chloride ion, whereas conjugative electron release by the aryl groups assists loss of chloride ion.[49]

Analysis of medium effects upon solvolyses of benzoyl (and benzyl) chloride suggests that there is extensive bond making and breaking, so that the reactions can be regarded as being in the middle of the S_N1–S_N2 mechanistic spectrum and more S_N1-like than solvolysis of ethyl tosylate, for example.[27b] Consistently, we find similar micellar charge effects for reactions of benzoyl and cinnamoyl chloride and of alkyl halides.

The rate enhancement of the hydrolysis of 4-nitrophenyl chloroformate by cationic micelles (Table V) is an exception to the generalization of micellar inhibition of these spontaneous hydrolyses. It could be due to an interaction between the nitro group of the substrate and the cationic micellar head groups, but such an effect should be present in hydrolysis of bis(4-nitrophenyl) carbonate (Table IV). In any event, the effect of decreased water reactivity in a cationic micelle is more than offset by a rate-enhancing interaction. Probably the combined electronic effects of Cl and the nitro group assist proton loss in the transition state (Scheme I) so that it carries a net negative charge, and consistently a nitro group increases k^+/k^- for most substrates (Table I).

The rate enhancements are slightly larger with CTACl and CTA$_2$SO$_4$ than with CTABr (Table V). The properties of the micelle–water interface should depend to some extent on the bound counterions, which will affect the reactivity of water molecules at the interface.

Micellar Effects and Mechanism. Micellar effects upon these spontaneous hydrolyses are related to both substrate hydrophobicity and reaction mechanism. Reaction rates in the micelle, relative to those in water, are dependent upon substrate hydrophobicity, which controls the average location of the substrate in the micelle, but are not especially useful as reaction probes, in part because substrates may reside largely in an apolar region of the micelle, but reaction may occur in a water-rich region (cf. ref 10). Relative rate constants in cationic and anionic micelles are related to mechanism and reflect the charge distribution in the transition state.

The inhibition by cationic, as compared with anionic, micelles is most evident in the more S_N1-like hydrolyses in which the reaction center has the greatest carbocationic character, e.g., with diphenylmethyl halides. However, even with benzoyl and benzyl chloride, where the hydrolytic mechanisms involve nucleophilic participation,[27b] micellar effects suggest that there is appreciable charge development at the reaction center. We note that other indicators, e.g., secondary structural isotope effects, suggest that solvolyses of benzyl halides, for example, involve transition states with some covalent interaction between the reaction center and

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(38) Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 3295 and references cited.

(39) Ion pairs are intermediates in many S_N1 solvolyses[40] and could have a transient existence even in water.[41]

(40) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In "Ions and Ion Pairs in Organic Reactions"; Swarc, M.; Ed.; Wiley: New York, 1974; Vol. 2, p 247.

(41) (a) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161. (b) Postle, M. J.; Wyatt, P. A. H. *J. Chem. Soc., Perkin Trans. 2.* **1972**, 474. Ride, J. N.; Wyatt, P. A. H. *Ibid.* **1973**, 746. Bunton, C. A.; Huang, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 3436.

(42) For other views, see ref 43.

(43) Sneen, R. A. *Acc. Chem. Res.* **1973**, *6*, 46.

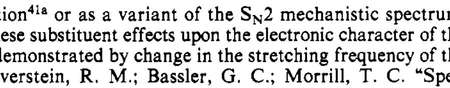
(44) McGarrity, J. F.; Smyth, T. *J. Am. Chem. Soc.* **1980**, *102*, 7303.

(45) Symons, M. C. R. *Acc. Chem. Res.* **1981**, *14*, 179.

(46) Arenesulfonate ions interact strongly with cationic micelles,[5b,47] and this interaction could offset unfavorable Coulombic interactions of a forming carbocation, provided that there is extensive bond breaking in the transition states.

(47) Sepulveda, L. *J. Colloid Interface Sci.* **1974** *46*, 372. Bartet, D.; Gamboa, C.; Sepulveda, L. *J. Phys. Chem.* **1980**, *84*, 272.

(48) Extensive C–Cl bond breaking in the transition state can be reconciled with a carbon addition mechanism, provided that water loss from a tetrahedral intermediate is faster than loss of Cl$^-$, or extensive oxygen equilibration by proton transfer. However, such a mechanism could be regarded as a



$$\mathrm{RCOCl} + \mathrm{OH_2} \rightleftharpoons \mathrm{R{-}\underset{O^-}{\overset{^+OH_2}{C}}{-}Cl} \rightarrow \mathrm{RCO_2H} + \mathrm{H^+} + \mathrm{Cl^-}$$

preassociation[41a] or as a variant of the S_N2 mechanistic spectrum.[23,27b]

(49) These substituent effects upon the electronic character of the carbonyl group are demonstrated by change in the stretching frequency of this group.[50]

(50) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; Chapter 3.

the entering and leaving groups.[51] Most of these studies were in organic or aqueous organic solvents, and the high ionizing ability of water, even in a micelle, should lead to more open transition states with considerable ionic character.

Our observations are consistent with, but do not require, a mechanistic continuum from the carbonyl addition reactions in which nucleophilic attack by water, concerted with proton transfer, is rate limiting, to the S_N2-like mechanisms with concerted bond making and breaking, and then to the S_N1-like mechanisms in which bond breaking is the key step. In the S_N1-like mechanisms of the secondary alkyl halides, the rear of the substrate is exposed to water, but its interaction with the reaction center can best be regarded as solvation rather than as a covalent interaction.[23]

Micellar effects upon the rates of spontaneous hydrolyses have been cited as evidence for a porous-cluster micellar model,[9] and the absence of capture of the carbocation (or ion pair) by halide ion is consistent with this model. A diphenylmethyl substrate should penetrate deeply into the micelle, and if substrate ionization occurred in that region, the halide ion should be attracted by cationic head groups at the micellar surface, leaving the carbocation to be captured by water that had penetrated the micelle. Alternatively, one could suppose that the carbocation is not trapped by halide ion because its lifetime is so short that a water molecule reacts on encounter with it.[41a] However, in so far as the diphenylmethyl cation does discriminate between water and halide ion in aqueous acetone,[22] this explanation also requires the cation to be generated in a water-rich region of the micelle although, on the average, substrate may reside in an apolar region of the micellar core.

All our observations on the effects of micellar charge upon these spontaneous reactions can be fitted to the assumption that in addition to effects due to water activity in the micelle, there are those related to the apparent charge of the transition state. This apparent charge arises because the positive charge on an attacking water molecule can be dispersed into other water molecules and the negative charge of a leaving halide ion attracts hydrating water molecules (Schemes I and II). Therefore cationic and anionic micelles interact differently with the transition states for the various reactions, depending upon the importance of bond making and breaking, even though all the transition states are formally neutral. These micellar effects appear to be diagnostic of mechanism.

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Registry No. $(PhO)_2CO$, 102-09-0; $(4\text{-}O_2NC_6H_4O)_2CO$, 5070-13-3; $(4\text{-}t\text{-}BuC_6H_4CO)_2O$, 22201-45-2; $(4\text{-}NCC_6H_4CO)_2O$, 16657-25-3; $(4\text{-}O_2NC_6H_4CO)_2O$, 902-47-6; $o\text{-}C_6H_4(CO)_2O$, 85-44-9; PhOCOCl, 1885-14-9; $4\text{-}O_2NC_6H_4OCOCl$, 7693-46-1; $PhSO_3Me$, 80-18-2; $PhCH_2Br$, 100-39-0; PhCHMeCl, 672-65-1; Ph_2CHCl, 90-99-3; Ph_2CHBr, 776-74-9; $(PhCO)_2O$, 93-97-0; PhCOCl, 98-88-4.

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[51] Shiner, V. J., Jr. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: Princeton, NJ, 1970; Chapter 2. Vitullo, V. P.; Grabowski, J.; Sridharan, S. *J. Chem. Soc. D* **1981**, 737.

Photochemistry of 1,1-Diazenes. Direct and Sensitized Photolyses of *N*-(2,2,5,5-Tetramethylpyrrolidyl)nitrene, *dl*-*N*-(2,5-Diethyl-2,5-dimethylpyrrolidyl)nitrene, and *N*-(2,2,6,6-Tetramethylpiperidyl)nitrene[1,2]

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Abstract: The photochemistry of the 1,1-diazenes *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene (**1**), *dl*-*N*-(2,5-diethyl-2,5-dimethylpyrrolidyl)nitrene (**2**), and *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**3**) is reported. The fluorescence spectrum of 1,1-diazene **1** has a 0–0 band at 607 nm, which is the maximum. The spacing between the peaks at 607 and 672 nm corresponds to the N=N stretch of S_0 consistent with the 1638-cm^{-1} stretch obtained from the infrared spectrum of **1**. The fluorescence quantum yields are $\phi_F = 2 \times 10^{-3}$ (MTHF, −78 °C), 7×10^{-3} (MTHF, −196 °C), and 1×10^{-3} (EPA, −196 °C). The fluorescence lifetime of **1** is $\tau_F = 2.3 \times 10^{-8}$ s ($CFCl_3$, −196 °C). Direct irradiation of **1** (466–610 nm, −78 °C) affords four hydrocarbon products, 54% **4**, 44% **5**, 2% **6** + **7** and tetrazene **8**. Triplet-sensitized photodecomposition afforded 74% **4**, 24% **5**, 2% **6** + **7** and tetrazene **8**. An approximate quantum yield for decomposition on direct irradiation is $\phi_D = 1.1 \times 10^{-2}$. From S_1, k_{N_2} is $>3.4 \times 10^5$ s^{-1}, and reaction of S_0 with S_1, k_{DIM}, is $>4.2 \times 10^7$ L mol^{-1} s^{-1} (at −78 °C). The spectrum of 1,1-diazene **2** reveals a structured absorption with λ_{max} 507 nm and a 0–0 band at 568 nm ($\epsilon = 20$). The vibrational spacing is 1270 cm^{-1}. The fluorescence spectrum of 1,1-diazene **2** has a 0–0 band at 620 nm, which is the maximum. The spacing between the maxima at 620 and 690 nm corresponds to the N=N stretch of S_0 consistent with the 1630-cm^{-1} stretch obtained for the infrared spectrum of **2**. The fluorescence quantum yield $\phi_F = 9 \times 10^{-3}$ (MTHF, −196 °C). The direct and sensitized irradiation of **2** in the visible affords hydrocarbon products **14**–**19** and tetrazene **20** in different ratios. The retention of stereochemistry in the cyclobutane products in the direct and sensitized photodecomposition was 98 and 68%, respectively, similar to the spin correlation effect seen in corresponding 1,2-diazene isomer. This indicates that for **2** (and by extension **1**) $k_{isc} << k_{N_2}$, consistent with a large S_1–T_1 gap in 1,1-diazenes. For 1,1-diazene **3** the fluorescence spectrum has a single maximum at 684 nm. The fluorescence quantum yield $\phi_F = 4 \times 10^{-4}$ (MTHF, −196 °C). The estimated fluorescence lifetime is $\tau_F = 4 \times 10^{-9}$ s. Direct irradiation of **3** in the visible at −78 °C afforded three hydrocarbon products, 29% **21**, 3% **22**, 68% **23** and tetrazene **25**.

The photochemistry of the 1,1-diazene (aminonitrene, *N*-nitrene) has not been examined due to this species transient nature.[5] Several theoretical groups have calculated the order of the electronic states of the 1,1-diazene during the past decade.[6]

0002-7863/82/1504-6660$01.25/0