Nucleophilically Assisted Deacylation in Sodium Dodecanoate and Dodecyl Sulfate Micelles. Quantitative Evidence on Premicellar Complexes

Dilma M. O. Marconi, Vera L. A. Frescura, Dino Zanette, and Faruk Nome*

Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC 88040-900, Brazil

Clifford A. Bunton

Department of Chemistry, University of California, Santa Barbara, California 93106 Received: June 4, 1994[®]

Hydrolyses of 2,4-dinitrophenyl acetate and octanoate (DNPA and DNPO, respectively) and benzoic anhydride (Bz₂O) in the pH range 8.9-10.2 are inhibited by anionic micelles of sodium dodecyl sulfate (SDS), and reactions of fully micellar-bound substrates are very slow. The effect of micellized sodium dodecanoate, SDOD, depends on pH. At high pH reactions of DNPA and Bz₂O involve OH⁻ and are inhibited by SDOD, but there are significant rates at high [SDOD]. At low-pH reactions of DNPA and Bz₂O are inhibited at low [SDOD] and assisted at high [SDOD]. The inhibition is due to formation of kinetically ineffective premicellar complexes and rate—surfactant profiles can be fitted quantitatively in terms of this model. When the substrates are fully micellar-bound rate constants in mixtures of SDOD and SDS follow the mole fraction of SDOD and second-order rate constants of nucleophilic attack by the dodecanoate ion at micellar surfaces are similar to those for the reactions of OAc⁻ in water.

Introduction

Aqueous micelles control rates of bimolecular reactions by compartmentalizing reagents. Anionic micelles inhibit reactions of nonionic organic substrates with anions by incorporating the substrates and, at least partially, excluding the anions.¹ Conversely cationic micelles incorporate both nonionic substrates and anionic reagents and increase rates of anionic nucleophilic reactions. This general principle has been extended to reactions of functional surfactants in micelles or comicelles, where, with fully bound substrate, reaction rates increase with increasing mole fraction of functional surfactant in the micelle.

Most studies of functional micelles and comicelles have involved cationic or nonionic surfactants, and we extended the study to micellized functional plus inert anionic surfactants. Long-chain sodium alkanoates are obvious candidates for this work, because carboxylate ions effectively catalyze hydrolyses of activated esters and carboxylic anhydrides and the catalytic mechanisms have been elucidated.²⁻⁴

Acetate ions catalyze hydrolysis of benzoic anhydride (Bz_2O) by generating the labile mixed anhydride,⁴ and other alkanoate ions should behave similarly. Similarly alkanoate ions increase rates of hydrolyses of 2,4-dinitrophenyl alkanoates by forming anhydrides which can be trapped by, for example, aniline⁵ (Scheme 1).

We examined hydrolyses of benzoic anhydride, Bz_2O , and 2,4-dinitrophenyl acetate and *n*-octanoate (DNPA and DNPO, respectively) in micelles of sodium dodecyl sulfate (SDS) and sodium dodecanoate (SDOD) and in mixed micelles (SDS and SDOD) where the dodecanoate ion should participate nucleo-philically.

This system is of considerable historical interest because in one of the earliest quantitative treatments of micellar rate effects Menger and Portnoy⁶ showed that inhibitions of deacylations by sodium dodecanoate micelles could be ascribed to transfer of the ester into the anionic micelles which excluded OH⁻. They noted the possibility of reactions involving carboxylate ions of





^{*a*} $\mathbf{R'} = \mathbf{Me}$, *n*-C₁₁H₂₃; $\mathbf{R} = \mathbf{Me}$; Ar = 2,4-dinitrophenyl.

the surfactant but fitted the data on the assumption that they could be neglected, possibly because reactions were followed at pH 9.59. Subsequent work has showed that there are residual reactions of OH^- in anionic micelles, but they are of minor importance except at very high pH.⁷

Micellar rate effects were originally treated on the assumption that monomeric surfactant did not affect reaction rates. This assumption fails for reactions of hydrophobic substrates and our new, quantitative evidence shows that it may also fail with weakly hydrophobic substrates such as acetates.

Incorporation of sodium dodecanoate into SDS micelles should not markedly perturb micellar structure because chain lengths are similar and at pH \approx 9 protonation of the carboxylate residue can be neglected.

Results

Reactions in Water. First-order rate constants, k_{obs} , extrapolated to zero buffer, at 25.0 °C, increased with pH >6 for DNPA and >7 for Bz₂O (Table 1) in agreement with earlier results.^{3,7,8} We could not examine hydrolysis of DNPO because of its insolubility.

Using the data in Table 1, the second-order rate constant for attack of hydroxide ion upon DNPA, extrapolated to zero buffer, is 82.1 M^{-1} s⁻¹ at 25.0 °C, and we found ca. 1.5×10^{-5} s⁻¹ for the spontaneous hydrolysis of DNPA. A value of 5.1×10^{-4} M⁻¹ s⁻¹ was calculated for the second-order rate constant for the attack of AcO⁻ upon DNPA, from the dependence of the rate constant on [buffer], at different pH values (data not shown). These values are consistent with earlier results.³

4.50/0 © 1994 American Chemical Society

^{*} Abstract published in Advance ACS Abstracts, August 1, 1994.

 TABLE 1:
 Hydrolyses of DNPA and Bz₂O in Water at Various pH^a Values

	$10^3 \times k_{\rm obs}$, s ⁻¹			$10^3 \times k_{\rm obs}, {\rm s}^{-1}$		
pH	DNPA	Bz ₂ O	pH	DNPA	Bz ₂ O	
4.03	0.015	0.34	8.87	0.85		
4.59	0.019	0.37	8.99	0.81		
5.05	0.019	0.37	9.18	1.72	4.50	
5.59	0.021	0.40	9.25	1.93		
6.44		0.36	9.57	2.98		
6.50	0.037		9.69	4.82	12.90	
6.96	0.058		9.86		22.70	
7.04		0.49	9.99	7.47		
7.51	0.099	0.64	10.15	10.60		
7.95		0.90	10.17	11.50		
8.05	0.170		10.25	13.70	39.80	
8.69		2.27				

^a At 25.0 °C, extrapolated to zero buffer.

 TABLE 2:
 Critical Micelle Concentrations at Different

 Molar Fractions of SDOD in SDS/SDOD Mixtures^a

χ_{sDOD} 10 ² cmc, M	0	0.2	0.5	0.7	0.8	1.0
	0.75	0.82	1.12	1.38	1.64	2.48

^a At 25.0 °C, pH 8.98, 0.01 M borate buffer.

The second-order rate constant for attack of OH⁻ on Bz₂O in water⁸ is 427 M⁻¹ s⁻¹. The first-order rate constant for the spontaneous hydrolysis at pH 4–6, extrapolated to zero buffer, is 3.7×10^{-4} s⁻¹ at 25.0 °C (Table 1) which is similar to an earlier value of 3.3×10^{-4} s⁻¹ in unbuffered solution.⁹ The second-order rate constant for OAc⁻-catalyzed reaction, in 86: 14 dioxane:H₂O V/V, is 4.23×10^{-3} M⁻¹ s⁻¹ at 25.0 °C.⁴ Under our experimental conditions, borate ion (0.01 M) does not catalyze reactions of Bz₂O or DNPA.

Micellar Reactions. Most experiments were made with [surfactant] well above the critical micelle concentration (cmc) so as to minimize contributions of reactions in the aqueous pseudophase. The cmc of SDOD is 2.48×10^{-2} M (Table 2) so relatively high [surfactant] was needed to bind the more hydrophilic substrates to micelles of high dodecanoate content.

Reactions in SDS Micelles. Hydrolyses were followed at $pH \approx 9$ where the dominant reaction is of OH^- and inhibition is as predicted.¹ The dilute borate buffer (0.01 M) does not catalyze hydrolyses in water, and it is safe to assume that it is excluded from anionic micelles.

Rate constants of hydrolysis of DNPA (Figure 1) decrease smoothly with increasing [SDS] and very sharply for the more hydrophobic substrates DNPO (Table 3) and Bz_2O (Figure 2) even with [SDS] < cmc.

Reactions in SDOD Micelles. Rate-surfactant profiles for reactions of DNPA and Bz₂O are sensitive to small changes in the pH of the solution (Figures 3 and 4). At low pH, with $[SDOD] > cmc, k_{obs}$ increases with increasing [surfactant], but it goes through a minima with [SDOD] < cmc. At low pH there is very little contribution of reaction with OH- and carboxylate ion catalysis in the micellar phase is all important. At higher pH reaction in the aqueous pseudophase becomes more important and is suppressed as the anionic micelles take up substrate and exclude OH⁻. This inhibition of the OH⁻ reaction is not offset by a contribution of reaction with the dodecanoate ion in the micellar pseudophase, so k_{obs} decreases monotonically with increasing [SDOD]. The behavior is different for reaction of DNPO which is so hydrophobic that it is essentially insoluble in water and reaction is wholly in the SDOD micelles, or premicelles at low [surfactant], which effectively exclude OH⁻ so the reaction is with the dodecanoate ion and its rate is independent of [surfactant] (Table 3). Similarly, for reaction of Bz_2O , k_{obs} is independent of pH when



Figure 1. Effect of SDS concentration on the first-order rate constant (k_{obs}) for hydrolysis of 2,4-dinitrophenyl acetate (DNPA) at 0.010 M borate buffer, (\Box) pH 10.15, n = 3 and (\bigcirc) pH 9.00, n = 4, at 25.0 °C. Solid lines are calculated using eq 1.

TABLE 3: Hydrolysis of DNPO in Anionic Surfactant^a

[SDS], M	$10^{6}k_{obs},^{b}s^{-1}$	[SDOD], M	$10^4 k_{obs}, c s^{-1}$
0.03	2.95	0.04	2.57
0.06	2.93	0.06	2.93
0.09	2.68	0.08	2.59
0.12	2.78	0.09	2.67
0.15	3.14	0.10	2.88
		0.15	2.87
		0.16	2.94
		0.18	2.71

^a At 25.0 °C, 0.01 M borate buffer. ^b pH 9.62. ^c pH 9.07.



Figure 2. Effect of SDS concentration on the first-order rate constant (k_{obs}) for hydrolysis of benzoic anhydride (Bz_2O) at 0.010 M borate buffer, (O) pH 9.58 and (\Box) pH 9.09, at 25.0 °C. Solid lines are calculated using eq 1.

the substrate is fully micellar-bound, a condition which is not reached with the more hydrophilic DNPA.

Reactions in Mixed Micelles. Hydrolyses in mixtures of SDS and SDOD were followed with constant [SDS] + [SDOD] = 0.10 M such that the substrates should be largely micellarbound, and k_{obs} increases with increasing mole fraction of SDOD (Figure 5). The cmc of mixtures SDS and SDOD are given in Table 2.

Indicator Measurements. Micellar effects upon proton equilibria involving weak acids or bases depend, for deproto-



Figure 3. Effect of SDOD concentration on the first-order rate constant (k_{obs}) for hydrolysis of 2,4-dinitrophenyl acetate (DNPA) at 0.010 M borate buffer, 25.0 °C, at different pH: (\bullet) 8.96; (\triangle) 9.18; (\blacksquare) 9.57; (\bigcirc) 10.00 and (\Box) 10.17. Solid lines are calculated using eq 2.



Figure 4. Effect of SDOD concentration on the first-order rate constant (k_{obs}) for hydrolysis of benzoic anhydride (Bz₂O) at 0.010 M borate buffer, pH 9.00 (\bigcirc) and 9.63 (\square), at 25.0 °C. Solid lines are calculated using eq 2.

nation, upon the extents of transfer of the indicator and its conjugate base between water and micelles and deprotonating power in the two media.^{1,9} The first problem is circumvented by using an indicator such as 1-dodecyl-3-pyridinium aldoxime bromide, which is sufficiently hydrophobic to be transferred quantitatively into the micelles, but the second problem is more difficult. However, for our kinetic work it is sufficient to observe the change in extent of indicator deprotonation on transfer from water to micelles, which gives the apparent pH (pH_{app}) at the micellar surface, on the assumption that the pK_a is the same in water and micelles (Table 4). For a quantitative analysis of micellar effects upon deprotonation see ref 10. As can be seen, increasing mole fraction of SDOD results in a slight increase in the apparent pH at the micellar surface.

Discussion

Reactions in the Presence of SDS. The inhibition of hydrolyses by micellized SDS is fitted by a simple pseudophase



Figure 5. Effect of increasing molar fraction of SDOD at 0.10 M of [SDS] + [SDOD] on the hydrolyses of 2,4-dinitrophenyl acetate (\Box) pH = 8.99, benzoic anhydride (\bigcirc) pH = 9.10 and 2,4-dinitrophenyl octanoate (\triangle) pH = 9.06, at 25 °C. Solid lines are calculated using eq 3.

TABLE 4: Apparent pH at Different Molar Fractions ofSDOD in SDS/SDOD Mixtures^a

χsdod	1.0	0.9	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
pH _{app}	7.68	7.60	7.68	7.66	7.65	7.71	7.87	7.82	7.93	8.16
^a At	25.0 °	C, 0.0	1 M b	orate t	ouffer,	рН =	10.01.			

treatment in which OH^- is largely excluded from the micelles. This approximation fails at high $[OH^-]$ or high [electrolyte] where micellar surface electrical potentials are reduced and coions are not completely excluded.⁷

The overall rate constant of reaction is given by

$$k_{\rm obs} = \frac{k'_{\rm W} + k'_{\rm M} K_{\rm S} [{\rm SDS}_{\rm M}]}{1 + K_{\rm S} [{\rm SDS}_{\rm M}]} \tag{1}$$

where k'_W and k'_M are first-order rate constants in the aqueous and micellar pseudophases respectively, and K_S is the binding constant of the substrate to micellized surfactant with $[SDS_M]$ = [SDS] - cmc. The cmc is assumed to give the concentration of monomeric surfactant⁶ and is affected by added solutes,¹ and we consider this question in more detail later.

The data for the inhibited hydrolysis of DNPA (Figure 1) were fitted with cmc = 0.0075 M, a kinetically derived value of $K_{\rm S}$ for DNPA of 75 ± 10 M⁻¹, which is in the range typical of moderately hydrophobic solutes and values of $k_{\rm W}$ taken from Table 1. We can fit the data for Bz₂O with $K_{\rm S} \approx 10^3$ M⁻¹ (Figure 2) and values of $k_{\rm W}$ and cmc taken from Tables 1 and 2, respectively. The fittings for [SDS] > cmc are satisfactory. However, values of $k_{\rm obs}$ for hydrolyses of DNPA and Bz₂O decrease with [SDS] < cmc, so that clearly premicellar effects are important and it does affect $k_{\rm obs}$. Since the rate decrease is monotonic, in order to fit the complete rate-surfactant concentration profile, we should use the cmc as a disposable parameter. We favor in this case the use of the experimental cmc, despite the fact that better fittings are obtained with cmc = 0, and we discuss premicellar effects latter.

The first-order rate constant, $k'_{\rm M}$, should have a small but finite value. Indeed, there is a residual reaction of DNPO at high [SDS] where the ester should be fully micellar-bound (Table 3). These residual reactions in SDS micelles could involve spontaneous, water-catalyzed hydrolyses which will be inhibited but not supressed by SDS micelles,⁹ and, as noted earlier, OH⁻ neglected in fitting kinetic data.

In aqueous ethanol DNPO is less reactive than DNPA toward lyate ion by a factor of ca. 2 (values of $k_{\rm obs}$ of 2.19 × 10⁻² s⁻¹

and 4.41×10^{-2} s⁻¹ were obtained for DNPO and DNPA respectively, at 25.0 °C, [KOH] = 0.001 M in 30% ethanol/ water), and therefore k_{obs} in water at pH 9.62 should be ca. 2.0 $\times 10^{-3}$ s⁻¹ based on data in Table 1, whereas in SDS micelles it is ca. 3.0 $\times 10^{-6}$ s⁻¹ (Table 3), consistent with almost complete exclusion of OH⁻.

Reactions in the Presence of SDOD. At high pH reaction of DNPA in water predominantly involves OH^- and therefore SDOD micelles inhibit the reaction (Figure 3), just as for SDS (Figure 1). At low pH where reaction of OH^- is relatively unimportant SDOD speeds hydrolysis, because of nucleophilic participation by the carboxylate moiety, and the independence of k_{obs} on [SDOD] at pH = 9.57 is due to compensation of these two effects.

There are rate effects well below the cmc in water, as in reactions in SDS. Added nonionic and ionic solutes decrease the cmc by interacting with, and stabilizing, micelles,¹ but these effects should be small because the borate buffer is dilute (0.01 M) and [DNPA] = 10^{-4} M, and the cmc was measured in borate buffer. We conclude that interaction of substrate with monomeric or premicellar surfactant aggregates is important, as in SDS. If DNPA forms a transient complex with anionic surfactant its reaction with OH⁻ will be inhibited. For reactions in SDOD this inhibition may be offset by a premicellar reaction with the carboxylate moiety to form a transient mixed anhydride. This reaction is apparently unimportant in premicellar SDOD ([SDOD] < 0.0248 M) at pH \approx 9 (Figure 3), probably because the conformation of premicellar complexes of DNPA and SDOD does not favor attack of the carboxylate moiety on the acetyl group of DNPA. We do not consider bimolecular attack of monomeric dodecanoate ion upon the substrates in water because it should be much slower than the overall reaction, based on second-order rate constants of reaction of OAc⁻ with DNPA and Bz₂O (see above).

The behavior of Bz_2O in micelles of SDOD as a function of pH (Figure 4) is very similar to that of DNPA and is explained similarly at a qualitative level.

Thus, we are forced to modify the accepted pseudophase model, in which only micellized surfactant is kinetically significantly,¹ and in treating the data we make two key assumptions: (i) the organic substrate can bind to both monomeric and micellized surfactant, and (ii) substrate-dodecanoate ion premicellar complexes inhibit the reaction. These assumptions lead to a simple kinetic treatment with a minor modification of eq 1 to

$$k_{\rm obs} = \frac{k'_{\rm W} + k'_{\rm M} K_{\rm S}[\text{SDOD}_{\rm M}]}{1 + K_{\rm S}[\text{SDOD}_{\rm M}] + K^{\rm F}_{\rm S}[\text{SDOD}_{\rm F}]}$$
(2)

In eq 2 we write $K^{F_{S}}$ as the binding constant of Bz₂O to "free" dodecanoate ions, whose concentration below the cmc will be equal to $[SDOD_{T}]$, and $[SDOD_{M}] = [SDOD_{T}] - cmc$. The difference between eqs 1 and 2 will essentially disappear as cmc $\rightarrow 0$ as with longer chain surfactants.

The value of $k'_{\rm M}$ for reaction in SDOD micelles is taken as constant because the concentration of the reactive carboxylate moiety at the micellar surface is independent of [SDOD], provided that micellar size and shape are essentially constant. We neglect contributions of reactions of H₂O and OH⁻ in the anionic micellar pseudophases. There is a very slow residual reaction of DNPO at high [SDS] (Table 3), but SDS inhibits water-catalyzed deacylations,⁹ and water attack probably contributes by less than 1% to reactions in the anionic micelles.

TABLE 5: Fitting Parameters for Reactions in SDOD^a

	Bz ₂ O	DNPA	DNPO
$\frac{10^{3}k'_{\rm M},\rm s^{-1}}{K_{\rm S},\rm M^{-1}}$ $K^{\rm F}_{\rm S},\rm M^{-1}$	6.4 ± 0.3 1000 ± 52 25 ± 4	2.8 ± 0.3 50 ± 5 21 ± 4	0.28 ± 0.02 1500

^{*a*} Values of k_W (for DNPA) and cmc taken from Tables 1 and 2.

The data for reactions of DNPA in SDOD were fitted with eq 2 with the parameters given in Table 5, as shown in Figure 3. The lower value of K_S in SDOD than in SDS is understandable in terms of differences in lengths of the hydrophobic alkyl groups.

Our simple assumptions regarding premicellar effects are consistent with the observed effects on the hydrolysis of Bz_2O in SDOD (Figure 4). The data for reaction of Bz_2O can be fitted at high and low pH, with the parameters given in Table 5.

Reactions in Mixed Micelles. Reactions of OH^- become relatively unimportant at high [surfactant] and when substrates are fully bound and k_{obs} in mixtures of SDS and SDOD should be that in micelles of SDOD multiplied by the mole fraction of micellized SDOD to micellized surfactant, and to a first approximation

$$k_{\rm obs} = k'_{\rm M} \chi_{\rm SDOD} \tag{3}$$

where $k'_{\rm M}$ is the first-order rate constant of hydrolysis at the surface of an SDOD micelle. We take this value as the firstorder rate constant of hydrolysis of bound substrate, neglecting contributions of reactions of OH⁻ and H₂O in the micellar pseudophase. This assumption should be worst for any contribution of the OH⁻ reaction because the shorter chain length of SDOD as compared with SDS means that, for a given aggregation number, the surface charge density will be lower and anions excluded less,⁷ consistent with the apparent pH values. However, these corrections are small and do not affect the overall conclusions. In addition the linearities of plots of k_{obs} against the molar fraction of SDOD for hydrolyses of DNPA, DNPO, and Bz₂O (Figure 5) indicate that reaction largely involves nucleophilic attack by the $-CO_2^-$ moiety of SDOD. In the case of DNPA, the contribution of the reaction in the aqueous phase was taken into account. Values of $k'_{\rm M}$ and K_S used in fitting the kinetic data in micelles are given in Table 5.

The first order rate constant, $k'_{\rm M}$, is proportional to the (constant) concentration of carboxylate ion at the interfacial reaction region at the micellar surface. The molarity is $1/V_{\rm M}$, where $V_{\rm M}$ (M⁻¹) is the molar volume of this region, which is generally identified with the micellar Stern layer. A range of values of $V_{\rm M}$ between 0.14 and 0.37 M⁻¹ has been used in fitting micellar rate data.¹ The second-order rate constant, $k^{\rm M}_2$, M⁻¹ s⁻¹ in the micellar pseudophase is given by

$$k_{2}^{M} = k_{M}^{\prime} V_{M} \tag{4}$$

Second-order rate constants in micellar pseudophases, $k_{2,}^{M_2}$, to that of $5.1 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ for reaction of OAc⁻ with DNPA in water. For reactions of DNPO $k_2^{M_2} = 3.92 \times 10^{-5}$ or 1.04 $\times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ for $V_M = 0.14$ or 0.37 M⁻¹, respectively. For reaction of Bz₂O, $k_2^{M_2} = 9.39 \times 10^{-4}$ or 2.48 $\times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for $V_M = 0.14$ or 0.37 M⁻¹, respectively. The second-order rate constant of reaction of OAc⁻ with Bz₂O⁴ in H₂O:dioxane 86:14 V/V is $4.2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$.

Role of Premicellar Complexes. Quantitative treatments of micellar rate data generally involve the assumption that monomeric or premicellar surfactant does not effect reaction rates.¹

The concentration of monomeric surfactant is taken to be the cmc and is assumed to be independent of [surfactant]. This assumption is incorrect,¹¹ but the error so introduced is small when [surfactant] \gg cmc. Added electrolytes reduce the cmc and the extent can be estimated,¹² but it is more difficult to allow for the effect of nonionic, hydrophobic substrates.

First-order rate constants of micellar-assisted bimolecular reactions with a constant reagent concentration go through maxima with increasing [surfactant], and this kinetic form is predicted by pseudophase treatments.¹ Formation of premicellar complexes is generally neglected, and as a result, fits of rate data in dilute surfactant are often suspect, as are predictions of the positions of rate maxima.

It appears that reactions of DNPA and Bz_2O with premicellar SDOD are relatively slow, but this behavior is probably not general. The reactivity in premicellar complexes of substrate and functional surfactants will depend upon conformation, and similar complexes of inert surfactants should be more reactive in general. Reactivity in premicellar complexes of substrate and functional surfactants will depend upon conformation, and similar complexes of inert surfactants should be more reactive to counterionic reagents than the free substrates.

We fit the rate data, including the rate minima in Figures 3 and 4 in terms of parameters given in Table 5, although for micellar-mediated reactions, fits are often not significantly impaired by modest changes in values of these fitting parameters.

Finally, we would like to comment that the "kinetic" cmc is usually taken as a disposable parameter,¹ but in most ratesurfactant profiles rates are affected by very dilute surfactant, so that we do not see the predicted independence of k_{obs} on submicellar [surfactant]. We cannot exclude the possibility that the substrate is inducing formation of normal micelles, although this behavior does not explain the rate minima for reactions in dilute SDOD (Figures 3 and 4) or the double rate maxima¹³ in some reactions of OH⁻ in cationic micelles. Besides, there is kinetic evidence that premicelles increase rates of some spontaneous cyclizations to form moderate-sized rings, and they are more efficient than micelles in this respect.¹⁴ We believe that premicellar complexes of substrate and surfactant play a significant kinetic role in many reactions in dilute surfactant, although when rates change monotonically with increasing [surfactant] the evidence for formation of premicelles is not compelling.

Experimental Section

Materials. The esters¹⁵ and Bz_2O^8 were prepared and purified as described. Purification of SDS (Sigma) has been described,¹⁶ and SDOD was prepared from dodecanoic acid (Aldrich) and NaOH. The cmc of the mixed surfactants was measured conductimetrically in 0.01 M borate buffer, pH 8.99 (Table 2).

Kinetics. Reactions were followed in aqueous 0.01 M borate buffer at 25.0 °C in a Shimadzu UV 210 spectrometer at 360 nm for DNPA and DNPO and 244 nm for Bz₂O, and k_{obs} (s⁻¹) is the observed first-order rate constant. The substrate concentration was 10^{-4} M and substrates were added in 1,4-dioxane and the kinetic solutions contained 0.3% 1,4-dioxane.

The second-order rate constant for attack of OAc⁻ on DNPA was estimated from data extrapolated to zero concentration in terms of the pKa of HOAc. Rate constants of hydrolyses of DNPA and Bz_2O over a range of pH were estimated by extrapolation of rate constants to zero buffer.

Trapping by Aniline. The intermediate anhydrides were trapped by 10^{-4} M aniline, which did not affect k_{obs} under kinetic conditions.⁵ The anilides were extracted (Et₂O) and were identified by HPLC (MeOH on a 4.6 mm × 25 cm, C₁₈ column) based on comparison of retention volumes with those of authentic samples.

Acknowledgment. We are deeply grateful to CNPq and PADCT/FINEP for financial support.

References and Notes

(1) (a) Bunton, C. A.; Nome, F.; Quina, F. H.; Romsted, S. L. Acc. Chem. Res. **1991**, 24, 357. (b) Berezin, I. V.; Martinek, K.; Yatsimirski, A. K. Russ. Chem. Rev. (Engl. Transl.) **1973**, 42, 487. (c) Romsted, L. S. In Micellization, Solubilization and Microemulsions; Mittal, K. L., Ed.; Plenum Press: New York, 1977; p 489. (d) Quina, F. H.; Chaimovich, H. J. Phys. Chem. **1979**, 83, 1844. (e) Bunton, C. A. In Surfactants in Solution; Mittal, K. L., Shah, D. O., Eds.; Plenum Press: New York, 1991; Vol. II, p 17.

(2) Gold, V.; Butler, A. R. J. Chem. Soc. 1961, 2305.

(3) Bender, M. L.; Turnquest, B. W. J. Am. Chem. Soc. 1957, 79, 1652.

(4) Johnson, S. L. J. Am. Chem. Soc. 1962, 84, 1729.

(5) Gold, V.; Oakenfull, D. G.; Riley, T. J. Chem. Soc. B 1968, 515.

(6) Menger, F. M.; Portnoy, C. E. J. Am. Chem. Soc. 1967, 89, 4698.

(7) Bunton, C. A.; Mhala, M. M.; Moffatt, J. R. J. Phys. Chem. 1989, 93, 7851.

(8) Al-Lohedan, H.; Bunton, C. A. J. Org. Chem. 1982, 47, 1160.

(9) Al-Lohedan, H.; Bunton, C. A.; Mhala, M. M. J. Am. Chem. Soc. 1982, 104, 6654.

(10) (a) Romsted, L. S. J. Phys. Chem. 1985, 89, 5107. (b) Chaimovich,
H.; Aleixo, R. M. V.; Cuccovia, I. M.; Zanette, D.; Quina, F. M. In Solution Behavior of Surfactants: Theoretical and Applied Aspects; Mittal, K. L.,
Fendler, E. J., Eds.; Plenum Press: New York, 1982; Vol. 2, p 949. (c)
Zanette, D.; Leite, M. R.; Reed, W.; Nome, F. J. Phys. Chem. 1987, 91,
2100. (d) Romsted, L. S.; Zanette, D. J. Phys. Chem. 1988, 92, 4690.

(11) Romsted, L. S. In Surfactants in Solution; Mittal, K. L., Lindmann, B., Eds.; Plenum Press: New York, 1984; Vol. 2, p 1015.

(12) Mukerjee, P.; Mysels, K. J. Critical Micelle Concentrations of Aqueous Systems; National Bureau of Standards, U.S. Government Printing Office: Washington, DC, 1970.

(13) Bunton, C. A.; Cowell, C. P.; Nome, F.; Romsted, L. S. J. Phys. Org. Chem. 1990, 3, 239.

(14) Cerichelli, G.; Savelli, G. Unpublished results.

(15) Chattaway, F. J. Chem. Soc. 1931, 134, 2495.

(16) Gonsalves, M.; Probst, S.; Rezende, M. C.; Nome, F.; Zucco, C.; Zanette, D. J. Phys. Chem. 1985, 89, 1127.