overall rate enhancements are due largely to concentration of the two reactants into the small volume of the micelles.[4,6b,c,9,20-22] For deacylation by oximate ion, Berezin and his co-workers concluded that second-order rate constants in the micellar pseudophase were slightly greater than those in water,[21] but for many reactions the reverse seems to be true. The comparisons depend slightly upon the assumed volume element of reaction and the method of estimating concentrations in the micellar pseudophase, so that exact agreement is not to be expected. In addition, the assumed volume element of reaction in the micelle should depend upon the specific reaction and the average location of reactants in the micelle. However, for dephosphorylations by amidoximate and oximate ion (**4**-**6**) the micellar rate enhancements are due almost wholly to concentration of the reactants into the small volume of the micellar pseudophase.

Intramolecular participation by the NH_2 moiety in deacylations and dephosphorylations has been suggested, because of the relatively high nucleophilicity of amidoximes,[7] but the similarity of the nucleophilicities of the oximate and amidoximate ions toward pNPDPP shows that participation is unimportant in reactions of the anions (cf. ref 8). However, undissociated amidoximes seem to be better nucleophiles than oximes.[7,8]

Although oximate and amidoximate ions have similar nucleophilicities, under practical conditions oximes are by far the more useful agent simply because with $pK_a \approx 10$ they give the reactive ion at relatively low pH, whereas amidoximes, with $pK_a \approx 12.6$, are deprotonated only in strongly alkaline solutions.

Acknowledgment. Support of this work by the U.S. Army Research Office is gratefully acknowledged. We are grateful to Drs. L. S. Romsted and G. Savelli for valuable suggestions.

Registry No. 1 (R = Ph), 613-92-3; **3a**, 80641-18-5; **3b**, 80641-19-6; **4a**, 80641-20-9; **4b**, 80641-21-0; *p*-hexyloxybenzonitrile, 66052-06-0; *p*-dodecyloxybenzonitrile, 29147-92-0; CTACl, 112-02-7; pNPDPP, 10359-36-1.

Ion Binding and Micellar Effects upon Reactions of Carboxylic Anhydrides and Carbonate Esters

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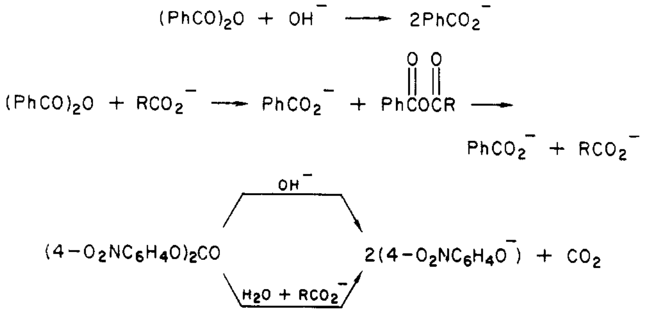
Cationic micelles speed reactions of benzoic anhydride and bis(4-nitrophenyl) carbonate with hydroxide and carboxylate ion. With micellized cetyltrimethylammonium bromide (CTABr) the variation of the first-order rate constant, k_ψ, with [CTABr] can be fitted to the pseudophase ion-exchange model, but this model fails when the counterion of the surfactant is OH^- or carboxylate ion. The variations of k_ψ with concentration of these reactive counterion surfactants fit a kinetic model in which the distribution of the nucleophilic anion between the aqueous and micellar pseudophases depends upon the concentration of nucleophilic ion. Despite the apparent differences between these two models, they predict similar values for the second-order rate constants of reaction of a given anion in the different types of micelles, and the implications of these findings to the interactions of micelles with counterions are discussed.

Micellar effects upon the reactions of nucleophiles with carboxylic esters have been extensively studied,[1] and the variations of rate constants with surfactant concentration have been explained quantitatively by considering the distribution of both reagents between aqueous and micellar pseudophases and the second-order rate constants in each pseudophase.[2-7]

Carboxylic anhydrides and diaryl carbonates are convenient substrates for study of micellar effects upon reaction rate because the reaction mechanisms are well understood,[8,9] and the reaction can be followed easily in dilute solution. We examined micellar effects upon reactions of benzoic anhydride or bis(4-nitrophenyl) carbonate with OH^- or carboxylate ion in water (Scheme I). These substrates should bind readily to micelles.[10] The reagents were chosen so that the first step is followed kinetically. For example, in the reaction of benzoic anhydride with carboxylate ion we used formate ion, because the first-formed mixed anhydride goes readily to products.[11] Reaction of bis(4-nitrophenyl) carbonate with H_2O gives a short-lived intermediate carbonate, and carboxylate ions are general-base catalysts of water reaction.[9a]

Scheme I



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Reactions were carried out in aqueous solutions of cetyltrimethylammonium surfactants (CTAX, $n\text{-}C_{16}H_{33}N^+Me_3X^-$, where $X^- = Br^-$, OH^-, or RCO_2^-). Typically the rate constants of bimolecular reactions go through maxima with increasing surfactant concentrations with constant concentration of the nucleophile and an inert surfactant counterion.[2-7] In carboxylic ester deacylation by OH^- in CTABr the rate maxima can be ascribed to the combination of competition between OH^- and Br^- for the micelle and distribution of the substrate between water and micelles.

However, if only relative counterions are in solution, the rate constants should become constant once all the substrate is micellar bound, provided that the micelle is saturated with counterions. This predicted behavior is observed for reactions of hydrogen ions in micellized alkanesulfonic acids,[12] and of *N*-alkylpyridinium ions in micellized CTACN.[13] Nucleophilic reactions in CTAOH and CTAF do not fit this pattern,[12,14,15] and it appears that here the concentration of micellar bound OH^- or F^- increases with increasing total concentration. We were interested, therefore, in studying reactions of other substrates in micellized reactive ion surfactants where the nucleophile or base was OH^- or RCO_2^- and in CTABr with added inert counterions.

Experimental Section

Materials. The preparation or purification of benzoic anhydride, bis(4-nitrophenyl) carbonate, and CTABr followed standard methods.[9,11,12] The other surfactants were prepared in solution from CTAOH[15] by neutralization with equimolar carboxylic acid. The preparation and manipulation of CTAOH was done under N_2 in the absence of CO_2. The surfactant concentration was calculated from that of CTAOH. The carboxylic acids were formic, acetic, and trimethylacetic, and their anions are designated as For, OAc, and Me_3CCO_2, respectively.

Kinetics. The slower reactions were followed spectrophotometrically by using Gilford or Beckmann spectrophotometers, and a Durrum stopped-flow spectrophotometer was used for the faster reactions. All reactions were followed in water at 25.0 °C, for the slower reactions substrate was added as a solution in MeCN to the reaction mixture in a 1-cm cuvette so that the concentration of benzoic anhydride was 5×10^{-5} M and that of bis(4-nitrophenyl) carbonate was 5×10^{-6} M, and the solutions contained 0.1% MeCN. For the faster reactions in CTABr one syringe contained CTABr plus substrate and the other the anionic reagent, and with reactive counterion surfactants the surfactant was in one syringe and the substrate in the other. Reaction of benzoic anhydride was followed at 245 nm and that of bis(4-nitrophenyl) carbonate at λ_{max} of 4-nitrophenoxide ion (403 nm) or at the isosbestic point (347 nm).

The first-order rate constants, k_ψ, are in reciprocal seconds. For hydrolysis of bis(4-nitrophenyl) carbonate in the presence of carboxylate ion there is a small contribution from reaction with OH^- generated by autoprotolysis. This reaction could be suppressed by addition of carboxylic acid which was added in some experiments. Attack of hydroxide ion upon benzoic anhydride was unimportant in solutions of sodium formate.

Reactions in the absence of surfactant were followed by using dilute nucleophile or base (<0.04 M) to minimize kinetic salt effects. The spontaneous, water-catalyzed reactions make only minor contributions,[9,11] and we neglect them in analyzing the rate data.

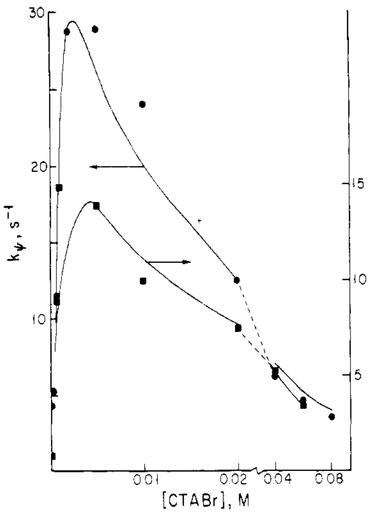

Figure 1. Reactions of benzoic anhydride in CTABr: ●, 0.01 M NaOH; ■, 0.02 M HCO_2Na. In this and the following figures the solid lines are calculated in terms of the models.

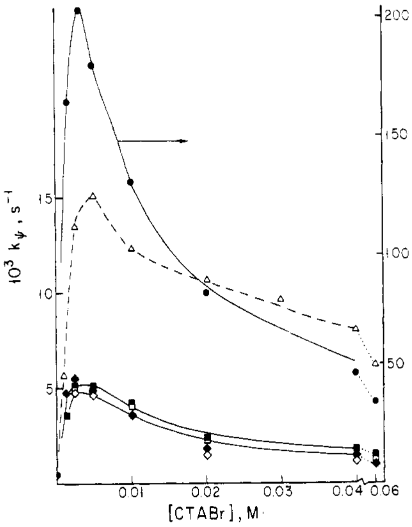

Figure 2. Reactions of bis(4-nitrophenyl) carbonate in CTABr: ●, 0.01 M NaOH; ■, 0.02 M HCO_2Na; ♦, 0.02 M $MeCO_2Na$; □, ◇, △, 0.02 M HCO_2Na, $MeCO_2Na$ and Me_3CCO_2Na, respectively, with equimolar carboxylic acid.

Results

Reactions in the Absence of Surfactant Benzoic Anhydride. The second-order rate constant (k_w) for reaction with OH^- at 25.0 °C is 427 M^{-1} s^{-1}, and for reaction with formate ion $k_w = 0.034$ M^{-1} s^{-1}. Reactions of noncommon carboxylate ions with anhydrides occur by nucleophilic attack, giving a mixed anhydride, which in our system should be short lived.[11] (The common carboxylate ion is a general-base catalyst, but this reaction is relatively slow.)

Bis(4-nitrophenyl) Carbonate. The second-order rate constant (k_w) for reaction of OH^- is 327 M^{-1} s^{-1}. Carboxylate ions catalyze reaction with water by acting as general bases,[9a] but this catalysis is observed only at a relatively high concentration of carboxylate ion. In the absence of surfactant there was essentially no carboxylate ion catalysis in the dilute solutions (<0.04 M) which we used.

Reactions in CTABr. Micellized CTABr speeds reactions with anions (Figures 1 and 2). As generally found, k_ψ goes through maxima with increasing [CTABr] and constant [anion], and added Br^- inhibits reaction by competing with the reactive anion for the micelle[3,5-7] (Table I).

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Table I. Inhibition by Bromide Ion of Reactions of Benzoic Anhydride in CTABr [a]

[NaBr], M	k_ψ nucleophile OH^{-b}	k_ψ HCO_2^{-c}
	12.4	0.0051
0.003	9.53 (9.1)	0.0044 (0.0045)
0.006	7.41 (7.6)	0.0034 (0.0036)
0.01	5.25 (5.9)	0.0030 (0.0031)
0.02	3.78 (4.0)	0.0023 (0.0023)
0.03		0.0020 (0.0018)
0.04	2.18 (2.3)	
0.06	1.41 (1.7)	0.0013 (0.0011)

[a] Values of k_ψ in reciprocal seconds at 25.0 °C; predicted values are in parentheses. [b] In 0.01 M NaOH and 0.02 M CTABr. [c] In 0.02 M HCO_2Na and 0.04 M CTABr.

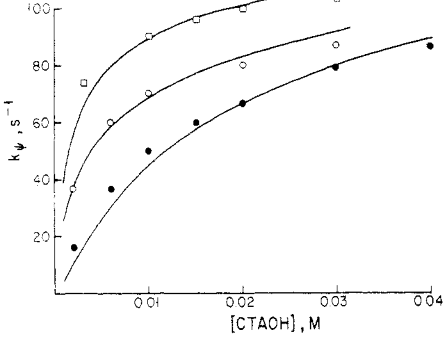

Figure 3. Reaction of benzoic anhydride in CTAOH: ●, no added NaOH; ○, 0.01 M added NaOH; □, 0.02 M added NaOH.

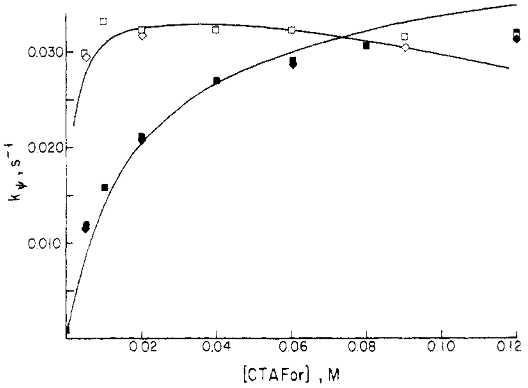

Figure 4. Reaction of benzoic anhydride in CTAFor: no added HCO_2Na, ■ and ♦; 0.12 M [CTA For] + [HCO_2Na], □ and ◇; ♦ and ◇ denote solutions with added 0.02 M HCO_2H.

The rate–surfactant profiles are similar for reactions of both substrates, and trimethylacetate ion is a better catalyst than formate or acetate ion of hydrolysis of bis(4-nitrophenyl) carbonate (Figure 2).

Reactions in Reactive Ion Micelles. Benzoic Anhydride. When only reactive anions are present, k_ψ increases steadily with [surfactant]. Added nucleophile increases k_ψ, but only to a small extent at higher [surfactant], and at high surfactant or nucleophile concentration k_ψ tends toward limiting values (Figures 3 and 4 and Table II; cf. ref 14 and 15). However, benzoic anhydride is hydrophobic and should be fully micellar bound at a [surfactant] well below those corresponding to limiting values of k_ψ. [This was confirmed by micellar effects upon the spontaneous hydrolysis (cf. ref 10).]

Bis(4-nitrophenyl) Carbonate. The variation of k_ψ with [CTAOH] is very similar to that found for reaction of Bz_2O, and added OH^- speeds the reaction (Figure 5). Although carboxylate ions are relatively ineffective catalysts in the absence of surfactant,[9a] we observed rate enhancements in micelles which appear to involve catalysis by carboxylate ion, because k_ψ is only slightly depressed by addition of carboxylic acid. When the counterion is acetate or formate, k_ψ increases steadily with increasing surfactant or carboxylate ion concentration (Figure 6), even under conditions in which the substrate should be almost completely bound to the micelle.[16] The situation is different when the counterion is trimethylacetate, because k_ψ increases sharply with the [surfactant], and except in dilute surfactant, addition of the counterion does not markedly increase k_ψ (Table III). This behavior is similar

Table II. Effect of Formate Ion on the Hydrolysis of Benzoic Anhydride [a]

[HCO_2Na], M	k_ψ, s^{-1}	[HCO_2Na], M	k_ψ, s^{-1}
	0.0266	0.09	0.0325 (0.034)
0.01	0.0267 (0.026)	0.12	0.0346 (0.035)
0.02	0.0279 (0.028)	0.17	0.0368 (0.036)
0.04	0.0298 (0.031)	0.21	0.0370 (0.037)
0.06	0.0306 (0.033)	0.23	0.0366 (0.037)

[a] At 25.0 °C in 0.04 M CTAFor. Values in parentheses are predicted by taking $K_X' = 80\ M^{-1}$ and $k_M = 0.4\ s^{-1}$.

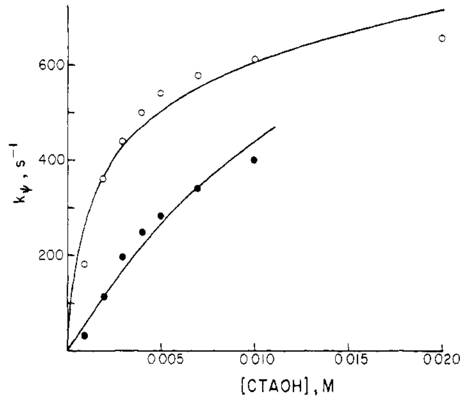

Figure 5. Reactions of bis(4-nitrophenyl) carbonate: ●, no added NaOH; ○, 0.01 M NaOH.

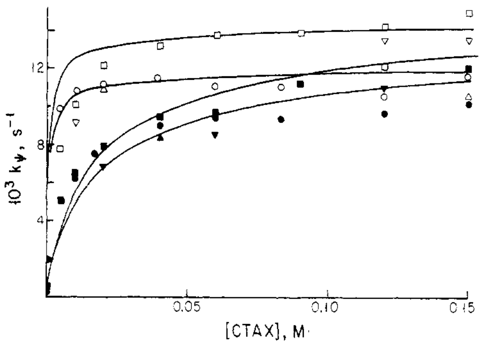

Figure 6. Reaction of bis(4-nitrophenyl) carbonate in CTAFor and CTAOAc: ■, CTAFor alone; ▼, CTAFor with equimolar HCO_2H; ●, CTAOAc alone; ▲, CTAOAc with equimolar HOAc; □, CTAFor with 0.06 M HCO_2Na; ▽, CTAFor with 0.06 M HCO_2Na and 0.06 M HCO_2H; ○, CTAOAc with 0.06 M NaOAc; ▼, CTAOAc with 0.06 M NaOAc and 0.06 M HOAc.

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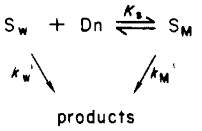
[16] On the basis of data at 50 °C[10] we estimate that ca. 90% of the substrate should be micellar bound in 10^{-2} M CTABr, and the binding should be similar to other C_{16} surfactants.

Table III. Reaction of Bis(4-nitrophenyl) Carbonate in Cetyltrimethylammonium Trimethylacetate[a]

$[\mathrm{CTAMe_3CCO_2}]$, M	$10^2 k_\psi$, s^{-1}
0.002	0.40
0.005	0.98 (1.50)
0.01	1.65 (2.30)
0.02	2.20 (2.60)
0.04	2.99 (3.02)
0.07	3.10 (3.12)
0.10	3.20 (3.23)
0.13	3.34

[a] At 25.0 °C with 5×10^{-6} M substrate and 0.02 M $\mathrm{Me_3CCO_2H}$. Rate constants in parentheses are in the presence of 0.06 M $\mathrm{Me_3CCO_2Na}$.

Scheme II



to that observed for reactions in micelles of cetyltrimethylammonium cyanide or sulfonic acids where the micelles appear to be saturated with counterion, and limiting values of k_ψ are reached when the substrate is fully micellar bound.[12,13]

Observation of greater catalysis by carboxylate ions in the micelle, as compared with that in water, is understandable because the concentration of carboxylate ion at the micellar surface will be greater than in the aqueous pseudophase.[3]

Discussion

In considering micellar effects upon reactions of hydroxide and carboxylate ion, one finds it necessary to take into account possible competition between $\mathrm{Br^-}$ and the reactive ions for the micelle. It is simplest, therefore, to consider first reactions in the absence of $\mathrm{Br^-}$, i.e., in the reactive counterion surfactants.

The substrate, S, will be distributed between aqueous and micellar pseudophases, denoted by the subscripts w and M, respectively (Scheme II), with reaction occuring in either pseudophase. The micellized surfactant (detergent) is denoted as Dn, and its concentration is assumed to be given by [D] – cmc, where D is the surfactant and cmc the critical micelle concentration, which is assumed to be the concentration of monomeric surfactant.

Reactive Counterion Surfactants. We assume that the distribution of substrate between aqueous and micellar pseudophases follows Scheme II, so that the overall rate constant is given by eq 1,[17] where k'_w and k'_M are the

$$k_\psi = \frac{k'_\mathrm{w} + k'_\mathrm{M} K_\mathrm{s}[\mathrm{Dn}]}{1 + K_\mathrm{s}[\mathrm{Dn}]} \tag{1}$$

first-order rate constants in the aqueous and micellar pseudophases, respectively, and K_s is the binding constant of the substrate written in terms of the concentration of micellized surfactant, [Dn]. (The quantities in square brackets are concentrations in molarity in terms of total solution volume.)

Equation 1 is written in terms of the first-order rate constants for reactions in the aqueous and micellar pseudophases, and they are given by eq 2 and 3,[7] where k_w ($\mathrm{M^{-1}}$

$$k'_\mathrm{w} = k_\mathrm{w}[X_\mathrm{w}^-] \tag{2}$$

$$k'_\mathrm{M} = k_\mathrm{M} m_\mathrm{x}^\mathrm{s} \tag{3}$$

$\mathrm{s^{-1}}$) is the second-order rate constant for reaction in the aqueous pseudophase, $[\mathrm{X^-}]$ is the molarity of the nucleophilic anion (based on total solution volume and neglecting the small volume of the micelles), and k_M ($\mathrm{s^{-1}}$) is the second-order rate constant in the micellar pseudophase, corresponding to the concentration of $\mathrm{X^-}$ written as a molar ratio, i.e., eq 4.

$$m_\mathrm{x}^\mathrm{s} = [\mathrm{X_M^-}]/[\mathrm{Dn}] \tag{4}$$

Equations 1–4 give eq 5 and 6.

$$k_\psi = \frac{k_\mathrm{w}[\mathrm{X_w^-}] + k_\mathrm{M} K_\mathrm{s} m_\mathrm{x}^\mathrm{s}[\mathrm{Dn}]}{1 + K_\mathrm{s}[\mathrm{Dn}]} \tag{5}$$

$$= \frac{k_\mathrm{w}[\mathrm{X_w^-}] + k_\mathrm{M} K_\mathrm{s}[\mathrm{X_M^-}]}{1 + K_\mathrm{s}[\mathrm{Dn}]} \tag{6}$$

For a reactive ion surfactant the molar ratio, m_x^s, of bound ion to micellar head groups is given by β,[12,13,15] the fractional extent of charge neutralization of the head groups. Therefore, if β is independent of the concentration of the surfactant or added reactive ion, $\mathrm{X^-}$,[3,18] eq 7 holds

$$k_\psi = k_\mathrm{M}\beta \tag{7}$$

once the substrate is fully micellar bound, and k_ψ should then reach a constant value. This behavior is found for reactions in some reactive ion surfactants, e.g., in CTACN,[13] CTABr,[15a,19] and some sulfonic acids.[12] However, when the reactive ion is $\mathrm{OH^-}$ or $\mathrm{F^-}$, k_ψ increases with increasing concentration of nucleophile or surfactant, even when the substrate is fully micellar bound.[12,14,15] We see this apparently anomalous behavior for reactions of anhydride and carbonate with $\mathrm{OH^-}$ or $\mathrm{RCO_2^-}$ (Figures 3–6 and Table II). Therefore, for a number of reactions the rate–surfactant profiles cannot be explained in terms of the simple model which assumes constancy of β. But they can be fitted to a model which assumes that the apparent value of β increases with increasing concentration of the reactive counterion.[15b]

The distribution of the reactive counterion, $\mathrm{X^-}$, between the aqueous and micellar pseudophase is written in terms of eq 8, which is akin to the Langmuir isotherm, where K_x

$$K'_\mathrm{X} = [\mathrm{X_M^-}]/[\mathrm{X_w^-}]([\mathrm{Dn}] - [\mathrm{X_M^-}]) \tag{8}$$

can be regarded as a binding constant assumed to be independent of the charge neutralization of the micelle.

Equations 7 and 8 can be combined and a simple computer program used to predict the variation of $[\mathrm{X_M^-}]$ with surfactant concentration and added $\mathrm{X^-}$ and therefore of k_ψ. The second-order rate constants, k_w, are measured directly, and k_M, K_s, and K'_x are treated as adjustable parameters. However, for dephosphorylation and aromatic nucleophilic substitution in CTAOH, $K'_\mathrm{OH} = 55\ \mathrm{M^{-1}}$,[15b] and we use this value here. The critical micelle concentration, cmc, is also treated as an adjustable parameter, although its value in the kinetic systems is assumed to be similar to that of CTAOH or similar $\mathrm{C_{16}}$ surfactants in water. Most of our experiments were done at relatively high [surfactant] where the simulated rate–surfactant profiles are insensitive to the cmc and where substrates are strongly micellar bound and uncertainties in K_s are relatively unimportant, but we take $K_\mathrm{s} = 650$ and $1000\ \mathrm{M^{-1}}$ for benzoic anhydride and bis(4-nitrophenyl) carbonate,[10] respectively. The cmc was taken to be 10^{-3} M for CTAOH and 8×10^{-4}

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[19] Cowell, C., unpublished results.

Table IV. Values of k_M [a]

reaction	conditions [b] 1	2	3	4
$Bz_2O + OH^-$	180	175	200	160
$Bz_2O + HCO_2^-$	0.05 [c]	0.04 [c]	0.06	0.07
$(O_2NC_6H_4O)_2CO + OH^-$	1700	1500	1200	
$(O_2NC_6H_4O)_2CO + HCO_2^-$	0.017	0.017	0.022	
$(O_2NC_6H_4O)_2CO + OAc^-$	0.016	0.014	0.020	

[a] Values of k_M in reciprocal seconds at 25.0 °C. [b] 1, reactive counterion surfactant; 2, reactive counterion surfactant plus counterion; 3, CTABr; 4, CTABr + Br^-. [c] K'_{For} = 80 M^{-1}; in the other experiments a value of 70 M^{-1} was used.

M for the corresponding formate and acetate. Changes in these values had no effect except in very dilute surfactant. This general model is described in detail in ref 15b.

The variations of k_ψ for reactions of the substrates in solutions of CTAOH and the related formate and acetate surfactants, CTAFor or CTAOAc, can be simulated by using this treatment, and the fit is illustrated in Figures 3–6, where the solid lines are calculated. The treatment can also be applied to experiments with added OH^- or carboxylate ion. (In fitting the data we include formally a term for reactions in the aqueous pseudophase, but its contribution to the overall rate constant is negligible.) The ion binding parameters were K'_{OH} = 55 M^{-1} under all conditions, K'_{For} = 70–80 M^{-1} (the values are footnoted in Table IV), and K'_{OAc} = 75 M^{-1}. Our estimates of k_M are in Table IV.

Reactions in CTABr. The maxima in k_ψ with increasing [CTABr] and constant $[OH^-]$ or $[RCO_2^-]$ (Figures 1 and 2) are typical of micellar rate enhancements with varying concentrations of inert surfactant and a constant [nucleophile].[1-7] They can be treated quantitatively by using the pseudophase ion-exchange model based on eq 9, with the concentration of micellar-bound nucleophilic anion calculated by using the ion-exchange equilibrium (9).[3]

$$Br_w^- + X_M^- \rightleftharpoons Br_M^- + X_w^-$$

$$K_{Br}^{X} = [Br_M^-][X_w^-]/[Br_w^-][X_M^-] \qquad (9)$$

The values of ion-exchange constants have been estimated by several methods. One approach is to use physical methods. In favorable cases electrochemistry is useful,[20,21] or an indicator such as an arenesulfonate ion can be used, because of its spectral change on binding to a micelle.[22] Other methods include ultrafiltration or the use of thiocyanate ion as an indicator.[23]

The other general approach is to simulate the variation of rate or equilibrium constant with surfactant concentration by taking the ion-exchange constant as an adjustable parameter.[3-6,24,26] These various methods agree qualitatively that Br^- binds much more strongly than OH^- to cationic micelles, but values of K_{Br}^{OH} range from approximately 10 to 40. This spread of values is due in part to the inclusion of a term depending on surface potential in some of the treatments,[5] but there is a more fundamental problem which is that the treatments contain a variety of adjustable parameters, and the data can often be fitted by various combinations of these parameters.[26]

The general approach in fitting the variation of k_ψ with [surfactant] or salt is to use eq 9 and the mass balance relation, with assumed values of K_{Br}^{X}, to calculate $[X_M^-]$ and $[X_w^-]$, to insert these values into the rate equation, using assumed values of k_M and K_s and the measured k_w, and to simulate the variation of k_ψ with [CTABr], for example.

Our data could be fitted by taking K_{Br}^{x} = 10 M^{-1} for all the added anions, and we took β = 0.75 (cf. ref 3 and 18). We assumed that values of K_s are similar to those which fit the data for reactions in reactive counterion micelles (Figures 3–6), i.e., 650 and 1000 M^{-1} for benzoic anhydride and bis(4-nitrophenyl) carbonate, respectively. The cmc of CTABr was assumed to be lowered by added electrolyte to 3×10^{-4} M in NaOH and 5×10^{-4} M in HCO_2Na and NaOAc. Variations in the cmc or K_s had no effect on the predicted rate–surfactant profiles except in very dilute surfactant. The "best fit" values of k_M for reactions in CTABr and in the reactive counterion micelles are given in Table IV.

The value of K_{Br}^{OH} = 10 is similar to those determined in other kinetic or equilibrium systems.[6,23-26] The corresponding ion-exchange parameters for formate or acetate ion in CTABr are similar to K_{Br}^{OH} suggesting that these carboxylate ions are not hydrophobic enough to interact strongly with the micelles (cf. ref 23). We could not fit our rate data for reaction of bis(4-nitrophenyl) carbonate with trimethylacetate ion in CTABr (Figure 2) to the pseudophase ion-exchange model (eq 6 and 9) by taking reasonable values of the various of adjustable parameters. This failure suggests that the model is inapplicable when the solution contains relatively hydrophobic counterions which interact strongly with the micelle and change its local structure (cf. ref 15, 20, 22 and 27).

A major problem with this analysis of the rate or equilibrium data in CTABr or similar surfactants is that its application depends on the assumption that β is constant, despite changes in concentrations of surfactant of added electrolyte.[3,26] For example, if the apparent value of β for CTAOH, and similar surfactants, varies with concentration of surfactant or counterion, as we suggest, the ionic exchange equation (eq 9) and the associated mass balance relation may be no more than first approximations. We note that the concentration of counterions in the aqueous pseudophase (eq 9) depends critically upon the fractional degree of ionization of the micelle: $\alpha = 1 - \beta$.[3] The assumed constancy of β is probably an approximation, even when Br^-, for example, is the only counterion in solution.[18,28] Incorporation of trimethylacetate ion could

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change β, and the kinetic data do not fit the ion-exchange model. These uncertainties are probably present to some extent even with the less strongly bound ions OH^-, HCO_2^-, or OAc^-. The problem is ameliorated when inert counterion is added so that its concentration in the aqueous pseudophase is partially buffered.[15,25,26]

Comparison of Reactions in CTABr and Reactive Counterion Surfactants. The treatments of reactions in CTABr with added nucleophile or base (eq 9) and those in reactive surfactants (eq 6–8) appear to be based on completely different premises and use different approximates, but, nonetheless, they lead to similar values of such parameters as k_M and K_s. Application of the ion-exchange equation (eq 9) to the rate–surfactant profiles is typically dependent on the assumption that β is constant, which appears to fail when the only counterion in solution is hydrophilic with a high charge density, e.g., OH^- or F^-,[12,14,15] but it is probably reasonably satisfactory when the counterion is less hydrophilic, e.g., Br^- or CN^-,[13,15] and eq 8 predicts that β will vary little with the [counterion] when K'_X is large.[15b] Therefore, addition of a weakly bound anion, e.g., OH^-, to a solution of CTABr, for example, may not have a large effect upon ionic binding to the micelle, as given by β, so that the ion-exchange model is applicable.

Equation 8 treats the variable extents of binding of reactive hydrophilic counterions to a micelle and leads to a reasonable fit between observed and predicted rate–surfactant profiles (Figures 3–6, Tables I and II, and ref 15b), suggesting that it is describing the distribution of counterions between aqueous and micellar pseudophases. However, this distribution may be governed by a wide distribution of micellar sizes, ranging from relatively small micelles which bind the counterion weakly to normal-sized micelles which bind it more strongly.[14,15] The size distribution could be much wider when the counterion is hydrophilic and weakly bound, e.g., as with OH^-, than when it is more hydrophobic and relatively strongly bound, as with Br^-, but an increase of the [counterion] should, in any event, increase micellar size[29] and counterion binding. Each treatment, therefore, appears to have its own limited range of applicability and cannot be applied outside that range.

There is another major problem with both these models in that they involve parameters whose values are not well established. For example, although we fitted the variation of k_ψ with the [CTABr] for reaction of bis(4-nitrophenyl) carbonate with hydroxide, formate, and acetate ion by taking $K_{Br}^X = 10\ M^{-1}$ and $\beta = 0.75$ for each system, we can fit the data using other combinations of K_{Br}^X and β, which change k_M, but not markedly. There is no reason to believe that one set of values is better than another, on the basis of our kinetic evidence.[26] In treating the micellar binding of OH^- in CTAOH, for example, using eq 8, we set formal limits of 0 and 1 for β.[15b] The treatment can be modified by setting an arbitrary limit of $\beta < 1$. We can fit our data taking limits of 0 and 0.75, for example, for β, and then values for K'_X for hydrophilic anions are increased.

Comparisons of Reactions in Micellar and Aqueous Pseudophase. The relation between k_w, for reaction in water, and k_M, for reaction in the micellar pseudophase (eq 3), should provide information regarding the environmental effect of these two media on reactivity. The two sets of rate constants cannot be compared directly because of differences in their dimensions.[7] The second-order rate constant, k_M, is expressed in terms of concentration as a molar ratio of reactive anion to micellar head groups (eq 3), whereas for k_w the concentration is written, conventionally, as moles of nucleophile per liter of aqueous pseudophase, which is approximated as total solution. These rate constants can be compared provided that the volume element of reaction in the micellar pseudophase can be defined, which requires estimation of the molar volume of the region of the micelle in which reaction occurs.[2,3,7,24,31] If one assumes that reactants are distributed uniformly over the micelle, this volume element would be ca. 0.36,[2–6] whereas if one assumes that reaction occurs only in the Stern layer, the volume element would be approximately half this value.[7,31] In other calculations we have used a volume of 0.14 L for reaction in CTABr and similar micelles, and we use this value here, accepting that the selection is an arbitrary one. If different reactants are located preferentially in different regions of the micelle, it will be impossible to define a unique volume element of reaction.

Table V. Reactions in Water and in Micelles

	k_M, s^{-1}	k_2^m, $M^{-1}\ s^{-1}$	k_2^m/k_w
$Bz_2O + OH^-$	180	26	0.06
$Bz_2O + HCO_2^-$	0.05	0.007	0.21
$(4\text{-}O_2NC_6H_4O)_2CO + OH^-$	1500	210	0.70

On this basis the second-order rate constant, k_2^m ($M^{-1}\ s^{-1}$), for reaction in the micellar Stern layer is given by [7,31] eq 10. (If the volume element of reaction is taken to be

$$k_2^m = 0.14k_M \tag{10}$$

that of the micelle, values of k_2^m will be approximately doubled.) The various rate constants are compared in Table V by taking averages of the values in Table IV.

For reaction of bis(4-nitrophenyl) carbonate with OH^- values of the second-order rate constants k_w and k_2^m in the aqueous and micellar pseudophases are similar, as is often found for reactions of nucleophilic anions.[2,4,7,13] This result is consistent with both reactants being located in a waterlike region of the micelle, and Menger and co-workers have shown that the first-order rate constant for reaction of bis(4-nitrophenyl) carbonate with water is only slightly decreased by incorporation of the substrate in micelles of CTABr.[10]

The second-order rate constants for reaction of benzoic anhydride with OH^- and formate ion are considerably smaller in micelles than in water (Table V). These differences between the anhydride and the carbonate could be due to their being located in different regions of the micelle. For example, the polar nitro groups of the carbonate might cause it to reside on the average in a more aqueous region of the micelle than that occupied by benzoic anhydride, and both hydroxide and formate ion should be largely near the water-rich micellar surface. This explanation is supported by the observation that micelles of CTABr only weakly inhibit hydrolysis of bis(4-nitrophenyl) carbonate,[10] but they sharply inhibit hydrolysis of benzoic anhydride.[32] Micellar structure is not uniform, and recent treatments suggest that the hydrocarbon core is ordered at the center and liquidlike on the outside and that part of the core is exposed to water.[33] In addition, the some-

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[29] This suggestion is consistent with observation of light scattering by solutions of CTAOH, but only at relatively high [CTAOH] or [OH^-], well above the cmc.[30]

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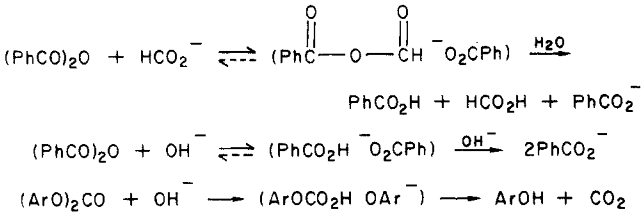
Scheme III



$$(PhCO)_2O + HCO_2^- \rightleftharpoons (PhC(=O){-}O{-}CH(=O)\ ^-O_2CPh) \xrightarrow{H_2O} PhCO_2H + HCO_2H + PhCO_2^-$$

$$(PhCO)_2O + OH^- \rightleftharpoons (PhCO_2H\ ^-O_2CPh) \xrightarrow{OH^-} 2PhCO_2^-$$

$$(ArO)_2CO + OH^- \longrightarrow (ArOCO_2H\ OAr^-) \longrightarrow ArOH + CO_2$$

what different geometries of the reaction centers of anhydrides and carbonates may influence the rate constants for nucleophilic attack in the micelles as compared with those in water.

But the differences between the two substrates could also be due to mechanism. Reaction of benzoic anhydride and formate ion goes via a mixed anhydride,[11] which in a micelle may readily recombine with benzoate ion (Scheme III) but should react rapidly with water in the absence of micelle. In reaction with OH^- in a micelle, benzoate ion may react with the adjacent benzoic acid, whereas in water, benzoic acid would be deprotonated before recombination could occur. On the other hand, the carbonate ester formed by nucleophilic attack upon bis(4-nitrophenyl) carbonate could rapidly and spontaneously lose CO_2 both in micellar and aqueous pseudophases so that intermediates would not recombine.[34]

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Registry No. Benzoic anhydride, 93-97-0; bis(4-nitrophenyl) carbonate, 5070-13-3; cetyltrimethylammonium trimethylacetate, 80737-51-5; CTABr, 57-09-0; CTAFor, 80721-50-2; CTAOH, 505-86-2; CTAOAc, 51374-75-5.

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Hydrolysis of Aldal Acetals

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Eleven aldal acetals were synthesized, and the kinetics of their hydrolyses in water and in water–acetonitrile were studied as model systems for the hydrolysis of sucrose. α,α'-Diethoxypropyl ether (an aldal acetal) hydrolyzes in water without hemiacetal buildup. The reaction is not subject to general acid catalysis and the value of $k_{D_3^+O}/k_{H_3^+O}$ = 2.44, both results being characteristic of an A1 mechanism. The energy of activation for the hydrolysis of α,α'-diethoxydipropyl ether was 84.98 kJ mol^{-1} in water and showed no temperature dependency over the range of 15–35 °C. The structural effects for the hydrolysis of aldal acetals parallel those for acetal hydrolysis.

The hydrolysis of acetals has occupied a central position in chemical kinetics and in physical organic chemistry.[1,2] Historically, the most important acetal in kinetic studies has been sucrose, and the continued general interest in acetals is because of the functional relationship to the glycosidic link of carbohydrates. Particular emphasis was given to the overall problem during the past decade because of the assignment of the structure of lysozyme and interest in the catalytic mode of lysozyme for the hydrolysis of polysaccharides.[3] Further interest in the problem has intensified due to the worldwide shortages of petroleum hydrocarbons and the need to be able to produce fuels and other materials from biomass.[4]

The hydrolysis of sucrose was the first chemical reaction to be studied as a function of time[5] and was one of the first reactions for which the influence of temperature on reaction rates was studied.[6] From the pioneering work of Wilhelmy in 1850 on the hydrolysis of sucrose up to 1947 there were over 1000 papers published on this subject, and the interest continues.[1,7] In spite of the continued and intense interest in the hydrolysis of sucrose there remain a number of specific and general problems to be solved for the process. Prominent among these problems are the following. (1) There is a marked change in the energy of activation with temperature.[1,8,9] The dramatic change in the energy of activation with temperature has not been explained. This well-documented fact is incredible when one realizes that the prominent reaction used by Arrhenius to establish the equation bearing his name is the hydrolysis of sucrose.[10] (2) Not only does the energy of activation for sucrose hydrolysis change with temperature but it also changes with the kind and amount of acid catalyst and with the supporting electrolyte.[8,11] (3) The specific rate constant (first order) for sucrose hydrolysis changes as the concentration of sucrose is changed.[8] The concentration effects have required that comparative studies be standardized as regards molarities of reactants and catalysts. (4) The site of protonation for bond cleavage and the bonds which cleave to yield the reaction products have not been established. The details of this complex process which includes protonation, bond cleavage, hydration, depro-

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