Reactions in Micelles of Cetyltrimethylammonium Hydroxide. Test of the Pseudophase Model for Kinetics

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The rate constants for reactions of OH⁻ with 2,4-dinitrochlorobenzene (DNCB), 2,4-dinitrochloronaphthalene (DNCN), and p-nitrophenyl diphenyl phosphate (pNPDPP) in micellized cetyltrimethylammonium hydroxide (CTAOH) do not conform to the pseudophase ion-exchange model. The rate constants do not become constant when substrates are fully micellar bound and increase on addition of NaOH. However, with the more hydrophobic substrates DNCN and pNPDPP we appear to reach limiting rate constants at high [CTAOH] or high [NaOH]. These observations can be explained on the assumption that the charge on a CTAOH micelle decreases on addition of OH^- , i.e., the concentration of OH^- in the micelle increases with increasing $[OH^-]$ in the aqueous pseudophase. The rate-surfactant profiles for reactions of DNCN and pNPDPP can be interpreted quantitatively in these terms. For reactions of DNCB the rate data can be interpreted if we assume that added OH⁻ also increases binding of DNCB to the micelle.

Micellar catalysis of bimolecular reactions in water depends primarily upon concentration of the two reactants into a small volume.² Rate-surfactant profiles have been interpreted quantitatively in terms of the concentrations of the two reactants in the Stern layer, and the secondorder rate constant in that layer.⁵⁻¹⁰ This pseudophase model suggests that second-order rate constants in the micellar pseudophase are similar to those in water.

The concentrations of organic reactants in the micellar pseudophase can often by estimated directly by solubility measurement, ultrafiltration, gel filtration, or spectrophotometrically.³ However, these methods are not generally applicable to hydrophilic inorganic ions. In some cases, their micellar incorporation can be measured electrochemically, but this method is not applicable to the hydroxide ion.¹¹ Micellar effects upon reactions of the hydroxide ion have been widely studied,³ and it is important to understand the distribution of this ion between water and micelles.

One approach is to examine the competition between various anions for a cationic micelle by using an indicator such as an arenesulfonate ion,¹² but generally kinetics or

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equilibrium methods have been used.^{8,13-17} It is assumed that the extent of charge neutralization, β , of a cationic micelle is, to a first approximation, independent of the nature and concentration of the counteranions.^{13,18} The other key assumption is that competition between counteranions for the micelle is governed by an ion-exchange equilibrium,¹³ similar to that which governs competition between counterions for an ion exchange resin, e.g., for interaction between X⁻ and OH⁻ for micellized cetyltrimethylammonium ions (CTA⁺) we write

$$OH_{M}^{-} + X_{W}^{-} \approx OH_{W}^{-} + X_{M}^{-}$$

where W and M denote the aqueous and micellar pseudophases respectively, and

$$K_{\mathbf{X}}^{\mathbf{OH}} = [\mathbf{OH}_{\mathbf{W}}^{-}][\mathbf{X}_{\mathbf{M}}^{-}]/[\mathbf{OH}_{\mathbf{M}}^{-}][\mathbf{X}_{\mathbf{W}}^{-}]$$
(1)

The experimental variations of rate or equilibrium constant with surfactant concentrations have been accounted for with equations which treat ion exchange in terms of eq 1, and assume constant β .

There are, however, problems with this approach. It is almost too easy to fit the experimental data because the equations contain several parameters, viz, β , $K_{\rm X}^{\rm OH}$, the rate constant in the micelle, and the concentration of monomeric surfactant, which is assumed to be given by the critical micelle concentration, cmc.¹⁹ The usual approach is to assume reasonable values for one or more of these parameters, e.g., β and the cmc, and to use the experimental rate or equilibrium constants to estimate values of $K_{\rm X}^{\rm OH}$, for example. These treatments depend critically upon the

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value of β , but, nonetheless, the fit with experiment is often good. However, this approach does not give unique values for any of the parameters, because equally good fits can often be obtained by using different combinations of assumed values of the various parameters.²⁰ An additional uncertainty is that while some treatments explicitly include a term for the surface potential of the micelle,⁶⁻⁸ others do not.^{13-17,20}

The treatments suggest that counterions differ in their affinities for ionic micelles,²¹ as toward ion-exchange resins.¹³ These differences suggest that β should not be independent of the nature of concentration of the counterions, as is generally assumed in the pseudophase ion exchange models. Values of β appear to depend upon the method of measurement,^{13,23,24} so that there is no objective evidence for its constancy. In addition, the β appropriate to kinetic measurements may be different from that measured by mobility, for example,²⁴ and quasielastic light-scattering measurements have been interpreted in terms of a variation of micellar charge (i.e., $1 - \beta$) with added counterion.25

Although the pseudophase model of micellar structure implicitly assumes constancy of β , ^{13,18,26,27} the alternative mass action model does not, although it can accomodate constancy of β ,²⁸ assuming compensation of opposing effects.18a

Another problem is that the various kinetic treatments assume a constant volume element of reaction in the micelle. One limit is to take the total volume of the micelle as the reaction volume,⁶ another is to assume that reaction occurs in the Stern layer, and to estimate its volume.^{5,14} Although the assumption of a constant volume element appears to be satisfactory, most of the tests have been made on reactions of relatively hydrophobic nonionic or anionic nucleophiles,^{5-7,9,10} and it may be unsatisfactory for reactions of very hydrophilic anions, e.g., OH- or F-, although it has been applied to some of these reactions. $^{8,14-17,22}$

The original Hartley model of an ionic micelle postulated a hydrocarbon-like core surrounded by an aqueous layer,^{3,29} containing the ionic head groups, and on this basis the volume of the micelle should be approximately twice that of the Stern layer.^{13,14} However, Menger has suggested that water penetrates the micelle, so that the interior may not be hydrocarbon-like.³⁰ Consideration of packing of surfactant into the micelle suggests that the extent of water penetration will depend upon the conformation of the alkyl groups of the surfactant and also upon the interactions between the head groups. Therefore, the volume of the Stern layer depends upon the nature and concentration

(21) Fortuitously Na⁺ and H₃O⁺ appear to have similar affinities for an anionic micelle,^{11b,22} but OH⁻ has a low affinity, as compared with anions such as halide or nitrate, for cationic micelles.^{8,11-17}

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Scheme I



of the counterions, and Aniansson has extended earlier suggestions of the "roughness" of a micellar surface using a model in which monomers oscillate about a mean position.³¹ In addition, the location of an organic substrate in the micelle should depend upon its structure,³² e.g., upon its hydrophobicity, and on its interactions with either water molecules or micellar head groups.

We have attempted to avoid the ion-exchange problem by using micelles of reactive counterion surfactants in which the reactive ion is the only counterion in the solution.³³⁻³⁵

The relation between rate and surfactant concentration can be written in terms of Scheme I for reactions of anions,¹⁹ where S denotes organic substrate, X⁻ the anionic reagent, D_n the micellized surfactant (detergent), given by ([D] – cmc), and K_s , the binding constant of S to D_n , is given by

$$K_{\rm s} = [S_{\rm M}] / [S_{\rm W}] ([D] - {\rm cmc})$$
 (2)

Scheme I leads to eq 3, where the bracketed quantities represent concentrations in moles per liter of solution and $m_{\rm x}^{\rm s}$ is the mole ratio of bound X⁻ to micellized surfactant, and $k_{\rm M}$, the related second-order rate constant^{5,14,22,36}

$$rate = k_{W}[S_{W}][X_{W}] + k_{M}[SD_{n}]m_{x}^{s}$$
(3)

where

$$m_{\rm x}^{\rm s} = [{\rm X}^-{}_{\rm M}]/[{\rm D}_n] \tag{4}$$

(A corresponding equation can be written for cationic reactions).²

The first-order rate constant with respect to S is given bv

$$k_{\psi} = \frac{k_{\rm W}[{\rm X}^-{\rm W}] + k_{\rm M}K_{\rm S}m_{\rm x}^{\rm s}([{\rm D}] - {\rm cmc})}{1 + K_{\rm S}([{\rm D}] - {\rm cmc})}$$
(5)

If X^- is the only counterion in solution³³⁻³⁵

 m^{s}

$$\xi = \beta \tag{6}$$

and with fully bound substrate:

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

i.e., k_{ψ} should be independent of [surfactant]. This predicted behavior is found for nucleophilic reactions of CN⁻³⁴ and Br^{-37,38} in micellized cetyltrimethylammonium cyanide

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and bromide (CTACN and CTABr, respectively) and for hydrogen ion catalyzed reactions in micellized alkanesulfonic acids.33

However, for aromatic nucleophilic substitution by OHin micelles of 1, X = OH³³ and dephosphorylation by F⁻

$$p-C_8H_{17}OC_6H_4CH_2NMe_3X^-$$

in micelles of CTAF,³⁵ the rate constants, k_{ψ} , increase with surfactant concentration even when all the substrate appears to be micellar bound, and added OH⁻ or F⁻ speeds the reaction.

One explanation of these observations is that an additional reaction path involves reaction across the micellar shear surface, i.e., nucleophilic anion in the aqueous pseudophase may react with micellar bound substrate.³³ There are several objections to this explanation. (i) Such reactions should not be restricted to nucleophilic attack by OH^- or F^- , and (ii) for attack of F^- on *p*-nitrophenyl diphenyl phosphate in micellized CTAF, k_{ψ} appears to reach a limiting value at relatively high [CTAF], i.e., ca. 0.1 M, or on addition of ca. 0.05 M F⁻ to less concentrated CTAF.35

The aim of the present work was to seek similar limiting rate constants for reactions in cetyltrimethylammonium hydroxide (CTAOH), and to examine alternative kinetic models. For example, we could assume that β for a cationic hydroxide or fluoride surfactant increases with increasing [OH⁻] or [F⁻], cf. ref 24 and 25. Alternatively one could assume that an increase in the counterion concentration shrinks the Stern layer, which would be equivalent to concentrating the reactants, and would, therefore, speed reaction. Another possibility is that the structure of the micelle, or other submicroscopic aggregate, changes with counterion concentration in such a way as to change the concentration of bound counterion.³⁵

The rate constants of reactions in CTAOH and CTAF, and the rate effects of added OH⁻ or F⁻, can be fitted to a simple, empirical, mass action equation.

We used two hydrophobic substrates, 2,4-dinitrochloronaphthalene (DNCN) and p-nitrophenyl diphenyl phosphate (pNPDPP), which bind strongly to micelles,^{33,39} so that uncertainties in the extent of binding and the contribution of reactions in the aqueous pseudophase will be relatively unimportant:



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We also used 2,4-dinitrochlorobenzene (DNCB), which is not so strongly micellar bound,⁴⁰ and its distribution between water and the micelles is kinetically important.



Experimental Section

Materials. The substrates were prepared or purified by standard methods.^{33,39,40} Solutions of CTAOH were prepared by treating CTABr with an approximately 50% excess of $AgSO_4$ in MeOH. The mixture was sonicated for 2 h; the solution was decanted off, additional Ag_2SO_4 was added, and the solution was resonicated. The solution was filtered and MeOH was removed in vacuo. The solid was redissolved in MeOH and recrystallized by addition of Et₂O. An aqueous solution of $(CTA)_2SO_4$ was treated with an equivalent amount of $Ba(OH)_2$ in the absence of CO_2 and $BaSO_4$ was removed by centrifugation. The solution of CTAOH was tested for the presence of either Ba²⁺ or SO_4^{2-} by standard methods. Solutions of CTAOH were stored in a refrigerator, although we saw no evidence of decomposition when they were left for several weeks at room temperature under N_2 . The stock solutions of CTAOH were approximately 0.25 M, and were diluted as necessary with CO₂-free water or NaOH or KOH. All manipulations of CTAOH were carried out in a CO₂-free atmosphere under N_2 .

Physical Properties. The apparent critical micelle concentration (cmc) of CTAOH was determined by measurement of the surface tension by the de Nouy method in a drybox under N₂. Plots of surface tension against log [CTAOH] had no minima and the break corresponded to a cmc of 8.6×10^{-4} M, which is similar to those for other C₁₆ surfactants, e.g., CTACl, CTABr, and CTANO₃ which are approximately 10⁻³ M.⁴¹

Conductivity was measured at 25 °C under N₂ in a cell whose temperature was controlled by circulating oil. There are typically sharp breaks in plots of specific conductivity, κ , against surfactant concentration at the cmc.³ The conductivity of CTAOH was measured up to 0.012 M and that part of the plot of κ against [CTAOH] which covers the apparent cmc is shown in Figure S1 (available as supplementary material; see paragraph at end of text regarding supplementary material). Some of the experiments were done with added NaOH and the values of κ are corrected for the contribution of NaOH, assuming it to be constant. In the absence of NaOH there was a linear relation between κ and [CTAOH] up to $\sim 1.8 \times 10^{-3}$ M CTAOH, the plot then was curved, as shown by the broken line (Figure S1), but became linear again for [CTAOH] > 3×10^{-3} M. With added NaOH plots of κ against [CTAOH] were linear and coincident with those in the absence of NaOH up to $\sim 10^{-3}$ M CTAOH. There was then curvature in the plot, followed by linearity at higher [CTAOH]. The curvature (broken plot) is markedly reduced by NaOH, and almost disappears in 10⁻² M NaOH.

The "break" in a plot of κ against [CTAOH] is at ~ 1.5 \times 10⁻³ M CTAOH in 10⁻² M NaOH, but it is too ill defined in the other solutions to be used as a measure of the cmc.

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Figure 1. Reaction of *p*-nitrophenyl diphenyl phosphate in CTAOH: (O) in absence of NaOH; (\bullet) in 5.52 × 10⁻³ M CTAOH with added NaOH.



Figure 2. Reaction of *p*-nitrophenyl diphenyl phosphate in CTAOH with added NaOH.

Indeed, these measurements in the absence of NaOH suggest that one cannot use conductivity to measure the cmc in this system.

Conductivity has been used to estimate β , and if we apply the equations of Evans⁴² to our system and assume an aggregation number of 50 we estimate $\beta \approx 0.6$, and it drops to 0.52 if we assume an aggregation number of 20. However, this treatment depends on assumptions in the Evan's treatment which are especially suspect for CTAOH.

Kinetics. All reactions were followed spectrophotometrically at 25.0 °C by methods described elsewhere.^{33,35} Solutions were made up under N₂, in the absence of CO₂, and for reactions in 1-cm curvettes the substrates were added as solutions in MeCN (2-4 μ L) to 2 mL of surfactant solution so that [substrate] = 0.5 × 10⁻⁵-3 × 10⁻⁵ M. At these low substrate concentrations micelles should contain no more than one substrate molecule, provided that [surfactant] > 10⁻³ M,¹⁹ as in most of our experiments. The first-order rate constants, k_{ψ} , are in reciprocal seconds. Small changes in [substrate] did not affect k_{ψ} and we obtained reproducible results using different batches of CTAOH.

Results

Kinetics. The variations of k_{ψ} with CTAOH and the effect of added NaOH or KOH are not as predicted by the simple pseudophase ion-exchange model with constant β , because k_{ψ} increases with increasing [CTAOH] and added OH⁻, even when the substrate should be fully micellar bound (Figures 1–5). These rate-surfactant profiles are



Figure 3. Reaction of 2,4-dinitrochloronaphthalene in CTAOH: (O) no added NaOH; (\bigcirc) in 10⁻² M CTAOH and added NaOH; (\blacksquare , \blacklozenge) at 0.05 and 0.1 M OH⁻_T, respectively.



Figure 4. Variation of k_{ψ} for reaction of 2,4-dinitrochloronaphthalene with [CTAOH]: (O) no added KOH; (\blacksquare) 0.05 M KOH; (\blacklozenge) 0.1 M KOH; (\blacklozenge) 0.25 M KOH; (\bigstar) 0.5 M KOH.



Figure 5. Reaction of 2,4-dinitrochlorobenzene in CTAOH: (O) no added NaOH; and 0.25 (\triangledown), 0.5 (\blacktriangle) 0.7 (\blacksquare), and 1.0 (\blacklozenge) M [OH⁻_T].

similar to those for reaction of pNPDPP in CTAF,³⁵ and aromatic nucleophilic substitution in 1, X = OH.³³

There is an effect of substrate hydrophobicity, because with the more hydrophobic substrates, pNPDPP and DNCN, limiting values of k_{ψ} are approached at high [CTAOH] or with added OH⁻ (Figures 1-4), and with

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relatively large amounts of added OH⁻ the variation of k_{ψ} with [CTAOH] is similar to that predicted by the ion-exchange model.^{33,34,37,38}

The kinetic form is different for reaction of the less hydrophobic substrate DNCB, where added OH⁻ increases k_{ψ} , even at relatively high [CTAOH] (Figure 5).

The effects of added OH^- are too large to be ascribed to reactions in the aqueous pseudophase.^{33,39a} The present results agree with those for reactions in CTAF,³⁵ in contradiction to an earlier tentative suggestion of a reaction between micellar bound substrate and OH^- in the aqueous pseudophase,³³ and any explanation has to account for differences in the kinetic forms of reactions of chemically similar substrates of different hydrophobicities, e.g., DNCN and DNCB (Figures 3–5).

Micellization of CTAOH. Observation of breaks in plots of log surface tension vs. [CTAOH] and of conductance vs. [CTAOH] (Figure S1), together with evidence of light scattering in the presence of NaOH,⁴³ suggests that CTA-OH can form micelles in water.

Discussion

Kinetic Model. It is convenient to rewrite eq 5 in the form

$$k_{\psi} = \frac{k_{\rm W}[{\rm X}^-{\rm W}] + k_{\rm M}K_{\rm S}[{\rm X}^-{\rm M}]}{1 + K_{\rm S}([{\rm D}] - {\rm cmc})}$$
(8)

$$=\frac{k_{\rm W}([{\rm X}^-{}_{\rm T}] - [{\rm X}^-{}_{\rm M}]) + k_{\rm M}K_{\rm S}[{\rm X}^-{}_{\rm M}]}{1 + K_{\rm S}([{\rm D}] - {\rm cmc})}$$
(9)

We assume that the distribution of a counterion, X^- , between the aqueous and micellar pseudophases follows eq 10.

$$K'_{\rm X} = [{\rm X}^-{}_{\rm M}] / [{\rm X}^-{}_{\rm W}] ([{\rm D}_n] - [{\rm X}^-{}_{\rm M}]$$
(10)

Equation 10 is formally similar to eq 2 which governs micellar binding of nonionic solutes, and we write $K_{X'}$ as independent of the concentrations of counterions in the aqueous and micellar pseudophases. (An alternative way of considering ion binding would be to describe it in terms of dissociation of a counterion from a micelle. We use eq 10 because of its formal similarity to eq 2.)

Added electrolyte can contribute to $[X^-]$, and $[X^-_T]$ is the total amount of X⁻, regardless of its origin. Equation 10, as written, assumes that micellar charge varies with concentrations of surfactant and counterion, and we use it empirically in treating the kinetic data. Combining eq 9 and 10 and the mass balance give¹⁵

$$K_{X'}[X_{M}^{-}]^{2} - (K_{X'}[D_{n}] + K_{X'}[X_{T}^{-}] + 1)[X_{M}^{-}] + K_{X'}[D_{n}][X_{T}^{-}] = 0$$
(11)

(for solutions of only CTAOH or CTAF $[X_T]$ is the total concentration of surfactant [D]).

Equation 11 can be used to calculate the concentrations of the reactive counterion in the aqueous and micellar pseudophases as a function of $[D_n]$ and $[X_T]$ for various assumed values of the ionic binding constant $K_{X'}$. We include the concentration of X^- in water to allow for a contribution of reaction in the aqueous pseudophase, using known values of k_{W} ,^{33,39,40} but neglect of it has little effect on the predicted rate-surfactant profiles for reactions of the more hydrophobic substrates.

Tests of the Model. Hydrophobic Substrates. Our approach is to use eq 8–11 to simulate the variation of k_{ψ} (eq 9) with concentration of surfactant or added nucleophile, taking as parameters $k_{\rm M}$, $K_{\rm X}'$, $K_{\rm S}$, and independently

TABLE I: Rate Constants for Reaction ofpNPDPP with OH^{- a}

[OH ⁻ T], M	10^4 cmc, M	$k_{\rm M}, {\rm s}^{-1}$	
0-0.12 ^b	8	0.78	
$0.05 - 0.1^{c}$	8	0.72	
0.02^{b}	4	0.68	
0.04^{b}	3	0.68	
0.10^{b}	1	0.68	

 a At 25.0 °C, taking $K_{\rm S}\approx 10^4$ M⁻¹ and $K_{\rm OH}{'}=55$ M⁻¹. b Variable CTAOH. c 5.51 \times 10⁻³ M CTAOH.

TABLE II: Rate and Equilibrium Constants for Reaction of DNCN with OH^{-a}

[OH ⁻ T], M	$k_{\rm M}, {\rm s}^{-1}$	[OH ⁻ _T], M	$k_{\rm M}, {\rm s}^{-1}$
0-0.11 ^b	0.11	0.10^{c}	0.10
0.05^{c}	0.10	$0-0.5^{d}$	0.10

^{*a*} At 25.0 °C, taking $K_{\rm S} \approx 1600 \text{ M}^{-1}$, $K_{\rm OH}$ = 55 M⁻¹, and cmc = 8 × 10⁻⁴ M. ^{*b*} No added OH⁻. ^{*c*} Variable CTAOH. ^{*d*} 0.01 M CTAOH.

measured values of $k_{\rm W}$, with the stipulation that $K_{\rm S}$, the binding constant of substrate to micelle, should be similar to that in the corresponding bromide ion surfactant. The other parameters are adjustable, with the proviso that $K_{\rm X}'$ and $k_{\rm M}$ should be insensitive to changes in surfactant or nucleophile concentration.

We made the usual assumption that the cmc gives the concentration of monomeric surfactant,¹⁹ and treated it in mixtures of surfactant and electrolyte as an adjustable parameter, with the requirement that added electrolyte decreases the cmc. Variations in the cmc have little effect on most of our simulated rate-surfactant profiles and, in any event, taking the cmc as the concentration of monomeric surfactant is at best a crude approximation.²⁴ For the more hydrophobic substrates the simulated rate-surfactant profiles are insensitive to changes in $k_{\rm W}$, $K_{\rm S}$, and cmc.

The calculated solid lines in the rate-surfactant profiles fit the experimental values under a variety conditions (Figures 1-4). The values of the parameters are in Tables I and II.

2,4-Dinitrochlorobenzene. This substrate does not bind strongly to micelles, e.g., $K_{\rm S} = 75 \, {\rm M}^{-1}$ in CTABr,^{39b,40} and its distribution between water and micelles of CTAOH may be affected by added NaOH, cf. ref 15.

Hydrophilic electrolytes, such as NaOH, "salt out" nonionic solutes from water,⁴⁴ and therefore may drive the substrate from water into the micelles. Added OH^- may also interact with CTAOH to change the structure of the aggregates, and change the distribution of a relatively weakly bound substrate between water and micelles. (These effects should be relatively unimportant with hydrophobic solutes which bind very strongly to micelles.)

In treating the reaction of DNCB we allowed for reaction in both micellar and aqueous pseudophases, and an increase of K_s with [NaOH]. An important observation is that relatively high [NaOH] sharply increases k_{ψ} for reaction of DNCB in CTAOH (Figure 5), but has a relatively small effect upon the corresponding reaction of DNCN (Figures 3 and 4).

The relatively hydrophobic substrate, DNCN, should be extensively micellar bound with [CTAOH] >> 10^{-2} M (Table II and ref 33), and the only effect of added OH⁻ is to increase bound OH⁻. The micelle should become saturated with OH⁻ ($K_{OH'} \approx 55$ M⁻¹) so that an increase of [OH⁻] above 0.2 M should have little effect on k_{ψ} , as is found. But increasing [OH⁻] should increase the amount

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⁽⁴⁴⁾ Long, F. A.; McDevit, W. F. Chem. Rev. 1952, 51, 119.

TABLE III: Rate and Equilibrium Constants forReaction of DNCB with OH^{-a}

[OH ⁻ T], M	10 ⁴ cmc, M	$K_{\rm S},{\rm M}^{-1}$	$10^{3}k_{\rm M},{\rm s}^{-1}$
0-0.12	8	100	5.1
0.25	1	110	7.2
0.50	0.6	170	8.7
0.70	0.4	200	9.6
1.00	0.2	250	11.3

^{*a*} At 25.0 °C, taking $K_{OH}' = 55 \text{ M}^{-1}$.

TABLE IV: Comparison of Second-Order Rate Constants in Aqueous and Micellar Pseudophases

substrate	reaction medium	$k_{2}^{m}, M^{-1} s^{-1}$	$k_2^{\mathbf{m}}/k_{\mathbf{W}}^{\mathbf{a}}$	
pNPDPP	СТАОН	0.11	0.23	
<i>p</i> NPDPP	CTAOH + OH⁻	0.10	0.21	
<i>p</i> NPDPP	CTAF	0.06	0.6	
DNCN	CTAOH	0.015	2.3	
DNCN	CTAOH + OH-	0.014	2.2	
DNCB	CTAOH	0.0007	5	
DNCB	$CTAOH + OH^{-}$	0.001	7	

^a Based on $k_{\rm W} = 0.48$, 6.4×10^{-3} , and 1.4×10^{-4} M⁻¹ s⁻¹ for reactions of OH⁻ in water with *p*NPDPP,^{39a} DNCN,³³ and DNCB,⁴⁰ respectively, and 0.1 M⁻¹ s⁻¹ for reaction of F⁻ with *p*NPDPP in water.^{39a}

of bound DNCB, so that k_{ψ} should increase even when the micelles are saturated with OH⁻ (Figure 5). The fit between experimental and predicted values of k_{ψ} for reaction of DNCB is good (Figure 5), using the parameters in Table III.

Reactions in Other Surfactants. Our model can also be applied to the reactions of pNPDPP with F^- in CTAF³⁵ (Figure S2) and of DNCB and DNCN with OH⁻ in 1, X = OH³³ (Figure S3) (supplementary material).

The rate-surfactant profiles for reactions in 1, X = OH (Figure S3) were fitted to eq 9–11 by using the parameters $K_{\rm OH}' = 8 \ {\rm M}^{-1}$ and cmc = $2 \times 10^{-2} \ {\rm M}$;⁴⁵ for DNCB, $K_{\rm S} = 10^2 \ {\rm M}^{-145}$ and $k_{\rm M} = 4 \times 10^{-3} \ {\rm s}^{-1}$; for DNCN, $K_{\rm S} = 10^3 \ {\rm M}^{-1}$ and $k_{\rm M} = 9 \times 10^{-2} \ {\rm s}^{-1}$. For reaction of pNPDPP in CTAF (Figure S2) we used the parameters $K_{\rm F}' = 40 \ {\rm M}^{-1}$, cmc = $2 \times 10^{-3} \ {\rm M}$,³⁵ $K_{\rm S} = 10^4 \ {\rm M}^{-1}$, and $k_{\rm M} = 0.44 \ {\rm s}^{-1}$.

The fit of experimental to calculated rate constants is insensitive to the values of $K_{\rm S}$ and cmc, especially at higher [surfactant].

Comparison of reactivities of DNCB and DNCN in CTAOH and 1, X = OH, suggests that $k_{\rm M}$ is similar for the two systems; however, values of $K_{\rm OH}$ are different and suggest that micellized 1 does not bind counterions strongly, and the cmc of CTABr is lower than that of 1 (X = Br) by approximately one order of magnitude.^{41,46} Interaction between counterions and surfactant assists micellization so that the higher cmc of 1, X = Br, as compared with CTABr is consistent with weaker binding of counterions.

The agreement between experimental and calculated rate constants (Figure S3) does not depend critically upon the binding constant of the substrate to the micelle, $K_{\rm S}$, but with other nonionic solutes the binding constants to micelles of 1 and CTABr are similar.³³

Validity of the Model and Constancy of β . The variation of k_{ψ} with surfactant or nucleophile concentration can be fitted to the kinetic model (Figure 1-5) with the parameters shown in Tables I-IV. The "best fit" rate constants, $k_{\rm M}$, are essentially independent of concentrations



Figure 6. Predicted variation of charge neutralization of head groups, β , with surfactant concentration and counterion binding constant, $K_{x'}$.

of surfactant or nucleophile, and binding constants, $K_{\rm S}$, M^{-1} , are similar to those in a bromide ion surfactant, e.g., CTABr. The treatment therefore, appears to be satisfactory, at least empirically, although its physical implications are less obvious. However, it is consistent with evidence that counterion binding is a specific property of the ion.^{5,7–9,13–17,47}

Our use of a mass action equilibrium between a micelle and a hydrophilic anion, e.g., OH⁻, appears at first sight to disagree with the generally accepted ion-exchange model. Equation 10 puts no restriction on the extent of charge neutralization of the micellar head groups by counterions, within the formal limits of 0 and 1 for β . In practice there is no reason to believe that these limits will be reached, as shown in Figure 6, where the predicted variation of β with [surfactant] is shown for various values of $K_{\rm X}'$. A hypothetical strongly bound anion, with $K_{\rm X}' \approx$ 2000 M⁻¹, would give a micelle with $\beta \approx 0.85$ over a wide concentration range. Our preliminary results suggest that $K_{\rm Br}' > 10^3 \,{\rm M}^{-1}$, so that we would expect β to be relatively constant for CTABr in the presence of added Br⁻ (Figure 6). However, even with a relatively weakly bound anion, e.g., OH⁻ (K_{OH} ' = 55 M⁻¹), the lower limit of β = 0 would not be observed under practical conditions because hydroxide ions are generated in the aqueous pseudophase by ionic dissociation from the micelle, and by the cmc.

We expect β to be relatively constant for a solution of, for example, CTABr + OH⁻, because Br⁻ binds so much more strongly than OH^{-8,12-17} that it will be the predominant bound counterion and will control the extent of charge neutralization in the micelle. There is, however, a problem with the accepted ion-exchange model which assumes strict constancy of β , because a small uncertainty in the estimated amounts of OH⁻ in the aqueous and micellar pseudophases introduces a large uncertainty in the estimated ion-exchange constant, K_X^{OH} , eq 1, because of application of the mass balance relation to both counterions.⁴⁸ This question is considered in more detail elsewhere.²⁰

⁽⁴⁵⁾ The cmc of 1, X = Br, is 7×10^{-3} M⁴⁶ and we assume that it will be higher for 1, X = OH.

⁽⁴⁶⁾ Bunton, C. A.; Savelli, G.; Sepulveda, L. J. Org. Chem. 1978, 43, 1925.

⁽⁴⁷⁾ Bunton, C. A. In "Reaction Kinetics in Micelles"; Cordes, E. H., Ed.; Plenum Press: New York, 1973; p 73.

⁽⁴⁸⁾ The problem with the ion-exchange model is most acute for experiments in the absence of added salt. In these systems the concentration of surfactant counterion, e.g., Br⁻, in the aqueous pseudophase depends upon $1 - \beta$ and the concentration of monomeric surfactant, which is assumed to be given by the cmc. Small changes in β , and the uncertainty in the concentration of monomeric surfactant, have a large effect on the estimate of $K_{\rm B}^{\rm B}$. This problem is decreased by addition of Br⁻ which buffers Br⁻_W.¹⁶

Although the mass action model, eq 10, fits our kinetic results it does not define the nature of the counterion binding. With CTAOH and CTAF we may have a wide spread of micellar size such that with dilute surfactant only small particles are present, but that increasing surfactant or counterion concentration allows the particles to grow and become normal micelles.

The formation of normal micelles is a cooperative phenomenon with head group repulsions balanced by hydrophobic attractions and attractions of head groups and counterions, and when the counterions are not very hydrophilic, e.g., Na⁺ or Br⁻, micellization occurs over a small range of concentration. If hydrophilic anions, e.g., OHor F⁻, bind weakly to the head groups the size distribution may be skewed toward small particles which could incorporate hydrophobic organic molecules, but because of their low charge density be incapable of strongly binding counterions, or catalyzing reaction.⁴⁹ However, with increasing counterion concentration increased ionic screening of the head groups would allow growth to the normal micelle, which would bind substrate and counterion and allow the reaction to proceed. This concept is consistent with electrostatic theories of counterion binding to relatively large polyions which predict that counterion binding to them should be independent of counter or polyion concentration. However, counterion binding should depend on polyion concentration in a salt-free solution, for a spherical polyion.²⁴

In this picture the apparent increase of β with increase of counterion concentration (Figure 6) would be the consequence of a size increase from relatively small *n*-mers to normal micelles. This change would occur over a wide concentration range for OH⁻ or F⁻, and over a much smaller range when the anion is more hydrophobic, e.g. with Br⁻, i.e., it would reflect differences in K_X' , depending upon the hydrophilicity of the counterion.⁵⁰

This description is consistent with the physical evidence. (i) There is a sharp break in the surface tension–[CTAOH] plot, which is consistent with only the monomers being surface active, whereas conductivity does not change sharply with concentration (Figure S1) because monomers, *n*-mers, and counterions are conductors. (ii) We see no light scattering by dilute CTAOH, although scattering is observed on addition of NaOH.⁴³

Comparison with the Ion-Exchange Model. Our kinetic data can be fitted with $K_{\rm OH'} = 55$ and 8 M⁻¹ for CTAOH and 1, X = OH, respectively, and $K_{\rm F'} = 40$ M⁻¹. We have no estimates of the values of $K_{\rm X'}$ for a more hydrophobic anion, e.g., Br⁻, but if it were $\sim 10^3$ M⁻¹ we would not expect β to vary much with surfactant or salt concentration, cf. Figure 6. The ion-exchange constant, $K_{\rm X}^{\rm OH}$, as defined by eq 1 should be given by $K_{\rm X'}/K_{\rm OH'}$. Published values of $K_{\rm Br}^{\rm OH}$ range from 10 to ~ 40 ,^{8,13-17} so that an estimated $K_{\rm OH'} = 55$ M⁻¹ and a value of $K_{\rm Br}^{\rm OH}$.

Reactions in CTAOĤ or CTAF fit the equations based on eq 10 with variable β . But reactions of H_3O^+ , CN^- , or Br⁻ in the reactive ion surfactants^{34,37,38} can be interpreted either in terms of eq 10, with large values of $K_{\rm X}$, or in terms of the pseudophase model, with constant β . However, estimated values of $k_{\rm M}$, or of ion-exchange constants for mixtures of counterions, depend upon the assumptions on which the calculations are based.⁴⁸

The ion-exchange model, with constant β , should be satisfactory for the quantitative treatment of salt effects upon micellar rates and equilibria when the reactive and unreactive counterions have similar affinities for the micelles, or when the more hydrophobic ion is in large excess.⁴⁸ For example, estimated values of $k_{\rm M}$ for cyanide addition to N-alkylpyridinium ions are similar for reactions in CTACN and in mixtures of CTABr and CN^{-.34} There is also reasonable agreement between $k_{\rm M}$ for acetal hydrolysis in micellized alkanesulfonic acid and in sodium lauryl sulfate with added HCl.³³

Rate Constants in Aqueous and Micellar Pseudophases. Although concentration of reactants into the micelles is the major source of the rate enhancements of bimolecular reactions, it is difficult to make precise comparisons of second-order rate constants in the aqueous and micellar pseudophases. Definition of concentration is a major problem whenever second-order rate constants are compared in different media. Conventionally, second-order rate constants in solution are based on concentration in terms of molarity, although other units would be as logical. Therefore calculation of the second-order rate constant in the micelle depends directly upon the estimated volume element of reaction, either that of the total micelle $^{6-10}$ or that of the Stern layer.¹⁴ This volume element is assumed to be independent of surfactant or counterion concentration, which is reasonable for the approximately spherical micelles of CTABr, for example, but not if micellar structure depends markedly upon concentration of counterion, e.g., with CTAOH or CTAF. Shrinkage of the micelle, or its Stern layer, with increasing $[OH^{-}]$ or $[F^{-}]$, would be equivalent to increasing concentration of micellar bound counterion, which would speed reaction.

The volume element of reaction may also depend upon the nature of the reactants.⁵¹ For example, very hydrophobic substrates may penetrate the micelle and be less exposed to a hydrophilic anion,³² and Menger has pointed out that water penetration should be sensitive to the conformations of the *n*-alkyl groups of the surfactant.³⁰

We estimated the volume of the Stern layer in 1 mol of micellized CTABr as 0.14 L,¹⁴ and if we apply this factor to reactions in CTAOH and CTAF we write the second-order rate constant, k_2^{m} , expressed in moles of nucleophile per liter of Stern layer as^{14,52}

$$k_2^{\rm m} = 0.14k_{\rm M} \tag{12}$$

Values of $k_2^{\rm m}$ and $k_{\rm w}$, the second-order rate constants $({\rm M}^{-1} {\rm s}^{-1})$ for reactions in the micellar and aqueous pseudophases, respectively, are in Table IV. Values of $k_2^{\rm m}$ are rounded off, and are averages for DNCB, for which we use only data with [NaOH] ≤ 0.25 M.

There appears to be a relation between $k_2^{\rm m}/k_{\rm w}$ and the hydrophobicity of the substrate, with the most hydrophobic substrate, pNPDPP, having the lowest reactivity with micellar bound OH⁻, relative to that in water, whereas the least hydrophobic substrate, DNCB, appears to be more reactive in the micelle than in water.

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⁽⁵⁰⁾ The relation between rate constant and [surfactant] can be rationalized in terms of an *n*-mer-micelle model. For reaction of DNCN in 0.5 M NaOH and CTAOH the limiting value of k_{ψ} is 0.12 s⁻¹ (Table IV) and should equal $\beta k_{\rm M}$ (eq 7). If we assume that in CTAOH reaction occurs only in the micelles and not in the *n*-mers the ratio of rate constants in CTAOH to that in 0.5 M NaOH and CTAOH should give the fraction of DNCN bound to micelles. For example, in 10⁻² M NaOH $k_{\psi} = 0.03 \, {\rm s}^{-1}$, so that the fraction bound is 25%, and in 0.1 M CTAOH the corresponding values are 0.068 s⁻¹ and 57%. We do not know how strongly DNCN binds to *n*-mers as compared to micelles, but these comparisons suggest that a relatively large amount of CTAOH is present as *n*-mers in dilute solution.⁴³

⁽⁵¹⁾ The estimated volume elements of reaction in the micellar pseudophase are at best crude approximations because dimensions of substrates, e.g., pNPDPP, may be similar to the thickness of the Stern layer. In addition, the composition of the micelle is not uniform.³⁰

⁽⁵²⁾ If we used the total volume of the micelle as the volume element our estimated values of k_2^{m} , eq 12 would be approximately doubled.

These comparisons suggest that the low value of $k_2^{\rm m}/k_{\rm w}$ for reaction of pNPDPP with OH⁻ is caused by a relatively deeper penetration of this substrate into the micelle as compared with that of DNCB. A similar conclusion has been made for reactions in functional micelles.⁵³ Values of $k_2^{\rm m}/k_{\rm w}$ for reactions of DNCB with phenoxide ion and pNPDPP with aryloxide and oximate ions are close to unity,^{39b,53,54} probably because the hydrophobicities of substrates and nucleophiles are such that both reside in the same region of the micelle.⁵⁵ Similar conclusions have

been drawn for reactions of other esters with relatively hydrophobic anionic nucleophiles.^{3b,6,9,10}

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Supplementary Material Available: Figures S1-S3, containing plots of κ vs. [CTAOH] and rate-surfactant profiles for reactions of pNPDPP with F^- in CTAF and of DNCB and DNCN with OH^- in 1, X = OH (3 pages). Ordering information is given on any current masthead page.

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Temperature Programmed Desorption Study of Water Adsorbed on Metal Oxides. 2. **Tin Oxide Surfaces**

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The type, the amount, and the adsorption bond strength of water adsorbed on SnO_2 were examined by temperature programmed desorption technique. SnO₂ samples, prepared from α - and β -stannic acid and calcined at 800 or 900 °C, showed essentially the same adsorbent characteristics. The samples, however, gave different desorption chromatograms of water depending upon the pretreatment atmosphere at 800 or 900 °C. When water was adsorbed on the samples pretreated in helium, two large water desorption peaks were observed at about 60 and 445 °C, while pretreatment in oxygen caused the appearance of four additional peaks at about 160, 250, 490, and 620 °C as well as the above two peaks. Except for the 60 °C peak which was ascribable to physisorbed water, all other peaks were found to reach saturation levels within a surface monolayer with increasing dose, indicating that they were all chemisorbed species. The 160 °C peak, which was very weak, was assigned to molecular water adsorbed on O^{2-} ions through hydrogen bonding, while the others were assigned to hydroxyl groups presumably on different crystal planes. The 620 °C water peak was accompanied by simultaneous desorption of oxygen at a ratio $H_2O/O_2 \simeq 1.8$ and was ascribed to the surface hydroxyls formed by the reaction of a water molecule with an adsorbed O^{2-} ion.

Introduction

It is known that the electrical conductivity of stannic oxide is highly sensitive to the gaseous environment. This phenomenon has been applied to the detection of inflammable gases, and many sensitive sensors have been devised by employing SnO_2 as a basic n-type semiconductor.¹⁻⁴ SnO_2 is also an important material for catalytic oxidation of organic molecules. A variety of binary oxide catalysts containing SnO₂ have been developed, including SnO₂-Sb₂O₄,⁵ -MoO₃,⁶ -V₂O₅,⁷ and -CuO.⁸ These sensors and catalysts are usually exposed to an atmosphere containing moisture under their operating conditions. Under such conditions, it is very likely that the surfaces are more or less covered with hydroxyl groups or adsorbed water molecules. Therefore, study of the nature of water adsorbed on SnO_2 is one of the necessary inputs to the elucidation of the related surface phenomena mentioned above.

There have been some previous reports on this subject. The infrared study by Thornton and Harrison⁹ revealed

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⁽⁵⁴⁾ The second-order rate constants for reactions of several nonionic nucleophiles in the micellar pseudophase are smaller than in water,^{5,14,1} but these rate differences are understandable in terms of the lower polarity of the Stern layer as compared with water.^{3b,t}

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