

Nucleophilic Reactions in Functional and Nonfunctional Micelles. Validity of the Pseudophase Ion-Exchange Model

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The dependence of the reaction of micellized *N,N*-dimethyl-*N*-(2-hydroxyethyl)-*N*-hexadecylammonium bromide (CDHABr) with *p*-nitrophenyl benzoate upon pH is analyzed, giving the apparent acid dissociation constant of the hydroxyl group, $pK_a \sim 12.3$. Salt effects upon this reaction are smaller than upon reactions of OH^- in nonfunctional micelles and are compared by using an empirical ion-exchange equation. This equation can also be applied to micellar reactions in the absence of added salt and in solutions of nonfunctional surfactants. It also allows comparison of rate constants in micelles of CDHABr + NaOH with those observed in the absence of inert counterion. Inhibition by SO_4^{2-} is compared with that due to univalent anions.

Micellar rate effects in aqueous solution are generally discussed in terms of the pseudophase model.¹⁻⁷ Reaction is assumed to occur in either a micellar or aqueous pseudophase, so that the overall rate of reaction is the sum of the rates in each pseudophase, with an equilibrium distribution of reactants between the pseudophases.⁸ For spontaneous, uni- or bimolecular reactions and micellar-inhibited bimolecular reactions variation of the first-order rate constant, k_p , with [surfactant] follows substrate distribution,⁹⁻¹⁰ but for nonsolvolytic bimolecular reactions one has to take into account the distribution of both reactants.³⁻⁷

The distribution problem is simple when both reactants are sufficiently hydrophobic to bind preferentially in the micelles,^{4,7a} but it is not so easy to discuss bimolecular reactions of hydrophilic ions. In favorable systems, ionic distribution between water and micelles can be estimated directly, for example, electrochemically,^{11,12} but these methods are not general. The development of the ion-exchange model by Romsted was a major step in our understanding of this problem.³ It involved several assumptions: counterions competed for ionic micelles, and large, low-charge density ions bound more strongly than small, high-charge density ions; reaction occurred at the micelle-water interface in the so-called Stern layer¹³ in

which ions bind specifically; and the fractional ionization of the micelle, α , was essentially independent of the nature or concentration of the counterion.³ The concentration of micellar-bound ions was therefore directly related to β , which is the fraction of micellar head groups neutralized by counterion, and $\beta = 1 - \alpha$. Ions not specifically bound to the micelle but in the diffuse layer were assumed not to react with micellar-bound substrate.

This general model explained the widely observed rate maxima for bimolecular ionic reactions with increasing [surfactant]. It also allowed estimation of second-order rate constants in the micellar pseudophase, and, where comparison could be made, these rate constants agreed reasonably well with those calculated from directly measured ionic concentrations in the micellar pseudophase^{3b,5} and were often similar to those for the reaction in water.^{3,5-7}

Added salts typically inhibit micellar-assisted bimolecular ionic reactions because of competition between reactive and inert ions, and this competition could also be treated quantitatively.^{3,5-7,15,16} Deprotonation of weakly acidic indicators in cationic micelles could also be treated quantitatively in terms of the amount of micellar-bound OH^- , calculated with the ion-exchange model.^{17,18}

There are problems with the model; for example, α is found experimentally to be dependent upon the counterion and increases in the sequence $\text{Br}^- < \text{Cl}^- < \text{OH}^-$, i.e., as the counterion becomes more hydrophilic.^{11,19-21} In addition, there may be a reaction across the micelle-water interface with hydrophilic ions, and effects due to changes in micellar structure are neglected. These assumptions were recognized in early discussions of the model.³⁻⁹

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(13) The term Stern Layer was originally applied to planar surfaces.¹⁴ It is widely applied to binding to micelles,^{1-3,5,8} but because of the curvature of their surfaces it might be better to refer to a specific binding layer.

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Sulfate ion behaves differently from monoanions such as Cl⁻ or Br⁻ in its ability to inhibit reactions of nucleophilic anions in cationic micelles.^{2,3,22,23} However, the solutions usually contained both inert mono- and dianions, and we have therefore examined reactions of OH⁻ in mixtures of Na₂SO₄ and cationic surfactants having sulfate as counterion. Chaimovich and Quina and their co-workers have developed equations which treat the competition between uni- and divalent ions for a micelle,²³ but inhibition by sulfate ion could not be explained in these terms, although the treatment was applied to a reaction of thio-sulfate ion.^{23a}

A clear example of the quantitative shortcomings of the model comes from a study of ion exchange using fluorescent probes.²⁴ Displacement of bromide ion from cationic micelles was followed, and for several anions, competition, measured with the probe, agreed with that estimated by kinetics or by other physical methods.^{3b,24} But very hydrophilic ions, e.g., OH⁻ or F⁻, were much less effective than expected in displacing Br⁻ from the micellar surface.

Another question is that of deprotonation of weakly acidic groups in functional micelles.^{5,26-29} We have examined the effects of OH⁻ and inert anions upon reactions in functional micelles or comicelles of *N,N*-dimethyl-*N*-(2-hydroxyethyl)-*N*-hexadecylammonium ion (CDHA⁺). Deprotonation of CDHA⁺ occurs at high pH, using OH⁻,²⁶ whereas buffers have to be used with more acidic functional groups,²⁹ and it is difficult to allow for micellar buffer effects.^{3b,30}



The zwitterion of CDHA⁺ is an effective nucleophile,^{26,29,31} and its micellar reactions in added OH⁻ can be analyzed in terms of an apparent acid (or base) dissociation constant.²⁶ Inert salts slow these reactions, but inhibition is much less than that typical of reactions in nonfunctional cationic micelles.^{26a} We have now examined these kinetic salt effects in more detail, but we cannot explain reaction rates in micelles of CDHAX in terms of an ion-exchange model based on the behavior of nonfunctional micelles.^{3b} Most work was on acylation of the functional surfactant by *p*-nitrophenyl benzoate (*p*-NPB).

Results

Functional micelles of the hydroxyethyl surfactant (CDHAX) effectively speed reaction with *p*-NPB at high pH. The alkoxide moiety is acylated by esters and is an

Table I. Reaction of *p*-NPB with OH⁻ in Micelles of CDHABr

[OH ⁻], M	<i>k_ψ</i> , s ⁻¹ , at various [CDHABr]		
	1.8 mM	5.5 mM	11 mM
0.005	20.5	15.8	11.0
0.01	28.7	23.6	17.8
0.02	42.3	33.9	26.2
0.05	55.7	49.9	38.6
0.10	70.3	62.3	53.6

^a At 25.0 °C.

Table II. Reaction of *p*-NPB with OH⁻ in Comicelles of CDHABr and CTABr

[OH ⁻], M	<i>k_ψ</i> , s ⁻¹ , at various [CDHABr]		
	0.15 mM	0.5 mM	1 mM
0.005	2.51	2.32	1.71
0.01	4.22	3.59	2.72
0.02	5.85	5.00	3.97
0.05	9.30	7.26	5.81
0.10	11.0	9.35	7.70

^a At 25 °C with [CTABr]:[CDHABr] = 10:1.

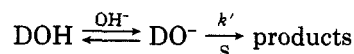
effective nucleophile toward other esters and activated halobenzenes,^{26-29,32} and the apparent p*K_a* is in the range 12.1–12.4.²⁶

Most kinetic estimates of the p*K_a* have been based on experiments at only one surfactant concentration, whereas the ion-exchange model predicts that the extent of deprotonation will depend upon the concentration of inert counteranion, e.g., Br⁻, and therefore upon the surfactant concentration,^{3b,7b,c} as is observed with weakly acidic indicators.^{17,18}

In this work we used micelles of CDHABr and comicelles of it and cetyltrimethylammonium bromide (CTABr) (Tables I and II).

The reaction in the micellar pseudophase with fully bound substrate, S, follows Scheme I,²⁶ where DOH denotes the functional surfactant.

Scheme I



The first order rate constant for overall reaction is given by

$$k_{\psi} = k[\text{DO}^-]/[\text{D}_n] \quad (1)$$

where [D_n] is micellized surfactant, so that

$$n/k_{\psi} = 1/k' + K_b/k[\text{OH}^-] \quad (2)$$

In eq 2 *n* is 1 and 0.1 for micelles and comicelles, respectively, in our experiments. The rate constant, *k*', and the apparent dissociation constant, *K_a*, (or *K_b*) can be calculated from eq 2 (Figure 1), from the variation of *k_ψ* with [OH⁻]. We neglected depletion of OH⁻ by deprotonation of DOH. This approximation is satisfactory except for the lowest [OH⁻] in micelles of CDHAX. The plots for the comicelles with CTABr are reasonably linear, values of *K_b* range from 0.015 to 0.02 and *k*' is 129, 110, and 100 s⁻¹ for reactions in 0.15, 0.5, and 1 mM CDHABr, respectively. For reactions in micelles of CDHABr values of *K_b* range from 0.02 to 0.024, and *k*' is 82, 71, and 67 s⁻¹ in 1.8, 5.5, and 11 mM CDHABr, respectively. Substrate should be extensively bound in these solutions.

The value of p*K_b* ~ 1.7 (p*K_a* ~ 12.3) agrees with earlier estimates,²⁶ but the unexpected observation is that these

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Table III. Quantitative Analysis of Reactions of OH⁻ Based on the Ion-Exchange Model^a

substrate	K_B, M^{-1}	$k_w, M^{-1} s^{-1}$	k_M, s^{-1}	$k_2^m, M^{-1} s^{-1}$
<i>p</i> -NPB ^b	1400	3.2	2.2 (3.5)	0.3 (0.5)
DNFB ^c	20	0.12	3.4 (4.8)	0.5 (0.7)
<i>p</i> -NPDHP ^c	1500	7.5×10^{-3}	6×10^{-3} (7.8×10^{-3})	0.9×10^{-3} (1.1×10^{-3})
<i>p</i> -NPDEP ^c	100	8.5×10^{-3}	12×10^{-3} (16×10^{-3})	1.7×10^{-3} (2.3×10^{-3})

^a Calculated with $K_{Br}^{OH} = 10$ and $\beta = 0.75$; values in parentheses are calculated with $K_{Br}^{OH} = 20$ and $\beta = 0.80$ except for *p*-NPB for which $\beta = 0.75$. ^b 0.005 M NaOH (ref 32). ^c 0.01 M NaOH (ref 22 and 26c). Abbreviations: DNFB, 2,4-dinitrofluorobenzene; *p*-NPDHP and *p*-NPDEP, *p*-nitrophenyl dihexyl and diethyl phosphate.

dissociation constants are, at most, only slightly dependent upon [surfactant] and are similar in micelles and comicelles, despite changes in [Br⁻], although Br⁻ is expected to decrease deprotonation.^{3b,17,18} The small decrease of k' (Figure 1 and Tables I and II) is consistent with only a modest effect of Br⁻.

Deprotonation of a micellar-bound weak indicator acid, BH, in a nonfunctional cationic micelle of CTAX can be treated quantitatively in terms of the basicity constant, K_B^M , in the micellar pseudophase:^{3b,17,18}

$$K_B^M = [BH_M]m_{OH^s}/[B_M^-] \quad (3)$$

where M denotes micellar bound material, CTAX is total surfactant, and

$$m_{OH^s} = [OH_M^-]/([CTAX] - cmc) \quad (4)$$

Equation 3 is analogous to eq 5 written for a rate process:^{3b,5,16}

$$k_M' = k_M m_{OH^s} \quad (5)$$

The concentration of micellar bound OH⁻ is assumed to follow the ion-exchange relation:³

$$K_X^{OH} = [OH_w^-][X_M^-]/\{[OH_M^-][X_w^-]\} \quad (6)$$

Micellar binding of substrate, S (or indicator, BH), is given by⁸

$$\frac{[S_M]}{[S_T]} = \frac{K_s([CTAX] - cmc)}{1 + K_s([CTAX] - cmc)} \quad (7)$$

where T denotes total substrate. Equations 3–7, with assumption of constant β , allow prediction of micellar or salt effects upon rates and equilibria.

For a deprotonated functional micelle, e.g., Scheme I, β should decrease with increasing deprotonation, because the zwitterion will not bind counterions,³³ but one can write an empirical relation, eq 8, where β_0 is the value in the absence of OH⁻:

$$\beta = \beta_0 (1 - m_N^s) \quad (8)$$

where m_N^s is the mole ratio of deprotonated to total surfactant calculated from the kinetically determined pK.

Equations 3–7 predict that the extent of deprotonation of a weak indicator acid in micelles or comicelles of CDHABr will go through a maximum with increasing [surfactant] at constant [OH⁻]. Qualitatively this behavior is observed for deprotonation of 5-nitroindole, in micelles or comicelles of CDHABr,³⁴ and, deprotonation in comicelles with CTABr follows the predictions of the ion-exchange model in 0.1 M NaOH and moderately well in 0.01 M NaOH, based on parameters similar to those which fit indicator deprotonation in nonfunctional micelles of CTABr.^{17,18}

It seemed reasonable therefore to attempt to explain deprotonation of the hydroxyl group of CDHA⁺ in these

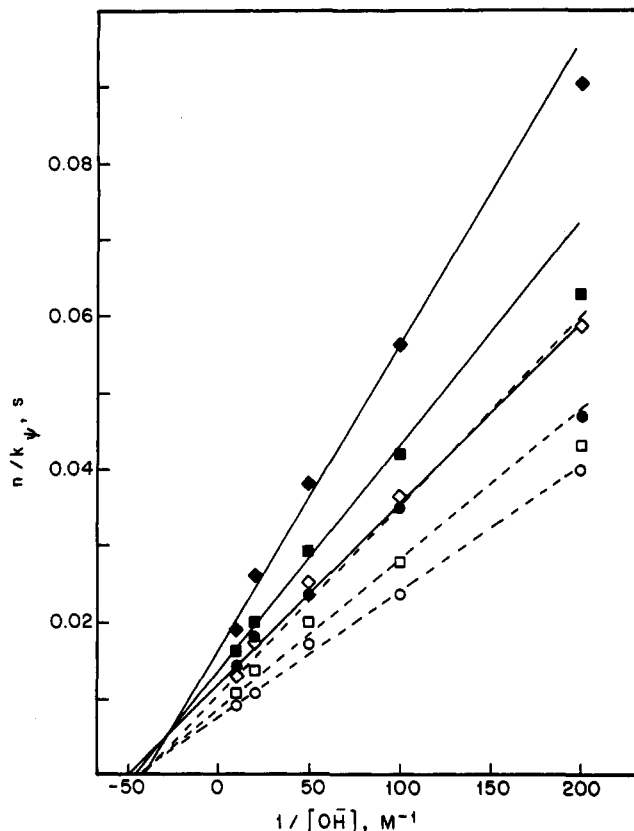


Figure 1. Estimation of K_b (apparent) for micelles and comicelles of CDHABr. Solid points represent micelles of CDHABr, $n = 1$, and open points represent comicelles of CDHABr-CTABr (1:10), $n = 0.1$: (\blacklozenge , \blacksquare , \bullet) 1.8, 5.5, and 11 mM CDHABr, respectively; (\diamond , \square , \circ) 0.15, 0.5, and 1 mM CDHABr, respectively.

terms, but we could not obtain a reasonable fit to the rate data (Tables I and II) taking values of the ion-exchange constant, K_X^{OH} , similar to those which fit reactions in nonfunctional micelles. Changes in the value of β to allow for deprotonation (eq 8) did not improve the situation.

However, the pseudophase, ion exchange, model fits the rate data for reaction of *p*-NPB with OH⁻ in CTACl and CTABr, (Figure 2 and ref 32), based on the parameters in Table III. The fits for dephosphorylation with OH⁻ in CTABr are shown in Figure S1 (supplementary material), and parameters for these reactions and an aromatic nucleophilic substitution are in Table III. Small changes in the parameters do not materially impair the fits. Other recent examples of the use of this model are in ref 3b and 35.

The variation of k_p with [OH⁻] for reaction of *p*-NPB with constant [CTABr] can also be fitted to the ion-exchange model for [OH⁻] < 0.05 M, but at higher [OH⁻] the predicted values of k_p are too low (Table IV). Similar deviations have been found for reactions of OH⁻ with DDT

(33) In any event the ion-exchange model fails if $\beta = 0$.

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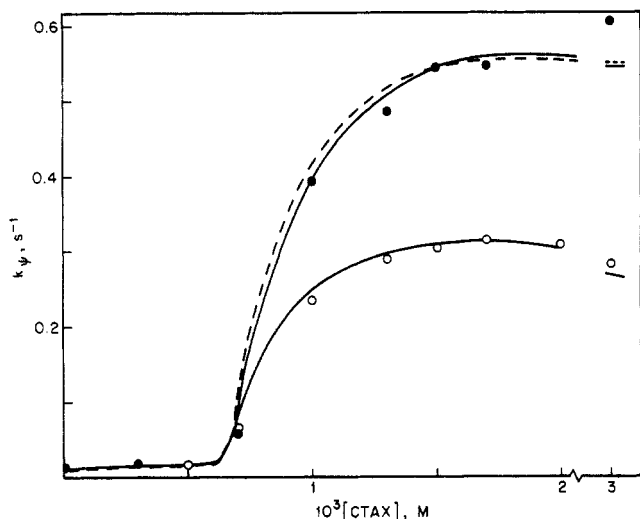


Figure 2. Quantitative treatment of the variation of k_ψ with [CTAX] for reaction of *p*-NPB: (●) X = Cl; (○) X = Br. The lines are theoretical: (---) eq 6-8; (—) eq. 10.

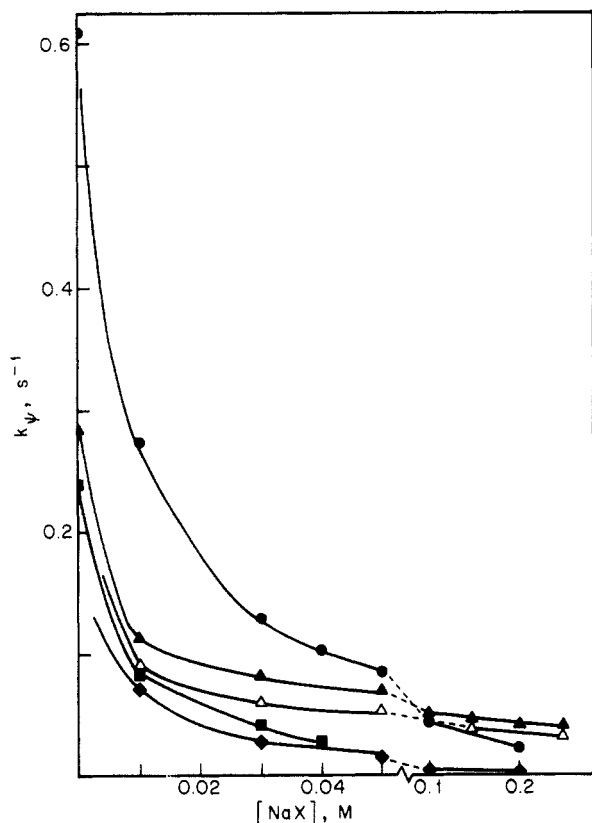


Figure 3. Salt effects upon reactions of *p*-NPB in CTAX micelles. The following plots are calculated, eq 6-8: (●) CTACl + NaCl; (■) CTABr + NaBr; (◆) CTABr + NaNO₃. Δ, and ▲ represent CTABr + 1/2 Na₂SO₄ and CTA(SO₄)_{1/2} + 1/2 Na₂SO₄, respectively. 0.01 M CTA⁺ and 0.01 M NaOH.

and related compounds, and Nome and co-workers have ascribed them to reaction across the micelle-water interface.³⁶

The second-order rate constants, k_M , (Table III and IV) are given with concentration written as a mole ratio (eq 4 and 5). The constants can be converted into k_2^m , M⁻¹

Table IV. Reaction of OH⁻ and *p*-NPB in CTABr^a

[NaOH], M	k_ψ , s ⁻¹	
	obsd	calcd
0.01	0.255	0.26 (0.27)
0.02	0.399	0.40 (0.42)
0.05	0.779	0.68 (0.76)
0.10	1.24	0.92 (1.03)

^a In 0.011 M CTABr at 25.0 °C. ^b Taking $K_s = 1400$ M⁻¹, cmc = 6×10^{-4} M, $\beta = 0.75$, and $k_w = 3.2$ M⁻¹ s⁻¹, $K_{Br}^{OH} = 10$ and $k_M = 2.2$ s⁻¹; values in parentheses are calculated by taking $K_{Br}^{OH} = 20$ and $k_M = 2.5$ s⁻¹.

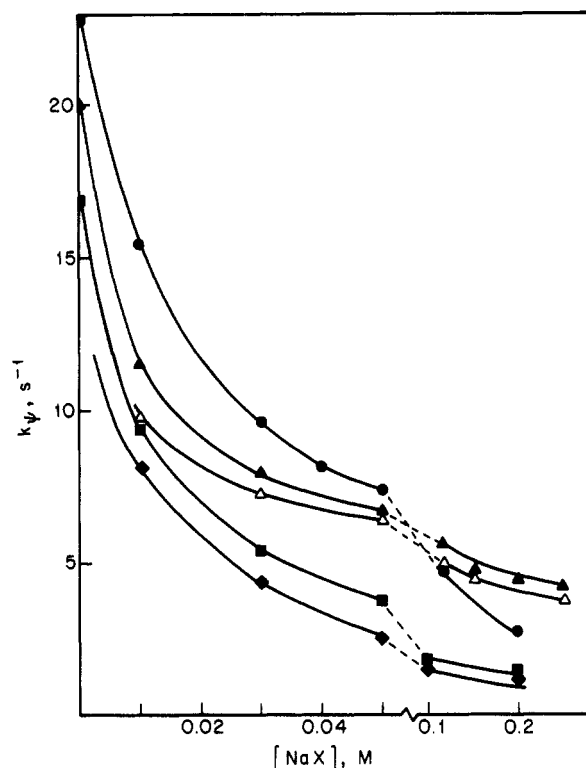


Figure 4. Salt effects upon reactions of *p*-NPB in functional micelles of CDHAX. The following plots are calculated, eq 10: (●) CDHAX + NaCl; (■) CDHAX + NaBr; (◆) CDHAX + NaNO₃. Δ and ▲ represent CDHAX + Na(SO₄)_{1/2} and CDHAX(SO₄)_{1/2} + Na(SO₄)_{1/2}, respectively. 0.01 M CDHAX⁺ and 0.01 M NaOH.

s⁻¹, by taking into account the molar volume of the reaction environment which is assumed to be 0.14 L,^{3b,5,16} so that

$$k_2^m = 0.14k_M \quad (9)$$

Other estimates of this volume range up to 0.37 L,^{6,7,37} which increases k_2^m correspondingly.

Evidence to date suggests that salt effects are smaller for reactions of functional, as compared with nonfunctional, micelles,^{26a} and SO₄²⁻ behaves differently from univalent anions. Substrate hydrophobicity appears to be unimportant, and in dilute salt, SO₄²⁻ is a better inhibitor than Cl⁻, but at higher concentrations the salt order is reversed (Figures 3 and 4 and ref 2,22,23b).

The effects of univalent anions upon reactions of *p*-NPB in nonfunctional cationic micelles can be fitted reasonably well to the ion-exchange model for CTACl-NaCl, with $K_{Cl}^{OH} = 3$, and CTABr + NaBr or NaNO₃, with values of K_X^{OH} for Br⁻ and NO₃⁻ of 10-12 and 15, respectively,^{3b,24,38}

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(38) In treating CTABr + NaNO₃ we assume that Br⁻ and NO₃⁻ have similar affinities for cationic micelles which leads to discrepancies in dilute NaBr.

Table V. Fitting Parameters for Salt Effects upon Reactions of *p*-NPB

surfactant	$K_X^{OH^a}$	y
CTACl + Cl ⁻	3	3 ^b
CTABr + Br ⁻	12	10 ^b
CTABr + NO ₃ ⁻	15	18 ^b
CDHACl + Cl ⁻		0.8 ^c
CDHABr + Br ⁻		1.7 ^{c,d}
CDHABr + NO ₃ ⁻		2.0 ^c

^a Calculated with $k_M = 2.2 \text{ s}^{-1}$, $K_s = 1400 \text{ M}^{-1}$, and $\beta = 0.75$.

^b Calculated with $k_0 = 1.75 \text{ s}^{-1}$. ^c Calculated with $k_0 = 42 \text{ s}^{-1}$. ^d $y = 1.5$ for reaction in absence of added salt.

Table VI. Empirical Treatment of Reaction of *p*-NPB in Comicelles^a

$10^4[\text{CDHABr}], \text{M}$	k_ψ, s^{-1}
	0.0029
0.3	0.0034
1.0	0.642 (0.76)
1.5	0.825 (0.87)
2.0	0.812 (0.83)
5.0	0.610 (0.50)

^a At 25.0 °C with 0.001 M NaOH and [CTABr]:[CDHABr] = 10:1. Values in parentheses are calculated from eq 10 with $K_s = 1400 \text{ M}^{-1}$, $k_0 = 5.2 \text{ s}^{-1}$, $y = 1.5$, and $\text{cmc} = 6 \times 10^{-4} \text{ M}$.

in agreement with earlier observations^{3b} (Figure 3). However, we could not fit salt effects upon reaction in functional micelles (Figure 4) in these terms taking parameters similar to those applied to reaction in nonfunctional micelles. The situation is similar to that noted earlier for reaction in functional micelles of CDHAX in absence of added salt.

The empirical equation (eq 10) fitted salt effects of univalent ions upon reactions of *p*-NPB in both functional and nonfunctional micelles:

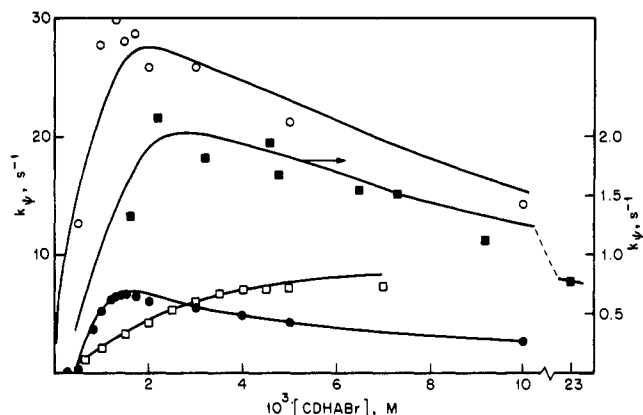
$$k_\psi = \left(\frac{K_s[\text{D}_n]}{1 + K_s[\text{D}_n]} \right) \frac{k_0}{(1 + yr)} \quad (10)$$

where r is the ratio of inert anion to OH⁻ and D_n is micellized surfactant.

The rate constant k_0 can be regarded as that in a hypothetical micelle which contains no inert counterion, and y indicates the sensitivity of the reaction to added salt. Values of k_0 and y are in Table V, together with ion-exchange parameters for nonfunctional micelles. The fit to the data is shown in Figure 4 for mixtures of CDHACl + NaCl and CDHABr + NaBr or NaNO₃. We could not apply eq 10 to the effects of SO₄²⁻.

Equation 10 also describes the effects of univalent ions upon reaction of *p*-NPB in nonfunctional micelles with fully bound substrate. We set the value of k_0 as βk_M because β gives the maximum value of m_{OH^-} (eq 5), so that for saponification of *p*-NPB $k_0 \sim 1.7 \text{ s}^{-1}$ and the fit of k_ψ against [salt] based on the values of y in Table V and eq 10 is essentially indistinguishable from that obtained using the ion-exchange treatment (Figure 3). Values of y are much smaller in functional than in nonfunctional micelles, as are the negative salt effects (Table V and Figures 3 and 4).

Equation 10 also describes rate-surfactant profiles for reaction of *p*-NPB in absence of added salt, provided that we take $k_0 = 1.9 \text{ s}^{-1}$. Figure 2 illustrates the fits in CTACl and CTABr, which are similar to those based on the ion-exchange model. Reaction of *p*-NPB in functional micelles and comicelles also fits eq 10 (Figure 5 and Table VI). Values of k_0 and y for reaction of *p*-NPB are similar in the presence and absence of salt, provided that allowance is made for "dilution" by CTABr in comicelles (Table VI).

**Figure 5. Fitting of rate constants for reactions in functional micelles of CDHABr to eq 10: (●, ○) *p*-NPB in 0.001 and 0.01 M NaOH, respectively; (□) 2,4-dinitrofluorobenzene in 0.01 M NaOH; (■) 2,4-dinitrochloronaphthalene in 0.01 M NaOH (ref 21 and 26b).****Table VII. Empirical Treatment of Reactions in Functional Micelles**

substrate	K_s, M^{-1}	k_0, s^{-1}
<i>p</i> -NPB ^a	1400	42
CNCN	1600	3.5 (4.0)
DNCB	75	0.13 (0.15)
DNFB	20	150
<i>p</i> -NPDPP	10 ⁴	2.1 (2.3)
<i>p</i> -NPDHP	3 × 10 ³	0.028
<i>p</i> -NBP	10 ³	0.032

^a Calculated from eq 10 with $y = 1.5$; for reaction in 0.001 M OH⁻ $k_0 = 48 \text{ s}^{-1}$. Values in parentheses are for reactions in CDHACl (ref 28). Abbreviations: DNCN and DNCB, 2,4-dinitrochloronaphthalene and benzene; *p*-NPDPP, *p*-nitrophenyl diphenyl phosphate; *p*-NBP, *p*-nitrobenzoyl phosphate.

Equation 10 can also be applied to aromatic nucleophilic substitution, dephosphorylation, and hydrolysis of 4-nitrobenzoyl phosphate in CDHABr + OH⁻ (Figure 5 and Table VII). Some of these reactions have also been followed in micelles of CDHACl where there is no interionic competition.²⁸ Values of k_0 are very similar to plateau rate constants in CDHACl for fully micellar bound substrate.

Although eq 10 fits the rate data for a number of reactions in functional and nonfunctional micelles, it is merely an empirical expression which allows us to calculate values of k_0 by extrapolation and to compare salt effects in functional and nonfunctional micelles. It is completely different from eq 6, which is based on a well-defined model,^{3,5,7,23,24,35,37} or the treatment based on individual binding constants for each ion, which has been applied as an approximate treatment³⁹ and on a more rigorous basis.⁴⁰

For reactions in functional micelles the rate constants k' (eq 2) and k_0 (eq 10) are calculated by extrapolation of observed rate constants k_ψ . For k' the extrapolation is to infinite [OH⁻] and the concentration of Br⁻ is not taken into account. For k_0 the extrapolation is to $[\text{X}^-]/[\text{OH}^-] = 0$, i.e., to $[\text{X}^-] = 0$, where X⁻ is Br⁻ or Cl⁻. As a result values of k' and k_0 differ somewhat, with $k' > k_0$; for example, for reaction of *p*-NPB in CDHABr with varying [OH⁻], k' ranges from 67 to 82 s⁻¹, whereas from experiments with added salts $k_0 = 40\text{--}50 \text{ s}^{-1}$.

Discussion

The ion-exchange model accommodates a great deal of kinetic and equilibrium data, for chemical reactions of

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univalent ions, and a mass-action-like model can be applied to reactions of hydrophilic anions in reactive-ion micelles.^{3,5-7,21,35,37,41} Reaction in the micelles is assumed to take place in a uniform region at the surface, the so-called Stern layer.

Micellar effects upon some inorganic reactions have been treated in terms of ionic distributions based on micellar surface potential.⁴² But these potentials were calculated from indicator equilibria,⁴³ so that micellar effects upon indicator equilibria were being related to effects upon rates of ionic reactions, which involves circular reasoning. Stigter has noted the problems which arise when attempts are made to estimate the potential of hydrophobic colloids from such data.⁴⁴ Thus this approach has no more predictive power than the pseudophase ion-exchange model (eq 6). However discussing ionic distribution in terms of surface potential avoids the artificiality of restricting reaction sites to the micellar Stern layer or the water, with no reaction across the micelle-water interface. Surface potentials and ion binding can be estimated by solving the Poisson-Boltzmann equation in spherical symmetry but neglecting specific effects.^{45,46} Specific effects have been described in a treatment of ion binding at a plane surface,⁴⁷ and reactivity in spherical micelles can be fitted to a model that includes both coulombic and specific effects and accounts qualitatively for inhibition by dianions and reactivity of a nucleophilic dianion.⁴⁸

The problem with the existing ion-exchange model seems to be that it unduly focuses attention on ion binding in the Stern layer and neglects any role for ions in the diffuse layer, cf. ref 36. But ions in the diffuse layer decrease the potential at the micellar surface, and SO_4^{2-} should be especially effective in this respect, because its double negative charge will skew its distribution strongly toward the micellar surface, in comparison with a hydrophilic univalent ion.⁴⁶ Thus the kinetic salt effect of SO_4^{2-} is probably not a manifestation of its ability to compete with reactive anions in the Stern layer but is a coulombic effect which can be understood in terms of a nonspecific interaction governed by a Poisson-Boltzmann distribution. We do not suggest that specific interactions are unimportant in interionic competition at a micellar surface, because of very clear specificity in the micellar binding of halide and nitrate ions, for example,^{3,5,7,24,25} but we believe that counterions can influence reaction rates in micelles by virtue of their nonspecific binding in the diffuse layer, as well as specific binding in the Stern layer.

This hypothesis is supported by evidence from light scattering by cationic micelles. Micelles with bromide counterion grow under conditions in which there is little growth when the counterion is Cl^- and probably none when it is OH^- .^{19b,c20,49} For a given micelle cmc and α decrease

in the sequence $\text{OH}^- > \text{Cl}^- > \text{Br}^-$, and the aggregation number increases in that sequence. But $(\text{CTA})_2\text{SO}_4$ has a very low cmc (0.2 mM⁵⁰), although from the evidence of dynamic light scattering it has a very low fractional charge, α , of 0.07,⁵¹ as compared with ca. 0.5, 0.27, and 0.22 for the related hydroxide, chloride, and bromide micelles, respectively.¹⁹ Despite this low value of α $(\text{CTA})_2\text{SO}_4$ shows little tendency to grow even in 1 M Na_2SO_4 , whereas with corresponding salt concentrations CTACl and especially CTABr show considerable growth.⁴⁹ Qualitatively these observations are consistent with little specific binding of SO_4^{2-} as compared with Br^- , for example, so that salt effects of SO_4^{2-} in micellar systems seem to be due not to competition in the Stern layer but to a decrease in surface potential caused by SO_4^{2-} in the diffuse layer. This hypothesis is consistent with the inability of the ion-exchange model to account for inhibition by SO_4^{2-} .

The differences in the parameters γ (Table V and eq 10) for functional and nonfunctional micelles are understandable on a qualitative basis because the hydroxyl group in a functional micelle will be located away from the cationic micellar head groups where there appears to be strong specificity in ion binding, whereas there should be little ion specificity in the diffuse layer, which would correspond to $\gamma \approx 1$. Values of γ for CDHAX + OH^- range from 0.8 for $\text{X} = \text{Cl}^-$ to 2.0 for NO_3^- and are much larger for CTAX (Table V), consistent with low specificity in the interionic competition. The differences arise in part because the hydroxyl group can be deprotonated by OH^- in the diffuse layer and also because deprotonation of the hydroxyl group of CDHAX decreases the ability of the micelle to attract anions. Analogy with anion-exchange resins is helpful. Competition between Cl^- and other anions for Dowex 1 and 2 depends specifically upon the anion but, except for OH^- , is very similar for the two resins. However, Dowex 2 contains a β -hydroxyethylammonium group, and its deprotonation by OH^- sharply decreases the ability of the resin to bind Cl^- .⁵²

Concentrations of OH^- in the diffuse layer, i.e., adjacent to the hydroxyl groups in a CDHA⁺ micelle, should approximately follow total concentration of OH^- . Therefore deprotonation of the hydroxyl group, as given by $\text{p}K_a$, should not be very sensitive to inert anions, e.g., Br^- . But these anions should markedly affect deprotonation of an indicator bound in the Stern layer.^{17,18}

Experimental Section

Materials. The preparation and purification of the surfactants and the other reagents have been described.²⁶

Kinetics. Reactions of *p*-nitrophenyl benzoate (*p*-NPB) were followed spectrophotometrically at 25.0 °C.³² Solutions were made up in CO_2 -free redistilled deionized water. The first-order rate constants, k_p , are in reciprocal seconds.

Binding of Br^- . The binding of Br^- to micelles of CDHABr was followed with a specific bromide ion electrode which was calibrated with NaBr and had a Nernst slope of 59.2 mV. Values of the fractional micellar ionization, α , were similar for CTABr and CDHABr and were 0.31–0.33 and 0.27–0.29, respectively. The values of CTABr are similar to other values estimated electro-

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chemically^{11,20a} and slightly higher than those estimated from diffusivity.^{11,19a,b,49c}

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Registry No. CDHABr, 20317-32-2; *p*-NPB, 959-22-8; DNFB, 70-34-8; *p*-NPDEP, 311-45-5; *p*-NPDHP, 102494-18-8; CTACl,

112-02-7; CTABr, 57-09-0; CDHACl, 24625-03-4; DNCN, 2401-85-6; DNCB, 97-00-7; *p*-NPDP, 10359-36-1; *p*-NBP, 20513-28-4; *p*-NO₂C₆H₄OC(O)Ph, 959-22-8; SO₄²⁻, 14808-79-8; OH⁻, 14280-30-9; Cl⁻, 16887-00-6; Br⁻, 24959-67-9; NO₃⁻, 14797-55-8.

Supplementary Material Available: A figure, of variation of k_p in the [CTABr] for reactions of *p*-nitrophenyl dialkyl phosphates with 0.01 M NaOH^{26c} (2 pages). Ordering information is given on any current masthead page.

Acid-Catalyzed Photooxidation of *m*-Nitrobenzyl Derivatives in Aqueous Solution

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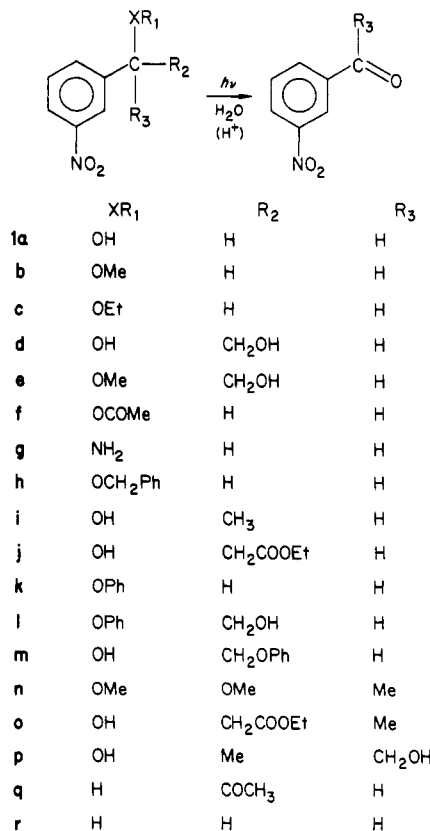
A variety of *m*-nitrobenzyl derivatives including alcohols, alkyl ethers, esters, and an amine undergo photooxidation reactions to produce *m*-nitrobenzaldehyde (or *m*-nitroacetophenone in two cases) as the major isolated product. The reaction is both solvent and pH dependent and only takes place in essentially aqueous media. The quantum efficiency of product formation reaches a maximum ($\phi = 0.3-0.4$) in the 20-50% sulfuric acid range, depending on the substrate, although the reaction is reasonably efficient even in neutral aqueous solution. The presence of benzylic hydrogen and a heteroatom (O, N) in the α -position appears to be essential for photooxidation to occur. The multiplicity of the reactive state is T₁. A solvent isotope effect ($\phi_{\text{H}_2\text{O}}/\phi_{\text{D}_2\text{O}} = 1.4$) was observed. The proposed mechanism involves rate-determining protonation of T₁ followed by rapid α -hydrogen abstraction by water.

Photochemical reactions of *o*-nitrobenzyl compounds are well-known and have been shown to involve intramolecular oxidation-reduction in several cases. For example, *o*-nitrobenzyl alcohol reacts photochemically¹ in organic solvents to give *o*-nitrosobenzaldehyde, while *o*-nitrobenzaldehyde undergoes photooxidation-reduction in various solvents and even in the solid state to give *o*-nitrobenzoic acid.² These reactions do not appear to involve catalysis by either external acids or bases and are clearly intramolecular in origin due to the proximity of the two groups involved.

In contrast, the photoredox reactions of analogous *m*- and *p*-nitrobenzyl derivatives take place only in aqueous media and are subject to catalysis.^{3,4} Surprisingly, irradiation of *p*-nitrobenzyl alcohol itself gives *p*-nitrosobenzaldehyde as the major product in a process which is strongly catalyzed by hydroxide ion,⁴ whereas the *m*-nitro isomer gives *m*-nitrobenzaldehyde via hydrogen ion catalysis.⁵ The detailed mechanism of these reactions has been the subject of several previous reports.³⁻⁵

We were interested in exploring the generality and possible synthetic utility of such photoredox reactions and because of the greater efficiency of the *m*-nitrobenzyl alcohol reaction,⁵ which has absolute quantum yields in the 0.05-0.4 range, depending on the pH, it was decided to

Chart I



concentrate initially on *m*-nitro systems. Their higher reactivity appears to be another example of the well-known meta effect⁶ in photochemical reactions.

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