Deprotonation of 5-Nitroindole in Micellized Cetyltrimethylammonium Bromide and Hydroxide

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The fraction, f, of deprotonation of 5-nitroindole (BH) in cetyltrimethylammonium bromide (CTABr) and NaOH goes through maxima with [CTABr]. In CTAOH micelles f increases smoothly with [CTAOH], even when the indicator is fully micellar bound, and is increased by added NaOH. These variations of f follow the concentrations of BH and OH⁻ in the cationic micelles and the basicity constant in the micellar pseudophase is smaller than in water by a factor of ca. 5.

The first examples of micellar effects upon reactivity were the observations that cationic micelles increased, and anionic micelles decreased, deprotonation of weak acids.^{1,2} These micellar effects have been treated quantitatively in terms of models which attempt to describe the concentrations of indicator acid and OH^- in the micelles, which are treated as a pseudophase $^{4-6}$ Similar treatments have been applied to micellar effects upon chemical reactivity.^{7–12}

In one quantitative treatment the effects of micellized cetyltrimethylammonium chloride and bromide (CTACl and CTABr, respectively; CTA⁺ = n-C₁₆H₃₃N⁺Me₃) upon deprotonation of benzimidazole and naphth[2,3]imidazole were explained in terms of the distribution of areneimidazole between the two pseudophases, and the distribution of hydroxide ion, governed by ion exchange between hydroxide and halide ion,⁶ and we follow this general approach here.

There is considerable evidence that β , the fraction of micellar head groups neutralized by counterions such as Br-, is insensitive to the nature or concentration of counterions.^{7,13} Therefore, rate constants in micelles of reactive ion surfactants should become constant once the substrate is fully micellar bound, because, if β is constant, the micellar Stern layer should be saturated with reactive

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counterions.¹⁴ The kinetic form is followed for reactions of anions such as cyanide¹⁵ or bromide,^{14b} but for reactions of more hydrophilic ions, such as hydroxide or fluoride, rate constants do not become constant when substrate is fully micellar bound, but increase on addition of surfactant or anion.^{14,16} It was originally suggested that this increase of rate, observed on addition of OH⁻, was the result of a reaction of micellar-bound substrate with OH- in the aqueous pseudophase.^{14a} This hypothesis was inconsistent with the generally accepted postulate that a reactant in the micellar pseudophase did not react with a reactant in the aqueous pseudophase,³ but it was applied to the effect of high concentrations of OH^- upon reactions of DDT and related compounds in cationic micelles,¹⁷ and to some amide hydrolyses.¹⁸

However, it was subsequently shown that rate constants of reactions in micellized cetyltrimethylammonium hydroxide (CTAOH) could be fitted to a rate equation in which micellar binding of OH- was governed by a massaction form of equation.¹⁶ In other words micelles were apparently not saturated with OH^- , and β appeared to increase with increasing OH⁻. This apparent variation of β could be due to a wide dispersion of size for micelles of CTAOH, with the smaller micelles being relatively ineffective at binding counterions, and the average micellar size increasing with surfactant concentration.

Reaction across the Stern layer introduces a new reaction path, without requiring an increase of β on addition of OH⁻. Therefore, it should be possible to distinguish between the two explanations by examining the effect of CTAOH upon equilibrium deprotonation of a weak acid, because introduction of a new reaction path should not affect an equilibrium reaction. We required an acid which would be partially deprotonated in CTAOH, and which would bind readily to the micelle. 5-Nitroindole (BH) is

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Figure 1. Extent of deprotonation of 5-nitroindole in CTABr + NaOH: (O) 0.01 and (●) 0.1 M NaOH. The lines are calculated.

a convenient indicator, with $pK_a = 14.75$,¹⁹ and an anion (B⁻) with λ_{max} at 398 nm.



We therefore examined deprotonation of BH in CTABr and OH⁻, where the anions should compete for the micelle, and also in CTAOH.

Experimental Section

Materials. The preparation or purification of CTABr and CTAOH has been described.¹⁶ 5-Nitroindole was decolorized (charcoal) and recrystallized twice (aqueous EtOH): mp 139-140 °C (lit.²⁰ mp 136, 141-142 °C).

Deprotonation. The fraction, f, of deprotonated 5nitroindole was estimated spectrophotometrically, at 25.0 °C, from the absorbance at λ_{max} of 398 nm where $\epsilon = 9690$. The concentration of 5-nitroindole was 9×10^{-5} M, and $f = [B^-]/([B^-] + [BH])$. Solutions were made up in redistilled, deionized, water under N_2 to exclude CO_2 .

Binding Constant. An estimate of the binding constant of 5-nitroindole to CTABr was based on the spectra in water and CTABr $(5 \times 10^{-3} \text{ M})$.²¹ The spectral shifts were small (<10 nm) but gave a binding constant of >2 \times 10² M⁻¹.

Results and Discussion

Deprotonation in CTABr. The extent of deprotonation of 5-nitroindole in 0.01 and 0.1 M NaOH goes through maxima with increasing [CTABr] (Figure 1). This behavior is very similar to that observed for deprotonation of phenols and areneimidazoles⁶ and can be explained qualitatively in terms of an increase in micellar binding of an acid, BH, and a competition between Br⁻ and OH⁻ for the cationic micelle.

A quantitative treatment of deprotonation in terms of the pseudophase ion-exchange model has been described, and we follow the earlier treatment.⁶ The anion of 5nitroindole should bind very strongly to the cationic micelles, but both 5-nitroindole and OH⁻ will be distributed between aqueous and micellar pseudophases.

The distribution of BH between water and micellized CTAX is assumed to follow eq 1:

$$K_{\rm s} = [\rm BH_{\rm M}] / \{[\rm BH_{\rm W}]([\rm CTAX] - \rm cmc)\}$$
(1)

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Figure 2. Extent of deprotonation of 5-nitroindole in CTAOH: (O) with no added NaOH, (
) 0.1 M NaOH. The lines are calculated.

where X = Br or OH.

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In eq 1 subscripts W and M denote aqueous and micellar pseudophases, respectively, and the concentration of monomeric surfactant is assumed to be given by the critical micelle concentration, cmc.²²

The basicity constant in the micellar pseudophase is written as⁶

$$K_{\rm B}{}^{\rm M} = \frac{[{\rm B}{\rm H}_{\rm M}]m_{\rm OH}{}^{\rm s}}{[{\rm B}_{\rm M}{}^{\rm -}]} = \frac{[{\rm B}{\rm H}_{\rm M}][{\rm O}{\rm H}_{\rm M}{}^{\rm -}]}{[{\rm B}_{\rm M}{}^{\rm -}]([{\rm CTAX}] - {\rm cmc})}$$
(2)

This basicity constant is defined in terms of the concentration of OH⁻ written as a mole ratio of bound OH⁻ to cationic head groups in the micelle. In CTABr the value of $m_{\text{OH}^{s}}$, or $[\text{OH}_{\text{M}}^{-}]$, is estimated from eq 3 and 4 and mass balance

$$m_{\rm OH}{}^{\rm s} + m_{\rm Br}{}^{\rm s} = \beta \tag{3}$$

where β is the degree of counterion binding, and

$$K_{\rm Br}^{\rm OH} = [OH_{\rm W}^{-}][Br_{\rm M}^{-}]/\{[OH_{\rm M}^{-}][Br_{\rm W}^{-}]\}$$
 (4)

Assuming that β and $K_{\rm Br}{}^{\rm OH}$ are independent of the nature of concentrations of the counterions, $m_{\rm OH}{}^{\rm s}$ can be estimated by using the quadratic equation 5:

$$(m_{\rm OH}^{\rm s})^{2} + m_{\rm OH}^{\rm s} \left(\frac{[\rm OH_{\rm T}^{-}] - K_{\rm Br}^{\rm OH}[\rm Br^{-}]}{([\rm CTABr] - \rm cmc)(K_{\rm Br}^{\rm OH} - 1)} - \beta \right) - \frac{[\rm OH_{\rm T}^{-}]\beta}{([\rm CTABr] - \rm cmc)(K_{\rm Br}^{\rm OH} - 1)} = 0$$
(5)

The fraction, f, of deprotonated 5-nitroindole can be written in terms of eq 6

$$f = [OH_{T}^{-}] / \{[OH_{T}^{-}] + K_{B}(app)\}$$
(6)

where

$$K_{\rm B}({\rm app}) = [{\rm BH}_{\rm T}][{\rm OH}_{\rm T}^{-}]/[{\rm B}_{\rm T}^{-}]$$
 (7)

In eq 6 and 7 subscript T denotes total concentration. Equations 1 and 7 give

$$K_{\rm B}(\rm app) = \frac{K_{\rm B}^{\rm M}(1 + K_{\rm s}([\rm CTABr] - \rm cmc))[\rm OH_{\rm T}^{-}]}{m_{\rm OH}^{\rm s}K_{\rm s}([\rm CTABr] - \rm cmc)}$$
(8)

Equations 5 and 8 can be combined and the data can be treated by computer simulation.^{6b}

Deprotonation in CTAOH. The extent of deprotonation of BH in CTAOH increases smoothly with [surfactant] and with added OH⁻, even under conditions such that 5-

TABLE I: Parameters Used in Fitting the Data

surfactant	$10^4 \times (\text{cmc}), \\ M$	$K_{s},$ M ⁻¹	K_B^{M} .
CTABr + 0.01 M OH-	6	350	0.14^{a}
$CTABr + 0.1 M OH^{-}$	4	400	0.15^{a}
CTAOH	8	300	0.14^{b}
$CTAOH + 0.1 M OH^{-1}$	4	400	0.09^{b}
^a Coloulated by taking ^a	0.70 and	W OH	I_ 15

^a Calculated by taking $\beta = 0.78$ and $K_{\rm Br}^{OH} = {}^{b}$ Calculated by taking $K'_{\rm OH} = 55 {\rm M}^{-1}$.

TABLE II: Effect of NaF upon Deprotonation in $CTAOH^a$

$\frac{10^{3} \times}{[CTAOH],}$	f	f ^b	10 ³ × [CTAOH], M	f	f ^b
4.0	0.29	0.38	20.0	0.48	0.71
8.0	0.36		50.0	0.68	0.80
10.0	0.38	0.64			

 a At 25.0 °C and 0.1 M NaF, unless specified. b In the absence of NaF.

nitroindole (and its anion) should be essentially fully micellar bound (Figure 2). These observations suggest that the Stern layer of CTAOH micelles is not saturated with OH^- , except at high $[OH^-]$, and we assume that the concentration of micellar-bound OH^- is given by¹⁶

$$K'_{\rm OH} = [OH_{\rm M}^{-}]/[OH_{\rm W}^{-}]([D_{\rm n}] - [OH_{\rm M}^{-}])$$
 (9)

where $[D_n] = [CTAOH] - cmc$.

The distribution of 5-nitroindole between aqueous and micellar pseudophases is assumed to follow eq 1, and eq 1-4 and 6-9 can be used to treat the data by computer simulation.^{6b}

Quantitative Treatment of Deprotonation. The variations of percentage of deprotonation of 5-nitroindole with [CTAOH] and [CTABr] and [OH⁻] in Figures 1 and 2 were fitted by using a simple computer program.^{6b,16} We used existing values of the various parameters, where available, and, where different values were in the literature, we chose values within postulated limits. For example, we required the ion-exchange constant, $K_{\rm Br}^{\rm OH}$ to be within the limits 10–20 (cf. ref 5–9 and 12). We assumed that the cmc would be decreased by added NaOH, consistent with observed electrolyte effects,²³ but fitting of the data was little affected by changes in the cmc.

In fitting the data we took $\beta = 0.78$ for CTABr,²⁴ and the kinetically estimated value of $K'_{OH} = 55 \text{ M}^{-1}$ for CTAOH.^{16a} The values of K_s in Table I are greater for solutions of higher [NaOH], which is consistent with evidence that electrolytes can "salt out" hydrophobic substrates from water and into the micelles.^{6,16a}

strates from water and into the micelles.^{6,16a} The values of K_B^M , and the other parameters, are in Table I. The quality of the fits in Figures 1 and 2 is little affected by small variations in those parameters, as is so often observed in treatments of micellar rate effects.

Effect of Fluoride Ion. Sodium fluoride decreases the extent of deprotonation of 5-nitroindole in CTAOH (Table II). The effect is not large and is qualitatively understandable in terms of a competition between F^- and OH^- for the micelle. Neither of these ions binds strongly to cationic micelles,²⁵ and their individual binding follows eq

9,^{16a} or its equivalent for F^- , so that it does not seem possible to apply the ion-exchange equation 4, and the concept of a constant β , to this system. We see no simple way of treating these data quantitatively.

Basicity Constants in Water and Micelles. The values of K_B^M in CTAOH or CTABr are approximately 0.14 (Table I), but these constants cannot be compared directly with those in water, K_B , M, because of the difference in dimensions. However, K_B^M can be converted into K_B^V , M, if the concentration of OH⁻ in the micellar pseudophase is written as a molarity.⁶ This can be done by using the molar volume of the micellar Stern layer, and we take this to be 0.14 L,^{12,26} so that

$$K_{\rm B}{}^{\rm V} = K_{\rm B}{}^{\rm M}/0.14 \tag{10}$$

giving $K_{\rm B}^{\rm V} \approx 1$ M.

In water $K_{\rm B} = 5.6$ M,¹⁹ so that the base dissociation constant is larger in water than in micelles, with $K_{\rm B}/K_{\rm B}^{\rm V} \approx 5.6$. This result is qualitatively similar to that observed with areneimidazoles,⁶ except that here the difference between the constants in water and the micelles is smaller, with $K_{\rm B}/K_{\rm B}^{\rm V} \approx 2.6^{\rm b}$ These micellar effects are understandable, because the cationic head groups in the micelle should interact favorably with the organic anions with their delocalized negative charge. However, this interaction is relatively unimportant as compared with the high concentration of OH⁻ in the Stern layer of the micelle.

Relation to Reactivity in Micellized CTAOH. The agreement between the values of $K_{\rm B}^{\rm M}$ in CTABr and CTAOH and the fitting of the variation of f with [CTAOH] (Table I) is consistent with an increase of the concentration of OH⁻ in the Stern layer of CTAOH micelles with increasing [OH⁻], and not with the postulation of reaction between OH⁻ in the aqueous pseudophase and substrate in the micellar pseudophase,^{14a,17,18} which should affect a rate, but not an equilbrium, constant. In both the kinetic and equilbrium systems it does not seem possible to explain the results in solutions of CTAOH in terms of a constant β , at least under the conditions of our experiments. However, the physical significance of the apparent variation of β with increasing [CTAOH] or [OH⁻] is uncertain and is probably related to an increasing average size of the micelles. The deviations from the predictions of the pseudophase ion-exchange model were observed by Nome and co-workers for reaction rates only in relatively concentrated OH^{-.17} Some of the assumptions of the ion-exchange model, e.g., constancy of β , or the ion-exchange constant, may be invalid for relatively concentrated solutions of electrolytes, which may also markedly perturb micellar structure. For example, very high concentrations of OH⁻ in the aqueous pseudophase could change not only the micellar structure but also the distribution of ionic and nonionic substrates between the pseudophases. However, we note that our basicity measurements were not made in very concentrated NaOH, so that, although we believe that they exclude reaction across the Stern layer in dilute NaOH, such a reaction may occur in very concentrated NaOH.¹⁷

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