Reagent Distribution and Micellar Catalysis of Carbocation Reactions[1]

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Abstract: Reactions of Malachite Green, MG$^+$, and the tri-*p*-anisylmethyl cation, R$^+$, with 1-benzyldihydronicotinamide (BDHNA) are catalyzed by anionic micelles of sodium lauryl sulfate (NaLS), and for MG$^+$ weakly by cationic micelles of cetyltrimethylammonium bromide (CTABr). Added sodium bromide and tosylate speed reaction in CTABr, probably by increasing incorporation of MG$^+$ into the cationic micelle, but they show the typical negative salt effects on the CTABr-catalyzed reaction of MG$^+$ with hydroxide ion. Tosylate, but not bromide, ion also inhibits the CTABr-catalyzed reaction of MG$^+$ with borohydride ion, suggesting that anion binding to micelles of CTABr follows the sequence OTos$^-$ > BH$_4^-$ > Br$^-$ > OH$^-$. For surfactant concentrations well above the critical micelle concentration, cmc, the rate constant–surfactant profile for reaction of MG$^+$ with BDHNA can be interpreted in terms of the distribution of both reactants between water and the micelles, using the binding constants of 8000 and 10 for MG$^+$ to NaLS and CTABr, and of 285 and 400 for BDHNA. Although the catalysis of this reaction is much greater for NaLS than CTABr (by factors of 15-fold as compared with twofold), this is the result of greater incorporation of MG$^+$, not of a greater rate constant in the micelle. The binding constants of MG$^+$ to CTABr are consistent with the rate–surfactant profiles of the reactions with hydroxide and borohydride ion. Second-order rate constants in the micellar pseudophase are compared with those in water.
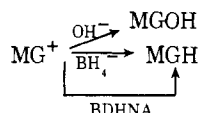
Catalysis by aqueous solutions of simple surfactants can be rationalized in terms of the ability of micelles to provide a new reaction medium and to concentrate reagents at the micelle-water interface, the so called Stern layer.[3] To date, added electrolytes have always inhibited bimolecular reactions by competing with an ionic reagent for the micelle. But some electrolytes increase micellar catalysis of unimolecular reactions by modifying the structure of the Stern layer[7] and perhaps this could also be so for bimolecular reactions.

Cationic micelles catalyze and anionic micelles inhibit reactions of triphenylmethane dye cations with hydroxide ion.[8,9] Reactions of amines are effectively catalyzed by anionic micelles, whereas cationic micelles are much less effective,[10] because hydrophobic and coulombic interactions bring reactants together on an anionic micelle, but for a cationic micelle hydrophobic interactions must overcome the coulombic repulsion between the carbocation and the micelle.

Our aim was to use inert added electrolytes to increase micellar catalysis of a bimolecular reaction[11] and to test models which interpret micellar catalysis in terms of the concentrations of both reactants in the micellar pseudophase.[12,13] In one model reactant concentrations in the micelle were determined by solubility measurements or spectrophotometrically.[12] In the other the concentrations of hydrophilic ions in the micellar pseudophase were estimated from their relative affinities for the micelle.[13]

Both models assume that the micellar properties are unaffected by reactants in low concentration. Carbocations interact very strongly with anionic, but not with cationic, micelles, and their reactions should provide a good test of these treatments of micellar catalysis.[12,13] A completely different model has recently been proposed based on cooperativity of binding of reactants to the micelle,[14] and the equations are similar to those applied to enzyme kinetics.

Most of our work was done using Malachite Green, bis(4-dimethylaminophenyl)(phenyl)methyl cation, (MG$^+$), but we also used the tri-*p*-anisylmethyl cation (R$^+$).[9b,10] The nucleophiles, hydroxide and borohydride ions and 1-benzyldihydronicotinamide (BDHNA),[15,16] differ strongly in their binding to micelles.

$$\text{MG}^+ \underset{\overset{\longrightarrow}{\text{BH}_4^-}}{\overset{\text{OH}^-}{\longrightarrow}} \begin{array}{l} \text{MGOH} \\ \text{MGH} \end{array}$$

BDHNA

The surfactants were cetyltrimethylammonium bromide (CTABr), sodium lauryl sulfate (NaLS), and Igepal, which is nonylphenyl polyethylene oxide.

Experimental Section

Materials. The preparation and purification of the reagents followed standard methods.[8,17]

Kinetics. Reactions of R$^+$ and the faster reactions of MG$^+$ were followed at 25.0 °C using a Durrum-Gibson stopped-flow spectrophotometer.[18] The slower reactions of MG$^+$ were followed by adding a small amount of the cation (1–3 × 10^{-5} M) to the reaction solution and following its disappearance at 620 nm, generally in a Gilford spectrophotometer. Reactions of BH$_4^-$ were carried out in the presence of a small amount of NaOH to suppress hydrolysis of BH$_4^-$ but the contribution of reaction with OH$^-$ was negligible under these conditions. The first-order rate constants, k_Ψ are in s^{-1}.

Products. The extent of formation of tri-*p*-anisylmethane was determined spectrophotometrically after complete reaction by allowing the hydride donor to decompose by air oxidation of BDHNA or hydrolysis of BH$_4^-$. The solution was then acidified to convert the alcohol, but not the alkane, completely to the cation. (Tri-*p*-anisylmethanol, present at the start of the reaction, is converted to cation on acidification, and the hydride donors react very rapidly with the cation, even in acid.) Reactions of BH$_4^-$ and BDHNA give RH quantitatively, cf. ref 16.

Micellar Incorporation of Reactants. The binding constant of BDHNA to CTABr and NaLS has been determined spectrophotometrically and kinetically.[19] We measured the binding constant to CTABr by the gel-filtration procedure,[20] with a G-10 Sephadex column and elution with varying [CTABr]. A plot of ($V_i/V_e - V_0$) against weight concentration of CTABr was linear (V_i, V_e, and V_0 are, respectively, the imbibed, eluted, and void volumes). The slope and intercept gave a partition coefficient[20] of 1100. This can be converted into the binding constant, K_{BH}:

$$K_{BH} = \frac{[\text{BH}_M]}{[\text{BH}_W]([D] - \text{cmc})}$$

using the partial molar volume of CTABr.[21] [The subscripts denote the hydride donor, BH, in the micellar and aqueous pseudophases, [D] is the total concentration of surfactant (detergent), and cmc is the critical micelle concentration.] The value of K_{BH} of 390 agrees with those of 453 and 460 determined earlier.[19] We use a value of 400 in CTABr and 285 in NaLS.[19]

Elution of MG$^+$ by CTABr from a G-10 Sephadex column was carried out in 10^{-3} M HBr (to prevent hydrolysis of the cation), but a plot of ($V_i/V_e - V_0$) against concentration of CTABr had a negative slope, corresponding to a very small binding of MG$^+$.[20] We attempted to confirm this result by ultrafiltration,[22] using a 50-mL Amicon 52
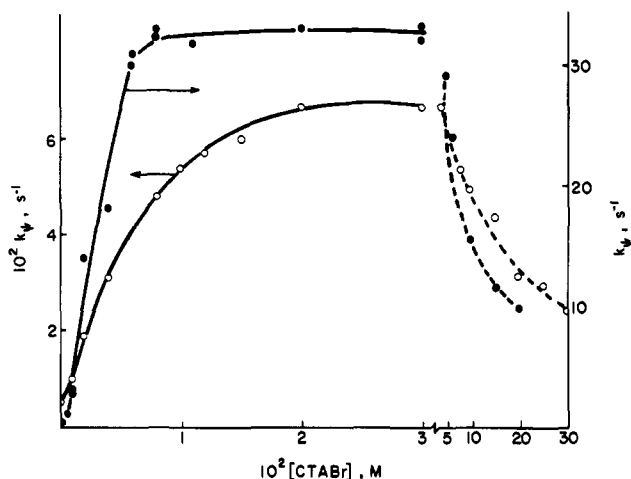
Figure 1. Reaction of MG$^+$ with 0.003 M NaOH (O) and 0.0037 M NaBH$_4$ (●) in CTABr at 25.0 °C. The broken line at high surfactant concentration is calculated.

Figure 2. Catalysis of the reaction of MG$^+$ with 10^{-4} M BDHNA in NaLS. The broken line is calculated.

Table I. Rate Constants in the Absence of Surfactants[a]

reagent	R$^+$	MG$^+$
OH$^-$	6600[b]	1.7
BH$_4^-$	2.0 × 10^6	31
BDHNA	2.1 × 10^{5b}	21

[a] Values of k_2 M^{-1} s^{-1} at 25.0 °C in water. [b] Ref 15.

Table II. Inhibition by NaLS of the Reaction of MG$^+$ with Hydroxide Ion[a]

10^3 [NaLS], M	10^3 k_Ψ, s^{-1}	10^3 [NaLS], M	10^3 k_Ψ, s^{-1}
	16.1	0.50	1.03
0.10	13.3	1.00	0.35
0.20	7.20	3.00	0.15
0.30	3.72	5.00	0.17
0.40	1.85	8.00	0.16

[a] At 25.0 °C with 0.01 M NaOH.

cell with a PM-10 membrane, and MG$^+$ in 10^{-4} M HBr was recycled until the absorbance, A_{fe} and A_{fd}, in the filtrate and filtrand, respectively, were constant, and then:

$$A_{fe}/A_{fd} = 1.25$$

This transport coefficient represents the relative diffusion rates of water and the solute and is assumed to be unaffected by the surfactant.[22]

This procedure was repeated using CTABr, and {($A_{fd}/1.25$) − A_{fe}}/A_{fe} was plotted against [CTABr]. The plot was linear, with a slope of 10 M^{-1}, but it did not intercept the abscissa at the cmc as predicted. This deviation was probably caused by changes in the absorption of MG$^+$ upon the membrane in the presence of CTABr. This absorption decreased on going from water to 5 × 10^{-4} M CTABr and then became constant, but K_{MG} is insensitive to small changes in the transport coefficient. The kinetic results, which will be described later, are consistent with the ultrafiltration values. Gel filtration has in the past been applied only to micellar incorporation of nonionic solutes.[20,23]

Interaction of Surfactant and Reactants. Catalysis by NaLS is observed at surfactant concentrations below the cmc in water, cf. ref 24.

The cmc of NaLS in 10^{-5} M MG$^+$ and 10^{-5} M HCl is ca. 8 × 10^{-4} M, by surface tension. (The cmc of our sample of NaLS was 7.5 × 10^{-3} M at 25 °C; cf. ref 25.) Added BDHNA (10^{-4} M) reduces the cmc of NaLS to 6 × 10^{-3} M.

The kinetic cmc of NaLS is therefore much lower than in water, suggesting that the reactants interact strongly with the anionic surfactant, and submicellar aggregates may be formed, because there is a slight minimum of ca. 1 dyn in a plot of surface tension against log [NaLS] in MG$^+$.

Results and Discussion

Reactants in the Absence of Surfactant. The second-order rate constants for reactions of MG$^+$ and R$^+$ with hydroxide ion and hydride donors in water are in Table I. The rate constant for reaction of R$^+$ with BH$_4^-$ is ca. 40% larger than the preliminary value given earlier.[15]

Micellar Effects upon Reactions of Hydroxide and Borohydride Ions. Reactions of R$^+$ and MG$^+$ with hydroxide and
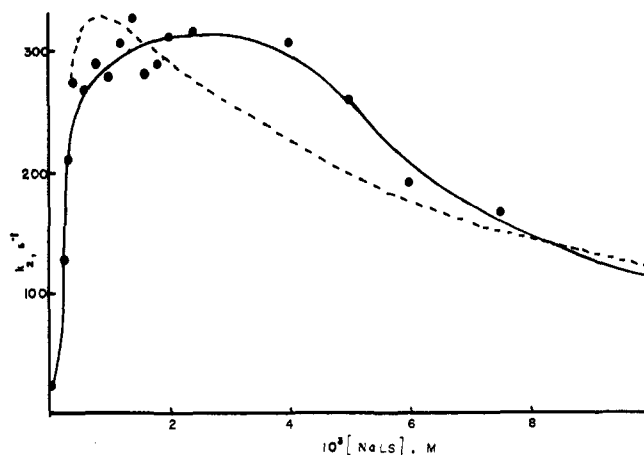
borohydride ion are strongly inhibited by anionic micelles of NaLS (ref 8 and 9 and Table II and SI and SII in the Supplementary Material). Cationic micelles of CTABr and nonionic micelles of Igepal have very little effect upon the reaction of R$^+$ with BH$_4^-$ (Table SII), probably because this cation is insufficiently hydrophobic to be incorporated into a cationic micelle; cf. ref 9b. However, the reactions of MG$^+$ with OH$^-$ and BH$_4^-$ are catalyzed by CTABr (Figure 1), cf. ref 8 and 9a, suggesting that this cation binds to cationic micelles despite the unfavorable coulombic interactions.

Although reaction of MG$^+$ with OH$^-$ is modestly catalyzed by CTABr (Figure 1 and ref 8 and 9a), we observe larger catalysis with BH$_4^-$ (Figure 1), probably because it is strongly incorporated into a cationic micelle. The maximum rate enhancements are by factors of 13 and 270 for reactions of hydroxide and borohydride ion, respectively. The rate constants go through broad maxima (Figure 1).

Micellar Effects upon Reactions with the Dihydronicotinamide. Micellar effects upon reactions with BDHNA are completely different from those found with OH$^-$ and BH$_4^-$, in that anionic micelles of NaLS are effective catalysts and under some conditions the reaction with R$^+$ becomes too fast to follow (Table SI). The catalyses by NaLS and Igepal of the reactions of R$^+$ and MG$^+$ with BDHNA (Table SIII and Figure 2) are very similar, and all the reactants should be taken up by the anionic micelles.

Reaction of R$^+$ with BDHNA is not catalyzed by CTABr (Table SIV), but there is a weak catalysis of the reaction of MG$^+$ (Table III). This table also contains values of k_M which are discussed later. These micellar effects are similar to those for reactions of R$^+$ with amines.[10]

The catalysis of the reaction of MG$^+$ with BDHNA by nonionic micelles is probably due to the concentration effect overcoming an unfavorable microenvironment effect of the micelle because addition of organic solvents retards reaction in water in the absence of surfactant.[15] Similar, but smaller, effects of Igepal were observed for reactions of R$^+$ with
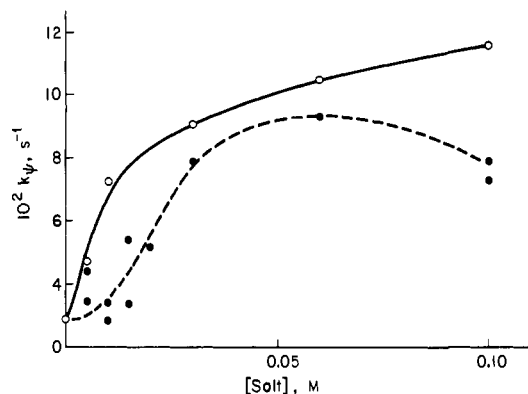
Figure 3. Positive salt effects upon the reaction of MG$^+$ with 10^{-3} M BDHNA in 0.01 M CTABr: (O) NaBr; (●) NaOTos.

Figure 4. Salt effects upon the reaction of MG$^+$ with 0.003 M NaOH in 2×10^{-2} M CTABr (open points) and with 0.0037 M NaBH$_4$ in 0.01 M CTABr (solid points): (□, ■) NaBr; (O, ●) NaOTos.

Table III. Reaction of MG$^+$ with BDHNA in CTABr^a

[CTABr], M	k_2, M^{-1} s^{-1}	k_M, s^{-1}
	21.0	
0.003	21.4	
0.004	22.8	
0.006	31.5	
0.007	32.5	
0.010^b	28.4	
0.010^c	28.8	
0.010	29.1	
0.010^d	27.2	
0.015^b	40.1	5.2
0.020^b	37.7	4.8
0.040^b	45.7	6.6
0.060^b	43.5	7.1
0.080^b	37.9	6.9
0.100^b	34.7	7.0

^{a} At 25.0 °C with 10^{-3} M BDHNA unless specified. ^{b} 10^{-4} M BDHNA. ^{c} 5×10^{-4} M BDHNA. ^{d} 2×10^{-3} M BDHNA.

amines.[10] Small amounts of cationic and nonionic surfactants can speed reactions of ionic reagents with hydrophobic substrates, although the effects may be due to dispersion or emulsification of sparingly soluble substrates as well as micellization.[26]

Salt Effects on the Micellar Reactions. Sodium bromide and tosylate were used, and the latter binds very strongly to CTABr.[7a,27,28]

Reaction with BDHNA. There is little catalysis of the reaction of MG$^+$ with BDHNA in CTABr (Table III) but both bromide and tosylate ion effectively speed the reaction (Figure 3). Our positive salt effects suggest that the added anions increase incorporation of MG$^+$ into the micelle or speed reaction in it.

Carbocations readily ion pair with low charge density anions,[18,29] and the cationic micelle may incorporate an ion pair rather than free MG$^+$, or the added anion may partially neutralize the charge on the micelle. (These descriptions are equivalent.)

These unusual positive salt effects can be understood only qualitatively, because bromide speeds up the reaction more than tosylate ion (Figure 3), which binds more strongly to both carbocations and cationic micelles. The salt effect therefore appears to depend upon both increased micellar incorporation of MG$^+$ and a salt-induced change in micellar structure.

Reactions with Anionic Nucleophiles. There is the typical salt effect on reaction of MG$^+$ with OH$^-$ in CTABr (Figure 4). Any salt-induced binding of MG$^+$ to the micelle is more than offset by exclusion of OH$^-$, especially by tosylate ion.
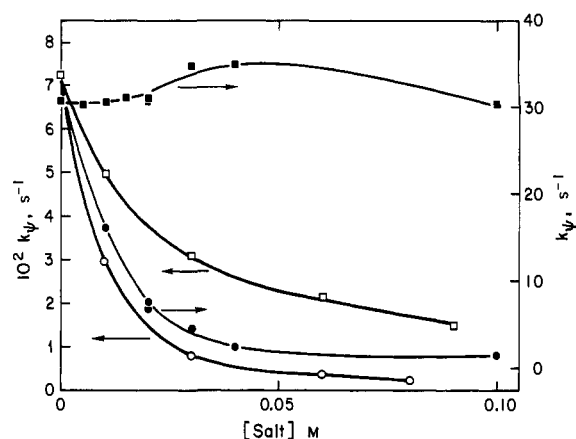
Tosylate ion reduces the micellar catalysis of the BH$_4^-$ reaction (Figure 4), suggesting that it competes with borohydride ion for the micelle, but Br$^-$, which has almost no effect, does not displace borohydride ion. Therefore, binding of the anions to micellized CTABr is: OTos$^-$ ≥ BH$_4^-$ > Br$^-$ > OH$^-$.

Quantitative Treatment of Micellar Catalysis. Rate constants can be related to surfactant concentration in terms of the distribution of reactants between water and the micelles.[12,13,30-32] In CTABr we can estimate the binding of MG$^+$ (Experimental and cf. ref 8) but not that of OH$^-$ or BH$_4^-$ to the micelles.

For reactions of MG$^+$ with BDHNA, we know the binding constants of the latter to CTABr and NaLS,[19] and we use the inhibition of the reaction of MG$^+$ with OH$^-$ by NaLS to estimate the binding constant of MG$^+$ to NaLS.

For reaction of a nucleophile, N, with MG$^+$, we use Scheme I,

Scheme I

$$MG^+ + D_n \xrightleftharpoons{K_{MG}} MG$$

$$k'_W \Big\downarrow N \qquad\qquad k'_M \Big\downarrow N$$

$$\text{products}$$
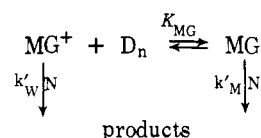
where the subscripts W and M denote material in water and the micelles, respectively, and D$_n$ is micellized surfactant.

The usual treatment gives the first-order rate constant, k_Ψ, with respect to substrate:[30]

$$k_\Psi = \frac{k_W' + k_M' K_{MG}([D] - cmc)}{1 + K_{MG}([D] - cmc)} \tag{1}$$

where [D] − cmc is the concentration of micellized surfactant.

The first-order rate constant k_W' and k_M' are related to the second-order rate constants k_W and k_M:

$$k_W' = k_M[N_W]; \quad k_M' = k_M m_M^N \tag{2}$$

We write k_W, M^{-1} s^{-1}, in terms of molarity and k_M, s^{-1}, in terms of the mole ratio of N to head group in the micellar pseudophase, i.e.,

$$m_M^N = [N_M]/([D] - cmc) \tag{3}$$

where [N$_M$] is the molarity of micellar bound N in terms of the total solution volume.[19]

Equations 2 and 3 give:

$$k_\Psi = \frac{k_W[N_W] + k_M K_{MG}[N_M]}{1 + K_{MG}([D] - cmc)} \tag{4}$$

Equation 4 can be used directly if values of K_{MG} and [N$_W$] or [N$_M$] are known. Because of uncertainties in the value of

the kinetic cmc, we calculate k_M from data at high surfactant concentration where possible.

Inhibition by NaLS of Attack by Hydroxide Ion. For reactions of OH$^-$ with carbocations in micelles of NaLS,[8,9] k_M' = 0 (Scheme I),[8,9] so that:

$$k_\psi = k_W'/[1 + K_{MG}([D] - \text{cmc})] \qquad (5)$$

where k_W' is the first-order rate constant for reaction of MG$^+$ in water with 0.01 M OH$^-$. We observe 50% inhibition at 1.8 $\times$ 10^{-4} M NaLS (Table II), where $K_{MG} = 1/([D] - \text{cmc})$. Our estimate of K_{MG} depends on the cmc; e.g., $K_{MG} = 5000$ if the cmc = 0 and ca. 10 000 if the cmc = 10^{-4} M. (The kinetic cmc is much lower than that in water.)

We can also use eq 6[30]

$$1/(k_W' - k_\psi) = 1/k_W' + 1/k_W'K_{MG}([D] - \text{cmc}) \quad (6)$$

and treat the cmc as a disposable parameter. A plot of $1/(k_W' - k_\psi)$ against $1/([D] - \text{cmc})$ is linear if the cmc = 10^{-4} M. The slope is then 6 $\times$ 10^{-3}, giving $K_{MG} = 8000$, and we use this value.

From the inhibition of the reaction of R$^+$ with OH$^-$ and BH$_4^-$ (Table SI and ref 9b), we calculate a binding constant of ca. 3500 for R$^+$ to micelles of NaLS; cf. ref 34. This value agrees with that estimated from the observation of 50% inhibition in 5 $\times$ 10^{-4} M, suggesting that R$^+$ binds less strongly than MG$^+$ to micelles.

Catalysis by CTABr of the Attack of Hydroxide and Borohydride Ion upon MG$^+$. Rate constants for reaction of MG$^+$ with OH$^-$ and BH$_4^-$ go through maxima with increasing CTABr (Figure 1).

The micellar catalysis of reactions of hydrophilic ions can be rationalized in terms of competition between the reactive ions and the micellar counterions for the micelle,[13] assuming that the charge of the head groups of micellized surfactant is neutralized to a constant extent by hydrophilic counterions regardless of their nature or external concentration.[13,35]

For the reaction of MG$^+$ with OH$^-$ at high concentrations of CTABr (eq 4), we obtain:

$$k_2 = (\alpha k_W + p\beta k_M K_{MG})/(\alpha + p\beta)(1 + K_{MG}[D]) \quad (7)$$

where α is the degree of ionization of the micelle, $\alpha = 1 - \beta$, and p is the ion-exchange constant:[13]

$$p = [N_M^-][Br_W^-]/[N_W^-][Br_M^-]$$

where N$^-$ is OH$^-$. Equation 7 gives:

$$\frac{1}{k_2} = \frac{\alpha + p\beta}{\alpha k_W + p\beta k_M K_{MG}} + \frac{(\alpha + p\beta)K_{MG}[D]}{\alpha k_W + p\beta k_M K_{MG}} \quad (8)$$

and plots of $1/k_2$ against [D] are linear (Figure 5), suggesting that $(\alpha + p\beta)/(\alpha k_W + p\beta k_M K_{MG})$ is constant under our conditions, and for reaction with OH$^-$ we obtain $K_{MG} = 8.7$ M^{-1} which is close to that of 10 estimated by ultrafiltration (see the Experimental Section).

The apparent constancy of $(\alpha + p\beta)/(\alpha k_W + p\beta k_M K_{MG})$ does not require constancy of the individual components of this term, because there may be a degree of compensation, but if $\alpha = 0.2, p = 0.4$ for OH$^-$,[13] and $k_W = 1.7$ M^{-1} s^{-1}, from the intercept of 0.033 and slope of 0.288 (Figure 5) we obtain k_M ≈ 5 s^{-1}. The salt effects (Figure 4) suggest that p may be small, and the calculated values (Figure 1) were obtained from eq 7, taking $p = 0.2$ and $k_M = 7.5$ s^{-1}, which fit the data slightly better than do $p = 0.4$ and $k_M = 5.3$ s^{-1}. Hydroxide competes poorly with bromide ion for cationic micelles, but an independent value of p would be very useful.

Bromide does not displace borohydride ion from a CTABr micelle (Figure 4), and we use the data at high surfactant concentration assuming that all the nucleophile is micellar bound. Equation 4 then gives:
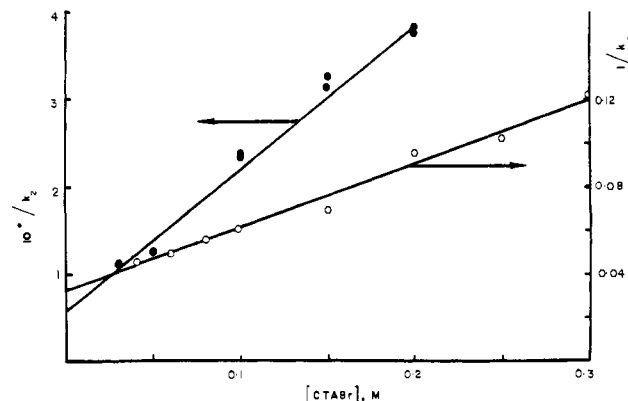

Figure 5. Quantitative treatment of the reactions of MG$^+$ in CTABr with 0.003 M NaOH (O) and 0.0037 M NaBH$_4$ ($\bullet$).

$$k_2 = k_M K_{MG}/(1 + K_{MG}[D]) \qquad (9)$$

where k_2 is the overall second-order rate constant (neglecting reaction with H$_2$O and OH$^-$).

A plot of $1/k_2$ against [D] $-$ cmc is linear when [CTABr] > 0.03 M, and the least-squares line gives $k_M = 590$ s^{-1} (from the slope of 1.66 $\times$ 10^{-3} s) and $K_{MG} = 29$ M^{-1} (from the intercept of 5.82 $\times$ 10^{-5} M s). Values of $k_\psi = k_2$ [BH$_4^-$] calculated using these parameters agree with the data (Figure 1).

The value of K_{MG} is larger than those of ca. 10 M^{-1} estimated independently, probably because BH$_4^-$ increases the micellar incorporation of MG,$^+$ just as do added bromide and tosylate ion (Figure 3). The value of $k_M = 590$ s^{-1} is probably a lower limit, because a lower value of K_{MG}, or partial incorporation of BH$_4^-$, would increase k_M. Our treatment ignores changes in micellar structure due to solute incorporation, and we note that there is no general agreement on the values of parameters such as α.[13] However, the calculations are insensitive to small changes in α, and the treatment rationalizes the decreases in the second-order rate constants at high surfactant concentration.

Quantitative Treatment of Micellar Effects upon Reactions with BDHNA in NaLS. Only reactions of MG$^+$ are treated in terms of Scheme I, because those of R$^+$ are very fast. We write the molar concentrations of the hydride donor in water [BH$_W$] and in the micelle [BH$_M$] in terms of total concentration and the binding constant to the micelle, K_{BH}. Equation 4 then gives:

$$k_2 = \frac{k_W + k_M K_{BH} K_{MG}([D] - \text{cmc})}{\{1 + K_{BH}([D] - \text{cmc})\}\{1 + K_{MG}([D] - \text{cmc})\}} \quad (10)$$

The assumption that low concentrtations of micellar-bound reactants do not perturb the micellar structure is least satisfactory when NaLS is not in large excess over the reactants, and there probably is solute-induced micellization or the formation of submicellar aggregates. Therefore, we did not analyze the rate constants obtained with the higher concentrations of BDHNA (Table SIII).

The first approach is to calculate k_M using eq 10, taking the kinetic cmc of NaLS as 10^{-4} M, where rate enhancements first appear. The binding constants K_{MG} and K_{BH} are 8000 and 285 M^{-1} respectively, and $k_W = 21$ M^{-1} s^{-1}. The values of k_M increase with increasing NaLS (Table IV), with a mean value of ca. 1.6 s^{-1}, and we use this rate constant to predict k_2. The expected rate maximum is obtained but at too low a surfactant concentration (Figure 2), probably because of solute effects on surfactant aggregation.

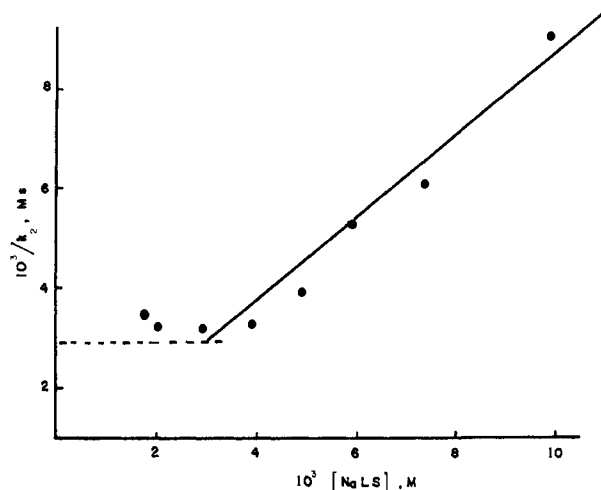Another approach is to use the rate constants for reaction

Figure 6. Treatment of the reaction of MG$^+$ with BDHNA in NaLS. The broken line indicates the value of $1/k_M K_{BH}$.

Table IV. Estimation of Rate Constant, k_M, for Reaction of MG$^+$ in Micelles of NaLS[a]

10^3[NaLS], M	k_M, s^{-1}	10^3[NaLS], M	k_M, s^{-1}
0.4	1.45	2.0	1.79
0.6	1.33	2.4	1.93
0.8	1.42	4.0	2.35
1.0	1.40	5.0	2.22
1.2	1.57	6.0	1.81
1.4	1.71	7.5	1.82
1.6	1.51	10.0	1.53
1.8	1.61		

[a] With 10^{-4} M BDHNA and 5×10^{-4} M OH$^-$.

Table V. Second-Order Rate Constants for the Reaction of MG$^+$ in the Micellar Stern Layer[a]

reagent	surfactant	k_{rel}[b]	k_M, s^{-1}	k_2^m, M^{-1} s^{-1}
OH$^-$	CTABr	13	7	1 (1.7)
BH$_4^-$	CTABr	272	590	83 (31)
BDHNA	CTABr	2	5[c]	0.7 (21)
BDHNA	NaLS	15	1.6	0.2 (21)

[a] The values in parentheses are second-order rate constants, k_w, M^{-1} s^{-1} for reaction in water. [b] At the rate maxima. [c] Application of eq 11b gives $k_M \approx 7.5$ s^{-1}.

in the more concentrated NaLS, so that eq 10 gives

$$1/k_2 = 1/k_M K_{BH} + ([D] - cmc)/k_M \qquad (11)$$

A plot of $1/k_2$ against [NaLS] is linear (Figure 6) and gives $k_M = 1.7$ s^{-1}; cf. Table IV. From k_M and K_{BH}, we estimate a cmc of ca. 3×10^{-3} M, which should be the monomer concentration at these relatively high concentrations (eq 11). This cmc is lower than that of NaLS in water,[25,33] because added hydrophobic solutes induce micellization.

These observations illustrate the problems in assuming that monomer concentration remains constant over a range of surfactant concentrations. The usual kinetic treatments involve this assumption,[4-6,14,30,31] but it fails when reactants bind very strongly to the micelles. The failure is least when [D] $\gg$ [reactants]. Equation 10 ignores the increase in the cmc toward that in pure surfactant as the surfactant concentration increases, which would lead to the observed increase in k_M with increasing [NaLS] (Table IV).

Reactions in CTABr. The constancy of reaction rates with BDHNA in CTABr (Table III) must be the result of opposing factors, because BDHNA is readily taken up[19] and if MG$^+$ was not incorporated we would observe inhibition.

We apply the approach used in NaLS and calculate values of k_M using eq 10, with the cmc = 4×10^{-4} M, estimated in BDHNA.[19,37] Taking $k_w = 21$ M^{-1} s^{-1}, $K_{MG} = 10$ M^{-1}, and $K_{BH} = 400$ M^{-1}, we estimate values of k_M, s^{-1} (Table III) for reaction with 10^{-4} M BDHNA. They are larger at the higher surfactant concentrations, as in NaLS (Table IV), probably because of micelle–reactant interactions. Applying eq 11 to this reaction gives $k_M = 6.8$ s^{-1} and $K_{MG} = 10$, in reasonable agreement with the values in Table III.

Comparison of Rate Constants and Limitations of the Kinetic Treatment. There are several obvious reasons for partial or complete failure of these kinetic treatments. (1) We cannot assume that the concentration of monomeric surfactant is always given by the cmc; cf. Figures 2 and 6. (2) The kinetic eq 1, 4, 8, and 10 neglect effects of reactants on the rate and equilibrium constants,[38] which is a problem if submicellar aggregates are present in very dilute surfactant solutions[39] and normal micelles in the more concentrated solutions. Kunitake and his co-workers have shown that some deacylations are strongly catalyzed by nonmicellar aggregates of hydrophobic quaternary ammonium ions.[40]

The kinetic equations are least satisfactory for reactions of hydrophobic reagents at low surfactant concentrations, and the catalyses at surfactant concentrations below the cmc

suggest that hydrophobic solutes induce micellization or form submicellar aggregates.

The aggregates of surfactants and reactants apparently depend on the relative concentration of reactants to surfactant, and the model of an unperturbed micelle seems to be unsatisfactory in dilute surfactant.

We have estimated the second-order rate constants, k_M, in terms of the mole ratio of bound nucleophile to head group, whereas second-order rate constants in water are usually measured in terms of molarity. We can estimate the volume of the Stern layer of 1 mol of micellized surfactant and calculate second-order rate constants in terms of moles of nucleophile per liter of Stern layer. Any approach is arbitrary and illustrates the difficulty of estimating the magnitude of medium effects upon the rates of bimolecular reactions.

Using Stigter's model of a micelle,[36] a micellar density of 1, Tartar's estimate of ca. 22 Å for the length of the C$_{16}$ chain in a CTABr micelle,[41] and a thickness of the Stern layer of 4.1 Å (from Dreiding models), we estimate a molar volume of ca. 140 mL for the Stern layer of both NaLS and CTABr micelles, giving:

$$k_2^m \approx 0.14 \, k_M$$

where k_2^m is the second-order rate constant, M^{-1} s^{-1}, in the Stern layer (Table V). (In an earlier paper, we used slightly different factors for the conversion of k_M into k_2^m.[19])

Generally, $k_w > k_2^m$, cf. ref 12, 19, 39, and so far as we know the only reported exceptions are deacylations by some anionic nucleophiles in CTABr,[12] where the apparently greater rate constants in CTABr may be an artifact of the method of calculating the rate constants using the apparent pK_a of the nucleophile.

The difference in catalysis of the reaction with BDHNA in CTABr and NaLS is due to greater incorporation of MG$^+$ in NaLS, and reaction in the CTABr micelle is faster than in NaLS (Table V), probably due to coulombic interactions which stabilize the initial state for NaLS and destabilize it for CTABr. The unfavorable coulombic interactions should decrease as the positive charge is dispersed in the transition state. (The reaction is often written as a hydride transfer, but our conclusions would be the same if it involved initial electron

transfer followed by transfer of a hydrogen atom; cf. ref 42.)

The reaction of BDHNA with MG$^+$ is slowed by addition of organic solvents to water,[15] and the lower polarity of the Stern layer as compared with water[4,43] should decrease $k_2{}^m$ (Table V).

A similar rationalization can be applied to reactions of MG$^+$ with OH$^-$ and BH$_4{}^-$ in the Stern layer of CTABr where the unfavorable initial state coulombic repulsions between MG$^+$ and the head groups are relieved in forming the transition state.

Organic solvents have relatively small effects upon the reaction of OH$^-$ in the absence of surfactants,[15,44] and there should be no large "microsolvent" effect upon this reaction due to the different polarities of water and the micellar surface (Table V).

For the reaction of BH$_4{}^-$, $k_2{}^m > k_w$ (Table V), and in the absence of surfactant the rate of this reaction increases sharply on addition of organic solvent to water.[15] Our value of $k_2{}^m$ for the reaction of BH$_4{}^-$ is a lower limit, and an initial state destabilization and a microenvironment effect work together to make this reaction an exception to generalizations about $k_2{}^m$ and k_w.

The Stern layer is treated as if it were a separate phase, but some of our reactants have diameters as large as the thickness of the Stern layer, so that they should only have two-dimensional motion in it. We should, therefore, perhaps regard the Stern layer as akin to an interface, rather than as a three dimensional medium, and consider the probability of the reactants coming together in this two-dimensional surface, with a loss of one degree of translational freedom and partial loss of translational entropy.

In other treatments, the reactant concentration has been estimated in terms of the total volume of the micelle,[12] although polar solutes appear to be located largely in the Stern layer. However, the volume of the Stern layer is often approximately half that of the micelle, so that the two methods give similar rate constants.

The distribution model is least satisfactory for the experiments in dilute surfactant where the micellar structure is perturbed to the greatest extent by the reactants. To this extent, our results accord with the cooperativity model suggested by Piszkiewicz,[14] but they give no support for this model at the higher surfactant concentrations, because it ignores incorporation of the second reagent, and we believe that the distribution model is reasonably satisfactory under these conditions.

Supplementary Material Available: Table SI, reactions of R$^+$ with BH$_4{}^-$ and BDHNA in anionic micelles of NaLS; Table SII, effects of surfactants on reaction of R$^+$ with BH$_4{}^-$; Table SIII, effects of B NaLS and Igepal upon the reaction of MG$^+$ with BDHNA; Table SIV, micellar effects upon the reaction of R$^+$ with BDHNA (4 pages). Ordering information is given on any current masthead page.

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