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Micellar Effects upon the Reaction of the Tri-*p*-anisylmethyl Cation with Aliphatic Amines[1]

Clifford A. Bunton,* Sylvia Chan,[2] and Sung K. Huang

Department of Chemistry, University of California, Santa Barbara, California 93106

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Anionic micelles of sodium lauryl sulfate, NaLS, catalyze the reaction of the tri-*p*-anisylmethyl cation, R^+, with butyl- and hexylamines and with 2-methylpyrrolidine. The catalysis increases with increasing length of the alkyl group of the amine, but is decreased by its branching. Cationic micelles of cetyltrimethylammonium bromide, CTABr, have little effect on the reaction rate, but nonionic micelles of Igepal are feebly catalytic.

Micellar effects upon the reaction of nucleophilic anions with stable triphenylmethyl dye cations have been extensively studied.[3,4] For example, cationic micelles catalyzed, and anionic micelles inhibited, attack of hydroxide ion. Micellar effects upon the attack of water on the more reactive tri-*p*-anisylmethyl cation (R^+) have also been ex-

$$R^+ + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} ROH + H^+$$

amined. Anionic micelles increase, but cationic and nonionic micelles decrease, k_b, but these micelles have no effect on k_f.[9] The reactions with hydroxide and azide ions were strongly inhibited by anionic micelles.

The present work covers micellar effects on the reaction of R^+ with aliphatic amines,[10] using cetyltrimethylammonium bromide (CTABr), sodium lauryl sulfate (NaLS), and Igepal (nonylphenyl polyethylene oxide, mol wt 1403).

Experimental Section

Materials and Rate Measurements. The purification of the surfactants has been described.[9] The tri-*p*-anisylmethyl cation was introduced as its chloride in dilute HCl. All solutions were made up using redistilled, deionized water, and were degassed.

The reactions were followed at 25.0° using a Durrum-Gibson stopped-flow spectrophotometer.[9] A solution of R^+ in dilute HCl, usually 0.1 *M*, was in one drive syringe, and the amine in NaOH was in the other (NaOH was in slight excess over HCl). The surfactant was in both syringes.

The first-order rate constants, k_ψ, in reciprocal seconds, were calculated using a Hewlett-Packard desk computer.

Results and Discussion

Effect of Micellar Charge. The effects of cationic and nonionic micelles upon the reaction of amines with R^+ are summarized in Table I, in which the values of k_ψ in the absence of surfactant are compared with those in the presence of CTABr and Igepal (Ig). Cationic micelles of CTABr have almost no effect on the rate of reaction, probably because R^+ is not taken up by the cationic micelles,[9] but these micelles markedly affect the equilibrium between R^+ and ROH in dilute acid.[11,12]

Nonionic micelles of Igepal catalyze the reaction of R^+ with *n*-hexylamine, which is the most hydrophobic amine used (Table I), suggesting that the rate enhancement is at least in part a proximity effect due to incorporation of the reagents in the micelle. This incorporation is almost certainly incomplete, and there is no rate maximum or plateau as is often observed in micellar catalysis.[4-8]

Anionic micelles of NaLS catalyze the reaction (Figures 1-3). At a constant amine concentration, the variation of rate constant with surfactant concentration is typical of micellar catalysis. There is little or no effect at very low concentrations of surfactant, but once micelles begin to form, the rate increases as reagents are incorporated into the micelle. The simple kinetic treatment predicts that the rate will not increase until the critical micelle concentration (cmc) of the surfactant is reached,[5-8,13] but the rate increase at NaLS concentrations well below the cmc[14] (Figures 1 and 2) is very common, especially with hydrophobic solutes, and arises because the reagents promote micellization, or there is some catalysis by submicellar aggregates.[5-8] The former explanation seems the more probable because the lowest surfactant concentrations necessary for catalysis are observed with the most hydrophobic amine.

The rate enhancements in the plateau region are given in Table II. They increase with increasing length of the amine chain, and decrease with chain branching.

One unusual feature of the micellar catalysis is that, with increasing surfactant concentration, the rates increase to plateau values, rather than to the maxima which are exhibited by most micellar-catalyzed bimolecular reactions.[16,17] These rate maxima have been ascribed to a dilution of the reagents in the micellar pseudophase once there are sufficient micelles to remove the reagents from the aqueous to the micellar phase;[16] *cf.* ref 7 for an alternative explanation.

The absence of rate maxima (Figures 1 and 2) may be due to the low surfactant concentrations required for catalysis, but formation of a reactive complex between R^+ and the amine should also give plateaux rather than rate maxima.

The rate of the water reaction of R^+ was unaffected by micelles, irrespective of their charge, and reactions of R^+

Table I
Effect of CTABr and Igepal on Reactions with Amines[a]

10^3 [amine], *M*	*n*-Butylamine None[c]	*n*-Butylamine CTABr[c]	*n*-Butylamine Ig[c]	*n*-Hexylamine None[c]	*n*-Hexylamine CTABr[c]	*n*-Hexylamine Ig[c]	Cyclohexylamine None	Cyclohexylamine CTABr	Cyclohexylamine Ig	2-Methylpyrrolidine None	2-Methylpyrrolidine CTABr	2-Methylpyrrolidine Ig
1.0										162	146	206
1.5										190		243
1.85	75	48	59									
2.0										234	233	300
2.5				97	92	144						
3.0										319	308	402
3.75	143	104	135				55	41				
4.0				164	179	361[b]				387	378	473
5.0				196	199	291 412[b]	65	53				
6.25				258	257							
7.5	299	289	277									
8.0				340	340	785[b]						
10.0				423	455	561 1035[b]						
12.5				657	635		128	109	134			
15.0							145		158			
17.5							170		184			
20.0							205		236			
25.0							245	207	286			

[a] Values of k_ψ, in reciprocal seconds at 25.0°, with 0.05 *M* NaCl. CTABr was 5×10^{-4} *M* and Igepal (Ig) was 2×10^{-4} *M* unless specified. [b] 4×10^{-4} *M* Igepal. [c] Surfactant.

Table II
Rate Enhancements in the Plateau Region[a]

Registry no.	Amine	k_{rel}[b]
109-73-9	*n*-Butylamine	2.5 (48×10^3)
13952-84-6	*sec*-Butylamine	2.4 (3.8×10^3)
111-26-2	*n*-Hexylamine	13 (50×10^3)
108-91-8	Cyclohexylamine	4.8 (9×10^3)
765-38-8	2-Methylpyrrolidine	4.3 (74×10^3)

[a] At 25.0° with [NaLS] $>1.5 \times 10^{-3}$ *M*. [b] Relative to the calculated second-order rate constant in the absence of surfactant. The values in parentheses are the second-order rate constants in the absence of micelles.[10]

with anionic nucleophiles were sharply inhibited by NaLS.[9] The micellar-catalyzed amine reaction thus differs from the other nucleophilic attacks upon R^+, but the catalysis is consistent with the generalization that attack of an electrophilic cation upon a neutral molecule is catalyzed by anionic micelles.[5-8]

Plots of k_ψ against amine concentration at a given concentration of NaLS curve upward (Figure 3), although

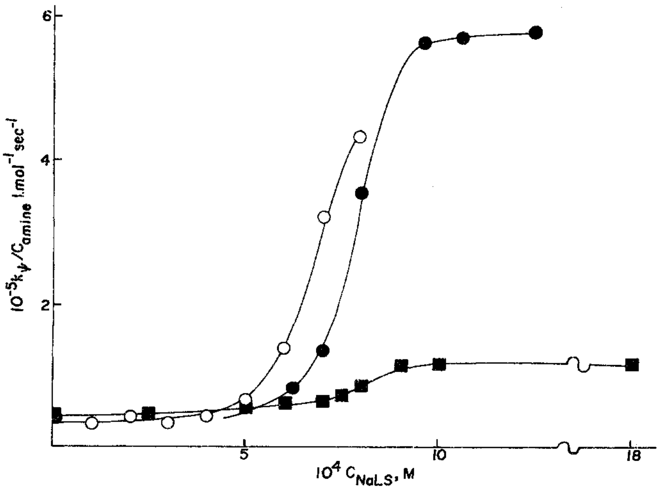

Figure 1. Rate enhancements by NaLS of the reactions of R^+ with primary amines: ■, n-$C_4H_9NH_2$, 7.5×10^{-3} *M*; ●, n-$C_6H_{13}NH_2$, 2×10^{-3} *M*; ○, n-$C_6H_{13}NH_2$, 3.75×10^{-3} *M*.

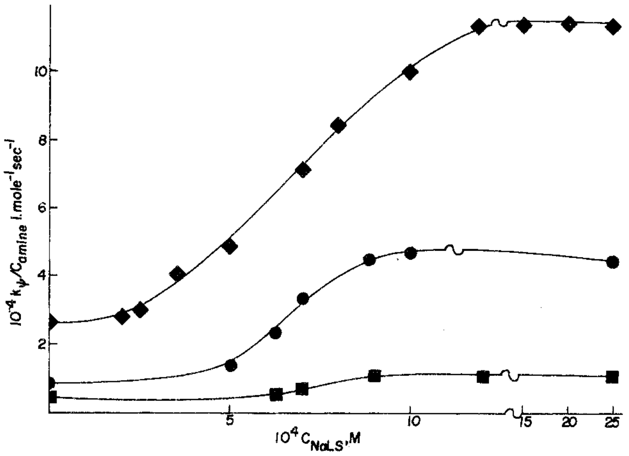

Figure 2. Rate enhancements by NaLS of the reactions of R^+ with secondary amines: ■, *sec*-BuNH$_2$, 5×10^{-2} *M*; ●, c-$C_6H_{11}NH_2$, 2×10^{-2} *M*; ♦, 2-methylpyrrolidine, 4×10^{-3} *M*.

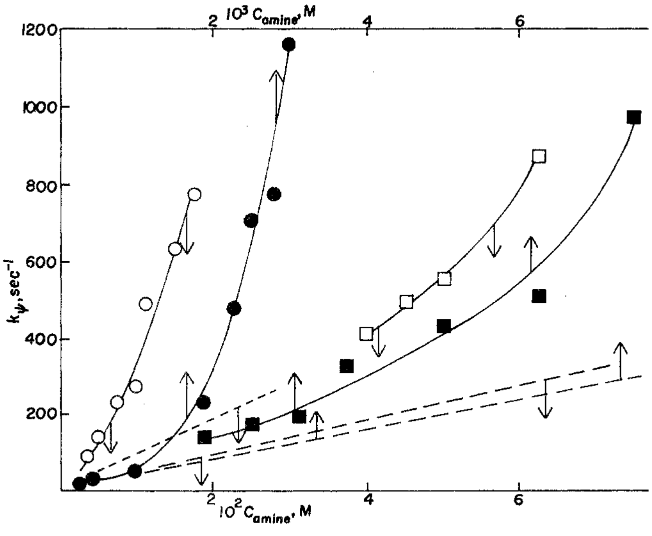

Figure 3. Relation between rate constant and amine concentration for reaction in 2.5×10^{-3} *M* NaLS: 1, ■, n-BuNH$_2$; 2, ●, n-$C_6H_{13}NH_2$; 3, □, *sec*-BuNH$_2$; 4, ○, c-$C_6H_{11}NH_2$. The broken lines are for reactions in the absence of surfactant.

Table III
Effect of Hydroxide Ion on the Reaction with Amines in NaLS[a]

10^2 [NaOH], *M*	*sec*-Butylamine[b]	2-Methylpyrrolidine[c]
0.5	119	
1.25	128	230 (12)
2.5	140	268
3.0		(14)
3.75	141	277
5.0	143	285
6.25	150	296
7.5	148	303 (26)

[a] Values of k_ψ, in reciprocal seconds, at 25.0° with 2.5×10^{-3} *M* NaLS, 10^{-3} *M* amine, 0.05 *M* NaCl; values in parentheses are in the absence of amine. [b] 1.25×10^{-2} *M*. [c] 10^{-3} *M*.

such plots usually have the opposite curvature. Amines probably modify the structure of the micelle so as to increase its catalytic efficiency, possibly by stabilizing the ammonium ion-like transition state by hydrogen bonding either to the amine or to the anionic head group of the surfactant.

Nature of the Reaction. For reaction of amines in water, it was necessary to allow for the contribution of the hydroxide ion which was generated in the equilibrium[10]

$$R_2'NH + H_2O \rightleftharpoons R_2'\overset{+}{N}H_2 + OH^-$$

but this problem is less serious for reaction in the presence of anionic micelles of NaLS, which stop the reaction of R^+ with hydroxide ion. In presenting the data, we do not correct for any reaction of R^+ with either water or hydroxide ion, because these should be very slow relative to the amine reaction.

For reactions in water, the slow step of the reaction of R^+ with ammonium or most amines is formation of the ammonium ion (I), which rapidly loses a proton,[10,19] and we assume that this is also true for reaction in an anionic micelle. However, proton loss is not rapid for reaction of

$$R^+ + R_2'NH \longrightarrow \underset{\text{I}}{R-\overset{+}{N}HR_2'} \xrightarrow{\text{fast}} RNR_2'$$

R^+ in water with pyrrolidine or 2-methylpyrrolidine,[10] and this may also be so for the micellar-catalyzed reaction of 2-methylpyrrolidine (Figure 2). (The reactions of pyrrolidine in micellized NaLS are too fast for convenient measurement.)

Added hydroxide ion has little effect upon the reaction of R^+ with primary amines in water, but it slightly increases the rate in the presence of micelles (Table III). This rate enhancement is probably not caused by a base-catalyzed decomposition of the ammonium ion (I) in the micelle, simply because hydroxide ion should be excluded from the Stern layer of an anionic micelle, and it is probably due to a suppression of the equilibrium formation of the ammonium and hydroxide ions, which should be increased by the anionic micelle. Because of the problem of allowing for this equilibrium in the presence of micelles, there is some uncertainty in the extent of catalysis by micelles of NaLS, especially for the most basic amine, 2-methylpyrrolidine, where $pK_a = 10.4$.[20]

Effect of Amine Structure. The rate enhancements in the plateau region (Table II) depend upon amine structure. For example, the rate enhancement with *n*-hexylamine is greater than with *n*-butylamine or cyclohexylamine. This effect of chain length of the reagent is often observed in micellar catalysis, even when the reagent is incorporated wholly into the micelle,[7] and it has been suggested that the larger *n*-alkyl groups bring the reaction center (the amine group) deeper into the Stern layer of the micelle because of favorable interactions between the *n*-alkyl groups of the reagent and the surfactant.[21] The decrease of reactivity with branching of the alkyl group of the reagent can be explained in the same way because a branched or cyclic alkyl group may not fit easily between the *n*-alkyl groups of the micellized surfactant. These observations suggest that hydrophobicity is not the controlling factor in micelle–substrate interactions.

The transition state for reaction of R^+ with an amine should have a structure similar to that of the ammonium ion (I), and hydrogen bonding to the ammonium protons should stabilize the transition state. Although there are water molecules in the Stern layer of the micelle,[5-8] the beneficial rate effects of bringing R^+ and the amine together on the micelle should be partially offset by a destabilization of the transition state relative to the initial state in the micellar phase. This counterbalancing effect is very common in micellar catalysis, and rate enhancements are generally small for reactions which have hydrophilic transition states. In this context, indicator measurements in aqueous NaLS show that anionic micelles stabilize the tri-*p*-anisylmethyl carbocation, R^+, much more than the *p*-nitroanilinium ion.[11]

Registry No.—CTABr, 56-09-0; Igepal, 9016-45-9; NaLS, 151-21-3; tri-p-anisylmethyl cation, 14039-13-5.

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