Micellar Effects on the Acid-Catalyzed Decomposition of Monoalkyl Xanthates[1]
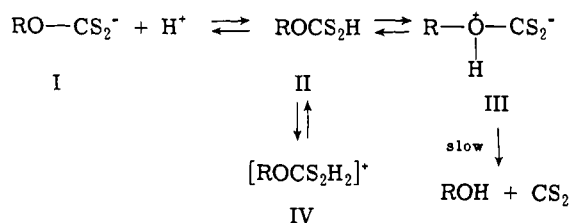
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At pH >2 the decomposition of ethyl, *n*-butyl, and *n*-octyl xanthate ion to the alcohol and CS_2 is inhibited by cationic micelles of cetyltrimethylammonium bromide (CTABr) and catalyzed by anionic micelles of sodium lauryl sulfate (NaLS) and nonionic micelles of Triton X-100. These effects can be rationalized in terms of micellar effects upon the protonation of the xanthate ion, and this rationalization is supported by micellar effects upon the apparent dissociation constants of the alkylxanthic acids. At low pH CTABr catalyzes the reaction in part because it decreases protonation of the xanthic acid to its unreactive conjugate acid; whereas under these conditions NaLS inhibits reaction, but the nonionic surfactant Brij 58 has no effect.

Monoalkyl xanthates (I) are rapidly hydrolyzed in dilute acid,[2] and the rate-limiting step is a spontaneous heterolysis of the undissociated acid (II).[4-6] The zwitterion (III) may be an intermediate formed in low concentration, or a proton transfer from sulfur to oxygen could be concerted with C–O bond breaking.

$$RO{-}CS_2^- + H^+ \rightleftarrows ROCS_2H \rightleftarrows R{-}\overset{\underset{|}{H}}{O}{-}CS_2^-$$

I II III

$$\downarrow\uparrow$$

$$[ROCS_2H_2]^+ \qquad \overset{slow}{\downarrow}$$

IV ROH + CS_2

The protonated ester (IV) is formed at low pH and is unreactive, unless the group R can be eliminated readily as a carbocation.[6]

The use of monoalkyl xanthates in ore flotation and cellulose processing stimulated work on their hydrolysis under homogeneous conditions,[3-6] but it seemed that synthetic surfactants might provide useful models for hydrolysis under industrial conditions because reaction in the presence of micellized surfactants could mimic that in the presence of colloids or larger sized particles. In addition alkylxanthate hydrolysis is often an undesired reaction which wastes material, so that its micellar inhibition could be useful.[7]

Experimental Section

Materials. The monoalkyl xanthates were commercial samples or were prepared, as the potassium salts, by standard methods.[3-5,11] The ionic surfactants, cetyltrimethylammonium bromide ($C_{16}H_{33}NMe_3Br$, CTABr) and sodium lauryl sulfate ($C_{12}H_{25}OSO_3Na$, NaLS), were purified by repeated recrystallizations, and the nonionic surfactants, Triton X-100 and Brij 58 (polyoxyethylene-20-cetyl ether) were used without further purification. Deionized and redistilled water was used to prepare the solutions.

Kinetics. The reaction was followed spectrophotometrically at 25.0° using methods already described.[6] The reactions at low pH, where the substrate is present as the xanthic acid, were followed at 270 nm, and Triton, which absorbs at this wavelength, could not be used under these conditions, so Brij was then used as a nonionic surfactant. Reaction at high pH was followed at 301 nm. Acetate buffer (0.02 *M*) was generally used to control the pH, and dilute HCl was used at low pH.

The products were the alcohol and CS_2, as in the absence of surfactants,[3-6] and trace metal effects were unimportant, as shown by the absence of any effect by added EDTA. The pH of the reaction solutions was measured in the presence of the surfactants. The observed first-order rate constants, k_ψ, are in reciprocal seconds, and the concentration of surfactant (detergent) is denoted as C_D.

The decompositions of ethyl and *n*-butyl xanthate have been examined over a wide pH range in the absence of surfactants.[4-6] The

Table I
Effect of pH on the Hydrolysis of *n*-Octyl Xanthate[a]

$10^3\ C_{HCl}$, M	pH[b]	$10^3\ k_\psi$, sec^{-1}	$\log k_\psi - \log C_{H^+}$[c]
	5.40	0.016	0.60
	4.50	0.11	0.53
	3.55	0.94	0.32
1.0		3.33	0.52
2.0		6.13	0.49
3.1		9.50	0.44
5.0		16.6	0.51
10.0		26.0	0.42
20.0		35.9	0.26
50.0		54.7	0.05

[a] In dilute HCl at 25.0° except where specified. [b] In buffer. [c] Log k_ψ + pH for reactions done in buffered solutions.

results for *n*-octyl xanthate show that its decomposition follows a pattern similar to that of the other alkyl xanthates. A plot of log k_ψ against pH has a slope of −1, and the rate levels off at low pH (Table I) for reaction in the absence of added surfactant.

Determination of Apparent Dissociation Constant. The absorbance at 301 nm of a solution of *n*-butyl xanthate at various pH in water or the appropriate surfactant was determined at various times, the absorbances were extrapolated back to the time of mixing, and the absorbances of an equimolar solution of *n*-butyl xanthate were measured under the same conditions. These experiments were repeated in solutions of various pH. The apparent dissociation constant "K_a" was calculated using eq 1, where A and A_x

$$\frac{A_x}{\epsilon_x(A_x - A)} = \frac{K_a}{a_H + \alpha} + \frac{1}{\alpha} \qquad (1)$$

are respectively the absorbances at a chosen pH and in alkaline solution, ϵ_x is the extinction coefficient of *n*-butyl xanthate in the surfactant solution, α is the difference between the extinction coefficients of xanthate ion and xanthic acid, and $a_{H^+} \equiv -\log$ pH in the presence of surfactant. The pH range for these experiments was 1.5–2.8, and the value of α for all the experiments was approximately 16,500.

Results and Discussion

Micelles could change the reaction rate in several ways: by affecting (1) conversion of xanthate ion (I) into the reactive xanthic acid (II), or (2) protonation of xanthic acid (II), giving the unreactive conjugate acid (IV), and (3) the rate of decomposition of xanthic acid (II) to products.

The simplest approach to this problem was to examine the micellar effects either at low pH (<1) where xanthate ion is absent or at higher pH (~3) where xanthic acid is fully ionized.[12] We also measured the apparent values of pK_a, and as expected we found that the acid dissociation of
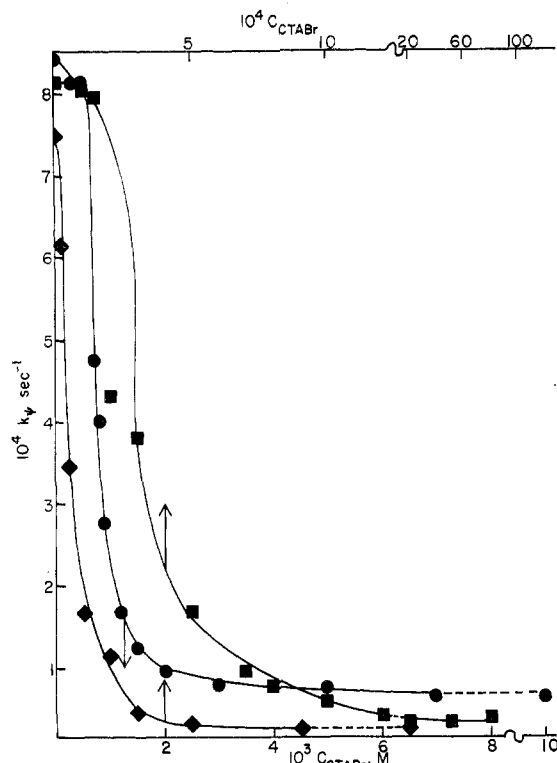
Figure 1. Effect of cationic micelles on the decomposition of n-alkyl xanthates at pH 3.65: ●, Et; ■, n-Bu; ♦, n-octyl.

Table II
Rate Enhancement by NaLS[a]

| $10^3 c_{NaLS}$, M | Alkyl group | | |
	Et	n-Bu	n-Octyl
	7.7	7.1	6.8
1		7.93	7.20
5	7.16	8.73	32.2
10	7.75	10.1	73.5
15		12.6	
20	7.65	14.0	
25		15.7	120
50	7.34	23.6	130
75	8.86		123
100	11.9	30.6	129
400		58	

[a] Values of $10^4 k_\psi$, sec^{-1}, at 25.0° and pH 3.7.

Table III
Effect of CTABr on the Hydrolysis of n-Butyl Xanthate[a]

$10^3 c_D$, M	$10^3 k_\psi$, sec^{-1}	$10^3 c_D$, M	$10^3 k_\psi$, sec^{-1}
	3.69	8.0	1.51
1.0	3.61	16.0	0.35
3.0	3.02	30.0	0.16
		60.0	0.17

[a] In 10^{-3} M HCl.

Table IV
Surfactant Concentrations for Half Rate Enhancement or Inhibition[a]

| Alkyl xanthate | Surfactant | | |
	CTABr[b]	NaLS[c]	Triton[c]
Et	8×10^{-4}		
n-Bu	3×10^{-4}	~0.1	5×10^{-3}
n-Octyl	4×10^{-5}	8×10^{-3}	1.3×10^{-3}

[a] Molarity of surfactant for 50% effect. [b] At pH 3.65. [c] At pH 3.7.

xanthic acid was increased by CTABr and decreased by Triton X-100 and NaLS; and these effects seem to be of key importance in determining the effects on reaction rate at pH > 3. Under all conditions the effects of micellized surfactants increase with increasing length of the n-alkyl group of the xanthate, as is generally found for micellar catalysis and inhibition.[8-10]

(1) At high pH where xanthate ion (I) is the bulk species, anionic micelles should increase the amount of reactive xanthic acid (II) present, and cationic micelles should have the opposite effect. (2) At low pH cationic micelles should decrease protonation of the reactive xanthic acid (II) which gives the unreactive conjugate acid (IV), and anionic micelles should have the opposite effect. (3) If we accept that the transition state is akin to the zwitterion (III) we would expect that incorporation of the substrate deeply into the micelle might hinder decomposition of the reactive xanthic acid by making it difficult for water molecules to hydrogen bond to the hydroxyl group of III, or to transfer a proton from sulfur to oxygen. However, there might be offsetting Coulombic interactions between the ionic head groups of the micelle and the anionic sulfur atoms, and evidence from reaction at pH 0 suggests that the decomposition step is slightly assisted by CTABr and hindered by NaLS.

Reaction at pH > 3. At this pH the xanthate ion is the bulk species, and because anionic micelles increase and cationic micelles decrease the reaction rate (Table II and Figure 1) their most important effect is to change the protonation equilibrium I ⇌ II, and effects on the rate of decomposition of alkylxanthic acid (II) seem to be less important.

The results at any given pH[13] are relatively simple. Cationic micelles of CTABr inhibit the reactions both in acetate buffer (Figure 1) and in 10^{-3} M HCl (Table III). The micellar inhibition increases sharply with increasing length of the n-alkyl group of the xanthate (Figure 1). The concentration of CTABr ($C_{1/2}$) required to halve the reaction rate (Table IV) gives an approximate indication of the strength of substrate–micelle bonding and shows the im-

portance of the hydrophobic n-alkyl group. Because the relation between rate constant and surfactant concentration depends on pH, these values in Table IV apply only at the pH specified.

Anionic micelles of NaLS and nonionic micelles of Triton catalyze the decomposition of n-alkyl xanthates at pH > 3 (Tables II and V). The catalysis increases, as expected, with increasing length of the n-alkyl group of the xanthate, and the concentration of surfactant needed for half rate enhancement similarly decreases (Table IV). The values of $C_{1/2}$ for n-butyl xanthate are approximate because we would have to go to very high surfactant concentrations to obtain rate plateaux.

Inhibition is observed with very low concentrations of CTABr, but much higher concentrations of NaLS are needed for rate enhancement, showing that the strongest interactions are between cationic micelles and alkyl xanthate ion (I).

Triton is as effective as NaLS in speeding the reaction (Tables II and V), and its nonionic micelles are effective in low concentration, showing the importance of hydrophobic as compared with Coulombic interactions.

The approximate maximum observed rate enhancements in micelles of NaLS at pH 3.7 follow: Et, 1.5-fold; n-Bu, 8-fold; n-octyl, 19-fold. With Triton they follow: Et, 2.5-fold; n-Bu, 7-fold; n-octyl, 16-fold (Tables II and V). However, it should be noted that these rate enhancements apply only

Table V
Rate Enhancement by Triton[a]

10^3 c_{Triton}, M	Alkyl group		
	Et	n-Bu	n-Octyl
	7.7	7.1	6.8
0.2	7.98	7.99	12.1
0.5	8.49	8.66	26.9
1.0	9.29	10.1	49.4
2.0	9.60	13.3	78.9
4.0	11.4	19.3	101
6.0	16.3	34.2	108
8.0	19.3	47.2	111
10.0	19.5	50.8	110

[a] Values of $10^4 k_\psi$, sec^{-1}, at 25.0° and pH 3.7.

Table VI
Effect of pH on the Hydrolysis of n-Octyl Xanthate in NaLS[a]

10^3 c_{NaLS}, M	Medium		
	10^{-3} M HCl	pH 2.9	pH 3.3
	33.0	45.7	18.4
1	33.5		16.3
3	40.6		
5			66.6
6	50.1		
10	158	122	99.1
15	186		
20	238		
25	277	158	144
40	299		
50	194	126	127
75		114	124
100		118	128

[a] Values of $10^4 k_\psi$, sec^{-1}.

for the specified pH. The results in Table VI, for example, show that the rate enhancements decrease with decreasing pH, and at these lower pH values we observe rate maxima in plots of k_ψ against C_D rather than plateaux.

The increasing protonation of the alkyl xanthate ion (I) in the presence of anionic micelles is easily understandable in terms of electrostatic interactions. There are no Coulombic interactions with nonionic micelles of Triton, but this surfactant should stabilize an undissociated alkylxanthic acid (II) relative to the more hydrophilic xanthate ion (I).

In the absence of surfactants plots of log k_ψ against pH are linear with slopes of −1 for decomposition of alkyl xanthates at pH > 2.5, but we do not observe this behavior in the presence of high concentrations of surfactants where these plots are curved, especially for CTABr and Triton (Figures 2–4). These experiments were carried out using relatively high surfactant concentrations, so that all the substrate should be taken up into the micelles.

There could be several reasons for this behavior. (1) Micelles affect the pH of buffered solutions by changing the acid dissociation constants,[14] and the substrates and buffer species will be distributed between the aqueous and micellar phases.[8-10] An uncharged alkylxanthic acid could be incorporated into a micelle, irrespective of its charge, especially if the alkyl group is hydrophobic, and the relatively hydrophobic n-octyl xanthate ion could be incorporated in anionic micelles of NaLS despite the electrostatic repulsions. (2) Micelles may change the rate of decomposition of
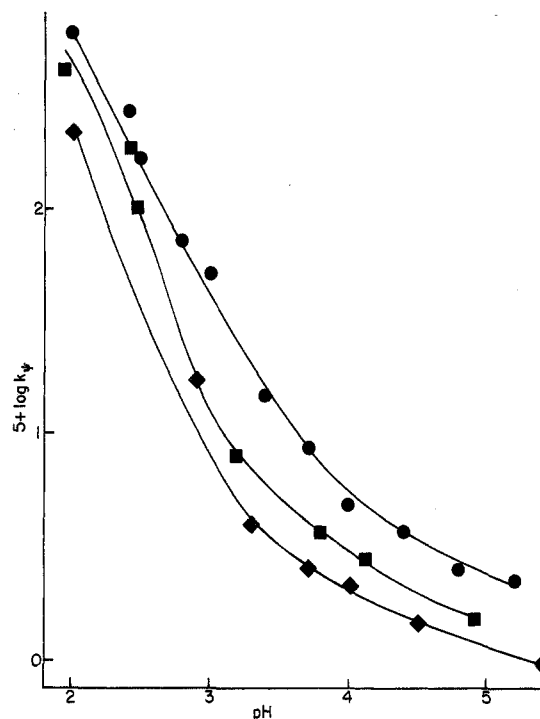

Figure 2. Variation of rate constant with pH in cationic micelles of CTABR: ●, ethyl xanthate in 5 × 10^{-3} M CTABr; ■, n-butyl xanthate in 2 × 10^{-3} M CTABr; ♦, n-octyl xanthate in 10^{-3} M CTABr.
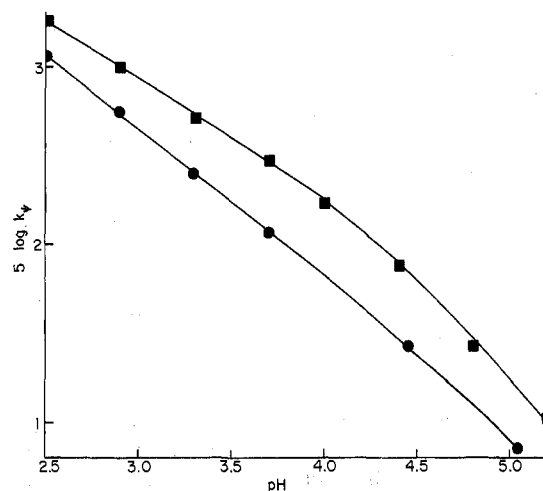

Figure 3. Variation of rate constant with pH in anionic micelles of 0.1 M NaLS: ●, ethyl xanthate; ■, n-butyl xanthate.

the xanthic acid (II). (3) There is a finite rate of reaction at high pH even in high concentrations of CTABr[15] (Figures 1 and 2), and when reaction is carried out in the presence of nonionic micelles of Triton X-100 the rates actually increase slightly at high pH (Figure 4). These observations are consistent with the appearance of a new reaction mechanism at high pH under these conditions. This reaction could be decomposition of the xanthate ion, which would generally be too slow to be observed but could be subject to catalysis by cationic and possibly nonionic micelles. How-

$$ROCS_2^- \longrightarrow RO^- + CS_2$$
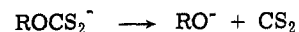
ever, anionic micelles should be ineffective in this role and we see no increase of reaction rate at high pH with micelles of NaLS (Figure 3).

An additional problem arises from the difficulty of knowing the pH on the micellar surface as compared with
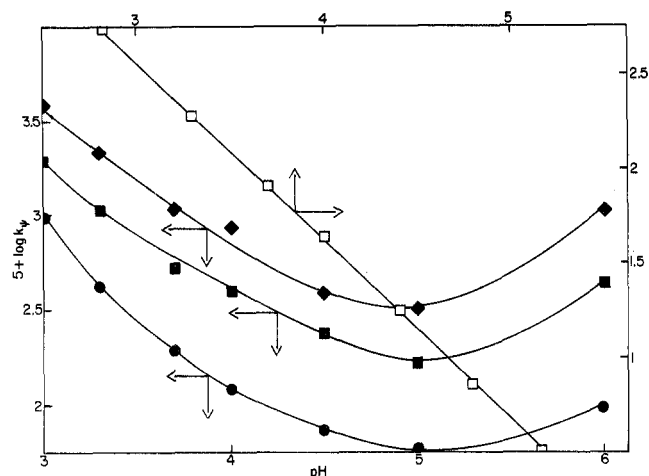
Figure 4. Variations of rate constant with pH in nonionic micelles of Triton: ●, ethyl xanthate; □ ■, n-butyl xanthate; ◆, n-octyl xanthate. The open points are for 5×10^{-4} M Triton and the solid points are for 10^{-2} M Triton.

that in the body of the solution,[16] and this problem is related to the appearance of rate maxima as shown in Table VI.

Micellar inhibition can generally be treated in terms of a partitioning of the substrate between the aqueous and micellar pseudophases,[8-10,17] and this treatment can occasionally be applied to micellar-catalyzed reactions.[18] However, these quantitative treatments cannot be applied to these xanthate reactions, in part for the reasons discussed above, but also because they require the assumption that changes in the critical micelle concentration (cmc) are small relative to the surfactant concentration. This approximation is a very dubious one for these reactions, because the relatively hydrophobic xanthic acid or xanthate ion could themselves promote micellization.

One major problem in studying micellar effects lies in deciding whether the micelles are acting by taking up the reactants, as is generally assumed, or whether they are merely affecting the properties of the solvent. With this in mind we observed that added sodium chloride in relatively high concentration decreases the inhibition by CTABr of the decomposition of n-butyl xanthate (Table VII) and increasing the concentration of acetate buffer has the same effect (Table VIII).[19] In the absence of surfactant the rate is almost unaffected by 10^{-2} M tetraethylammonium bromide. The salt effects upon the micellar inhibition could be caused either by exclusion of the substrate from the micelle, or by changes in micellar structure. The first explanation is generally applied to salt effects upon micellar catalysis and inhibition,[8-10] but changes in micellar structure are important in decarboxylations.[20]

Reaction at Low pH. An alkyl xanthate ion should be wholly protonated at pH < 1, so that micelles should affect the reaction rate only by changing the rate of decomposition of an alkylxanthic acid either directly, or indirectly by increasing the amount of the unreactive conjugate acid (IV). It is difficult to separate these factors, but decomposition of the xanthic acid is probably playing a role because in 0.1 M HCl anionic micelles of NaLS retard decomposition of n-butyl xanthate, and in 1 M HCl, where there should be some protonation of the xanthic acid,[21] reaction is also inhibited by NaLS. Nonionic micelles of Brij 58 have no effect on the reaction rate, which is consistent with this qualitative explanation, because they should not assist protonation of an alkylxanthic acid or its decomposition. However, CTABr slightly hinders reaction in 0.1 M HCl, suggesting that some n-butyl xanthate is then formed, but it catalyzes the reaction in 1 M HCl (Table IX) although

Table VII
Effect of Sodium Chloride on the Reaction of n-Butyl Xanthate in CTABr[a]

c_{NaCl}, M	$10^3 k_\psi$, sec^{-1}	c_{NaCl}, M	$10^3 k_\psi$, sec^{-1}
	0.033	0.10	0.31
0.001	0.051	0.15	0.42
0.005	0.063	0.20	0.51
0.01	0.076	0.50	0.92
0.025	0.11	1.00	1.40
0.05	0.20		

[a] At 25.0° in pH 3.89, 2×10^{-3} M CTABr and 0.02 M acetate buffer.

Table VIII
Effect of Sodium Acetate on the Reaction of n-Butyl Xanthate in CTABr[a]

c_{NaOAc}, M	$10^3 k_\psi$, sec^{-1}
0.0069	0.026
0.020	0.033
0.028	0.041

[a] At 25.0°, pH 3.89, and 2×10^{-3} M CTABr.

Table IX
Effect of Surfactants on the Acid Hydrolysis of n-Butyl Xanthate[a]

	NaLS		CTABr		Brij	
			c_{HCl}, M			
$10^3 c_D$, M	0.1	1.0	0.1	1.0	0.1	1.0
	98.0	96.0	98.0	96.0	98.0	96.0
1	82.0		82.0		93.0	
3	76.0	69.7	80.0	260	100	99.0
6	41.2					
8		41.2	80.7	302	103	103
16	26.0		80.5			
20					94.0	90.0
25	25.8					
30			83.0			
60			85.0			

[a] Values of $10^3 k_\psi$, sec^{-1}, at 25.3°.

Table X
Reaction of n-Octyl Xanthate in CTABr and 0.1 M HCl[a]

$10^3 c_{CTABr}$	$10^3 k_\psi$, sec^{-1}	$10^3 c_{CTABr}$	$10^3 k_\psi$, sec^{-1}
	34.9	16	62.7
3	39.2	30	67.2
8	53.3	60	72.2

[a] At 25.0°.

the enhancement is relatively small (less than threefold). This rate enhancement is understandable if the transition state is between the zwitterion (III) and product, with favorable Coulombic interactions between the micelle and the CS_2^- group, and such a transition state should be destabilized by NaLS. Some support is given for this hypothesis by the rate enhancement of the reaction of the relatively hydrophobic n-octyl xanthate by CTABr, even in 0.1 M HCl, where in the absence of surfactants protonation of the xanthate ion should be almost complete, but there should be no protonation of the xanthic acid (Table X).

Table XI
Micellar Effects upon the Apparent Dissociation Constants of *n*-Butylxanthic Acid in Water

Surfactant	"pK_a"	Surfactant	"pK_a"
	1.54	5×10^{-2} *M* NaLS	2.45
2×10^{-3} *M* CTABr	1.01	10^{-2} *M* Triton	1.92

Micellized alkyl sulfates are readily hydrolyzed in moderately concentrated acid; therefore we did not use highly acidic solutions in these experiments, and freshly made solutions were always used.

Apparent Dissociation Constants. Micellar effects upon the rates at pH > 3 can be explained qualitatively in terms of changes in the acid dissociation of the alkylxanthic acid. Similar observations have been made on a number of micellar catalyzed or inhibited reactions.[8-10,14b] We have calculated the apparent dissociation constant of *n*-butylxanthic acid in the presence of micelles by rapidly determining the total concentration of xanthate ion. (The values are apparent because we do not know the distribution of xanthic acid or xanthate and hydronium ions between water and the micellar pseudophase.[16])

Micelles change the dissociation constant in the expected directions (Table XI). Cationic micelles of CTABr should stabilize the xanthate ion relative to xanthic acid, and they increase the dissociation constant, whereas anionic micelles of NaLS and nonionic micelles of Triton should stabilize xanthic acid relative to its anion, and they decrease the dissociation constant.

References and Notes

(1) Support of this work by the National Science Foundation, The Comision Central de Investigacion of the University of Chile, and the University of Chile–University of California Cooperative Program supported by the Ford Foundation is gratefully acknowledged.
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(21) For the equilibrium II ⇌ IV p$K_a \simeq -1$.[4,6]

Kinetics of the Condensation of *N*-Methyl-4-picolinium Iodide with *p*-Dimethylaminobenzaldehyde in Aqueous Ethanol

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The kinetics of condensation of *N*-methyl-4-picolinium iodide and *p*-dimethylaminobenzaldehyde in 78.2% (v:v) aqueous alcoholic sodium hydroxide were determined at 25° spectrophotometrically by following the appearance of *p*-dimethylamino-4-styrylpyridinium methiodide at 470 nm. The reaction was first order in methiodide, aldehyde, and hydroxide with a third-order rate constant of 1.67×10^{-2} M^{-2} sec^{-1}. The kinetics of the proton exchanges of *N*-methyl-4-picolinium iodide in methanol-d_4-methoxide-d_3 were determined by nmr at 35°. The second-order rate constants for exchange of *N*-methyl, 2,6-, and *C*-methyl protons were 2.2×10^{-5}, 1.62×10^{-4}, and 7.5×10^{-2} M^{-1} sec^{-1}, respectively. The second-order rate constant for the *N*-methyl proton exchange of *N*-methylpyridinium iodide was 16×10^{-5} M^{-1} sec^{-1}. The kinetic data are in accord with a condensation mechanism in which the rate-determining step is carbon–carbon bond formation by reaction of the methylene base with the aldehyde. Nitrogen decoupling experiments showed the β protons of the *N*-methylpyridinium iodide to be coupled to nitrogen. Furthermore, the *N*-methyl group showed a positive nuclear Overhauser effect upon irradiation of nitrogen.

In conjunction with a study of the detection of alkyl halides by reaction with 4-picoline we have examined the rate of the 78.2% (v:v) aqueous alcoholic base induced condensation of *N*-methyl-4-picolinium iodide (**1**) with *p*-dimethylaminobenzaldehyde (**2**) to yield the highly colored *p*-dimethylamino-4-styrylpyridinium methiodide (**3**) (eq 1).

Phillips[1] has reported the analogous piperidine-induced condensation of *N*-methyl-2-picolinium iodide with **2**.

The objective of the kinetic experiments was to determine the reaction mechanism sufficiently to define the optimum conditions for alkyl halide detection. The central mechanistic questions were (1) the role of the conjugate