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Inhibition of Hydrolysis by Lamellar Liquid Crystalline Solvents

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The rate of hydrolysis of benzylidene *t*-butylamine *N*-oxide decreases as the concentration of dodecylammonium chloride in water increases until the lamellar liquid crystalline mesophase is formed. Based on the aggregate-substrate association constant plot the partitioning of the substrate into the hydrocarbon region and the electrostatic effect causes this maximum inhibition.

INTRODUCTION

Many reactions of fundamental importance occur at interfaces and the study of micellar catalyst and inhibition at the CMC represents an expanding area of research.[1] Equally important is the kinetic study of interfacial reactions at surfactant concentrations a hundred times the CMC occurring at interfaces between aqueous and liquid crystalline mesophases. These mesophases may provide favorable orientation of reactant molecules at the boundary between the micellar water phase and the surfactant layer as well as exerting a large electrostatic effect and providing an extensive hydrocarbon region for partitioning of the substrate from the water layer.

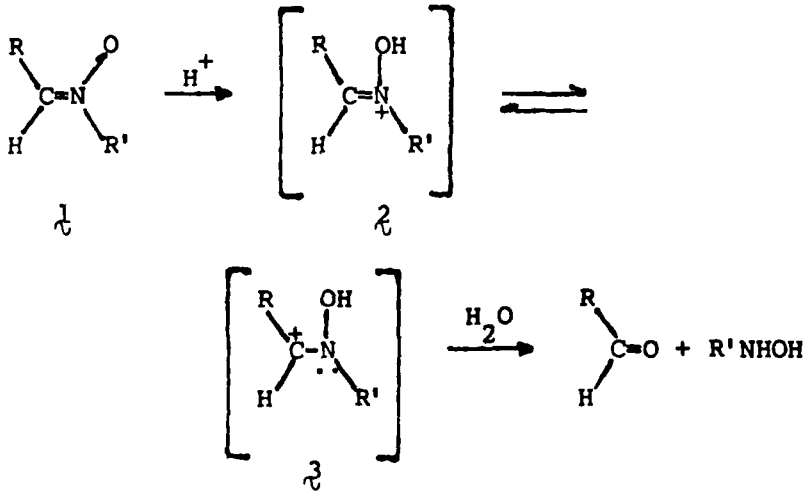
The aqueous hydrolysis of benzylidene *t*-butylamine *N*-oxide, **1** reaches its maximum inhibition in the lamellar mesophase[2] of dodecylammonium chloride solution (DdAC) while anionic micelles catalyze the reaction and cationic micelles at CMC do not affect the rate.[3] We wish to consider reasons for this inhibition and outline possible sites for the reaction in this paper.

The rate of acceleration or inhibition of organic reactions in micellar solutions arises from different rates of reaction of the substrate in the

micellar phase and in the bulk solution and the distribution of the substrate between these two phases. Basically these rate effects can be attributed to electrostatic and hydrophobic interactions between the substrate and the surfactant aggregate and in some cases to alterations in the structure of the surrounding water.[4] The role of the anisotropic interfacial structures on reactive molecules has not been fully investigated.

RESULTS AND DISCUSSION

The hydrolysis of **1** in aqueous DdAC solutions is shown below and the rate of hydrolysis decreases as the concentration of DdAC increases



$R = C_6H_5$; $R' = t\text{-}C_4H_9$.

as shown in Table I. The rate of hydrolysis forms a plateau above one molar concentration and this corresponds to the formation of the lamellar mesophase.[2] Electron microscopy indicates these lamellar mesophases contain multi-wall vesicles[5] and they are probably in equilibrium with dilute aqueous micellar solution. Light microscopy shows focal-conic structures and oily streaks typical of the smectic mesophase and the lamellar structure.[2]

Inhibition of reactions in micellar systems can be treated by assuming that the substrate, S, interacts chemically or physically with the micelle to generate a complex with a lower reactivity. Making the usual as-

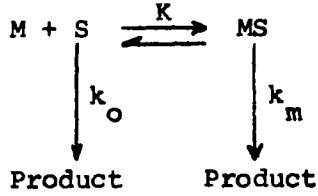
TABLE I

Rate constants for hydrolysis of benzylidene *t*-butylamine *N*-oxide in aqueous DdAC solutions. pH 1.00

DdAC M	0.391	0.494	0.605	1.052	1.368	1.559
Rate[a] $\cdot 10^4$ sec^{-1}	16.6	12.8	11.1[b]	5.24	5.40	5.50

[a] Pseudo first-order determined at 25°, substrate concentration 7.0×10^{-6} M.
[b] This value is higher than the rate reported in Ref. 2 and is more precise.

sumptions and simplifications[4] the kinetics of micellar inhibition has been successfully treated in terms of micelle-substrate binding and reaction in the aqueous bulk and micellar phases [Eq. (1) where k_0 and k_m are the rate constants for product formation in the bulk solvent and micellar phase respectively and K is the micelle-substrate binding constant].



(1)

The observed rate constant, k_ψ, for the hydrolysis of **1**, is given by Eq. (2)

$$k = \frac{k_0 + k_m K[M]}{1 + K[M]} \tag{2}$$

and using relationship (3), (where C_D and $[M]$ are

$$[M] = (C_D - \mathrm{CMC})/N \tag{3}$$

the concentration of surfactant and micellar concentration respectively, N is the aggregate number and CMC is the critical micelle concentration) and rearrangement leads to Eq. (4).

$$\frac{1}{k_0 - k_\psi} = \frac{1}{k_0 - k_m} + \left(\frac{1}{k_0 - k_m}\right)\left(\frac{1}{C_D - \mathrm{CMC}}\right)\frac{N}{K}. \tag{4}$$

Equation (4) predicts a rate plateau and is frequently used to calculate the binding or association constant, K.[6] Values for K/N and k_m were obtained from the slope and intercept of the line observed in the graph of the left side of Eq. (4) *vs* $1/(C_D - \mathrm{CMC})$ as shown in Figure 1.

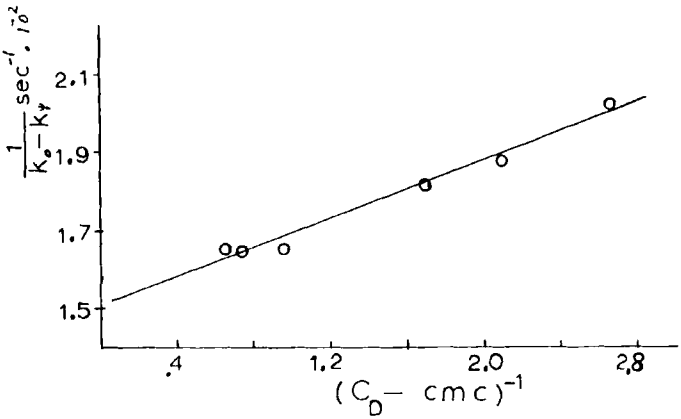


FIGURE 1 Aggregate-substrate association constant plot based on Eq. (4).

The intercept of the line calculated by least squares of the reciprocal plot is within experimental error of $1/k_0$, indicating the rate of hydrolysis of the *N*-oxide-substrate absorbed into the micelles, k_m, must be zero. The K/N ratio was evaluated from the slope and by substituting 55.5 for the aggregation number, *N* reported for DdAC[7] we find *K* to be 4.5×10^2 M^{-1}, indicating the cationic micelles readily incorporate the substrate. This value is similar to the values for association constants for acid hydration reactions in cationic micelles reported by Bunton, Rivera and Sepulveda.[8]

The partitioning between the aqueous and the hydrocarbon region parallels the partitioning between octanol-water solvent.[9] We determined the partitioning of **1**, in this solvent system from Beer's law relationship in water saturated with *n*-octanol and the reverse phase as eleven. This result suggests that **1** has a preference for the hydrocarbon environment and presumably in the lamellar system a concentration of eleven times more of **1**, resides in the hydrocarbon region than in the water. Such unfavorable partitioning results in a decrease in the rate of hydrolysis in the lamellar phase as we have demonstrated.

Inhibition of the hydrolysis reaction by the lamellar mesophase may be explained by two basic factors: (a) electrostatic repulsion of the protonated intermediates **2** and **3**, within the aqueous layer, and (b) partitioning of the substrate into the lipophilic region which interferes with the protonation step.[8] Considering the concentration of DdAC necessary to form the lamellar mesophase is about one hundred times the CMC it is expected that k_m in the lamellar mesophase would be smaller than at the CMC.

EXPERIMENTAL

Dodecylammonium chloride, DdAC was prepared by the procedures reported[10,11] and the salt was recrystallized from ethanol–ether mixtures several times. The solutions were prepared with deionized water just before each rate determination. The pH was adjusted with conc. hydrochloric acid at 25° using a Fisher Accumet pH Meter with an expanded scale equipped with a Corning combination electrode. Prolonged exposure of the glass electrode to the surfactant solution caused a slow response of the electrode to the pH of the solution. The response was restored by soaking in 0.1 M HCl.

KINETIC MEASUREMENTS

The hydrolysis of **1**, was followed by the consumption of reactant at 292 nm in one centimeter thermostatted curvettes at 25° ± .05 with a GCA McPherson EV 700 series recording spectrophotometer equipped with an automatic filter attachment. The reaction was initiated by the injection of nine microliters of the aqueous solution of **1** into the curvette and then stirred to assure a homogeneous solution. The pseudo first-order plots were linear to greater than 90% reaction and the reproducibility was within 5%. The correlation coefficient for Figure 1 is 0.98.

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