mum 2.67)[5] and the isomerization of 2-aryl-3-methyl-2-butene (2.34),[20] both in acetic acid.

Whether the maximum theoretical C–H isotope effect is reckoned to be 6.2 (zero-point energy only), 10 (allowing for bending vibrations), or higher still if the tunnel effect is included,[21] these are small isotope effects and are therefore indicative of an asymmetric transition state,[22] relatively close either to the carbonium ion or to the product. Since the former is of much higher energy, consideration of the Hammond postulate[23] suggests that the transition state for slow proton transfer will be in fact carbonium ion like.

Conclusion

This reaction, the dehydration of 1,1′-diadamantylmethylcarbinol in aqueous acetic acid, is unusual in that variation of the solvent composition causes the deuterium KIE to vary over a wide range. This phenomenon is attributable to the fact that one of the components of the reaction medium, water, causes the intermediate carbonium ion to revert to starting material, while the major component, acetic acid, is apparently inert. A very simple kinetic scheme leads to an equation which expresses the overall KIE in terms of the water concentration. The data provide values of the secondary isotope effect upon carbonium ion formation and of the primary isotope effect on deprotonation of this ion, the latter without it being necessary to compare elimination rates from labeled and nonlabeled groups. Though neither datum is completely resolved, both are relevant to the mechanism of dehydration and of olefin hydration in partially nonaqueous media. Our observations provide no information about the possible occurrence of π complexes but clearly do not require their involvement in the rate-determining step or steps of these reactions.

Experimental Section

Synthesis of 1,1′-Diadamantylmethylcarbinol, 2. The normal and deuterated alcohols were prepared by addition of 1,1′-diadamantyl ketone to the appropriate methyllithium compound in ether under argon at room temperature: mp 204.5 °C after recrystallization from hexane; IR (CCl$_4$) 3625 cm^{-1}; NMR (CCl$_4$) δ 1.03 (s, 3 H of methyl (absent in **2d**)), 1.70 and 1.94 (unresolved m, 30 H of adamantyl groups). The highest peak in the mass spectrum of the normal alcohol (*m*/*e* 296) corresponds to loss of water; in the case of **2d**, HDO is lost (*m*/*e* 298). Anal. Calcd for $C_{22}H_{34}O$: C, 84.01; H, 10.90. Found: C, 83.87; H, 10.88.

Dehydration Product of 1,1′-Diadamantylmethylcarbinol. Acid-catalyzed dehydration of the normal alcohol, **2h** (0.6 g), in anhydrous acetic acid containing 0.006 M sulfuric acid (100 mL) for 30 min at 25 °C gave the corresponding 1,1-bis(1-adamantyl)ethylene (0.55 g, 97% yield): mp 110–111.5 °C after recrystallization from hexane; IR (CCl$_4$) 1607, 895 cm^{-1}; NMR (CCl$_4$) δ 1.71 and 1.96 (unresolved multiplets, 30 H of adamantyl groups), 5.03 (s, 2 vinylic H). Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 88.98; H, 10.94. The amount of alcohol remainiing was estimated by GLC to be less than 0.1% and no IR absorption attributable to acetate could be detected in the crude reaction product.

Alcohol-Olefin Equilibrium. Alcohol 2 or the corresponding olefin (1–2 mg) was dissolved in anhydrous acetic acid (5 mL). An aqueous acetic acid solution of sulfuric acid was added to make 10 mL (final concentration 11.13 M water, 0.444 M sulfuric acid) and the mixture was thermostated at 25 °C for 2 h. GLC analysis of samples showed an identical alcohol/olefin ratio of 1.2/98.8 regardless of the starting material.

Kinetic Procedure. Rate constants for the dehydration of the alcohols were determined by measuring the rate of disappearance of the alcohol against an internal standard by gas chromatography on Carbowax 20M. The internal standard (1,1′-diadamantyl ketone)(3 mg) and the alcohol (10 mg) were dissolved in anhydrous acetic acid (Merck, 100%, analytical grade, 25 mL). Aqueous media were prepared by taking weighed amounts of water in graduated flasks and completing with stock solutions of 100% sulfuric acid in acetic acid. The reaction was started by adding to 5 mL of the acid medium enough reactant/standard solution to make 10 mL. Samples were taken at appropriate intervals, quenched in aqueous sodium carbonate, and extracted into *n*-hexane.

Since the dehydration is slightly reversible in the presence of water, the first-order kinetic plots depart from linearity after 2–4 half-lives, depending on the water concentration, unless correction is made for the equilibrium alcohol concentration. The forward rate constants given in Table I have been corrected appropriately. Rate constants are reproducible to 1–2%, isotope effects to 3–4%.

Acknowledgment. I am indebted to Professor J. E. Dubois for stimulating and helpful discussions.

Registry No. 2d, 75782-40-0; **2h**, 75782-41-1; 1,1′-diadamantyl ketone, 38256-01-8; 1,1-bis(1-adamantyl)ethylene, 75782-42-2.

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[20] Kieboom, A. P. G.; Bekkum, H. v. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1424.

[21] Bell, R. P. *Chem. Soc. Rev.* **1974**, *3*, 513. Saunders, W. H. *Chem. Scr.* **1976**, *10*, 82.

[22] Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265.

[23] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

Solvolyses of a Carbonate and a Benzhydryl Chloride inside Micelles. Evidence for a Porous Cluster Micelle

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Received September 16, 1980

Two water-insoluble compounds, bis(4-nitrophenyl) carbonate and *p*-chlorobenzhydryl chloride, solvolyze in micelles at rapid rates indicative of highly aqueous binding sites. This is used as evidence against the classical Hartley micelle and in support of a "porous cluster" model bearing water-filled regions where guests bind hydrophobically. The conclusions from the kinetic data agree with those from a variety of other approaches used in this laboratory including ^{13}C NMR, gas solubility, ORD, and molecular models.

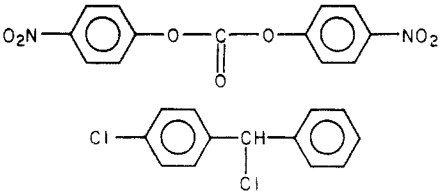
Reactivity inside a micelle generally differs from that in bulk water. This fact has been widely used to probe the nature of micellar environments.[1,2] Of course, it is seldom easy to interpret small catalytic or inhibitory effects with

Table I. Observed Rate Constants at 50.0 °C for the Hydrolysis of Bis(4-nitrophenyl) Carbonate[a,c,d]

entry	additive	$10^2 k_{obsd}$, min^{-1}
1	none	18.0
2	10% dioxane[b]	13.4
3	50% dioxane	6.0
4	50% dioxane + 1.0 M Me_4NBr	1.1
5	60% dioxane	3.3
6	60% dioxane + 1.0 M Me_4NBr	0.7
7	1.0 M KBr	13.9
8	2.0 M KBr	9.2
9	1.0 M KCl	16.4
10	1.0 M Me_4NBr	14.5
11	2.0 M Me_4NBr	11.7
12	3.0 M Me_4NBr	8.5
13	0.002 M HTAB[e]	13.8
14	0.003 M HTAB	13.2
15	0.005 M HTAB	12.5
16	0.0075 M HTAB	12.0
17	0.010 M HTAB	11.2
18	0.020 M HTAB	10.5
19	0.040 M HTAB	10.0
20	0.050 M HTAB	9.8
21	0.030 M HTAB + 0.10 M KCl	12.2
22	0.030 M HTAB + 0.20 M KCl	13.0
23	0.030 M HTAB + 0.30 M KCl	13.7
24	0.030 M HTAB + 0.10 M KBr	9.2
25	0.030 M HTAB + 0.20 M KBr	6.2
26	0.030 M HTAB + 0.30 M KBr	6.1
27	0.030 M HTAB + 0.40 M KBr	6.3

[a] Entries 1-12 used 0.01 M HCl; entries 13-27 used 0.01 M HBr. [b] v/v. [c] Rate constants represent the average of 3-5 runs. [d] 3.0×10^{-5} M carbonate. [e] Hexadecyltrimethylammonium bromide.

multistep reactions proceeding inside elusive and nonuniform aggregates. Even relatively straightforward bimolecular micellar reactions require a complicated rate expression to secure the gross kinetic features.[3] With the philosophy that complex systems are best investigated using *simple* experiments, we have studied two micellar processes each involving but a *single* organic reactant: (1) the "water reaction" of bis(4-nitrophenyl) carbonate and (2) the solvolysis of *p*-chlorobenzhydryl chloride. The



carbonate hydrolysis seemed useful for micelle work because it proceeds at a convenient rate without the aid of an acid or base catalyst.[4] Benzhydryl chloride solvolyses attracted our interest because of their great sensitivity to solvent (the reaction is roughly 10^4 times faster in 30% dioxane–water than in 80% dioxane–water). We could therefore use the reaction to explore the water content of micelles, a matter of considerable controversy. Thus, we have proposed[5] and supported[6,7] a micelle model which contains deep water-filled grooves. Others, however, still prefer the classical Hartley model consisting of a water-free "oil droplet" surrounded by an ionic shell.[8,9]

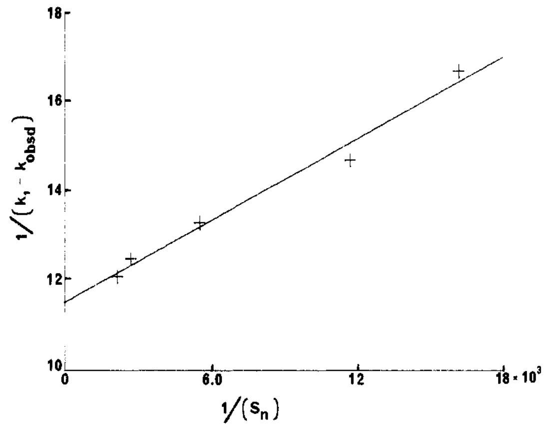
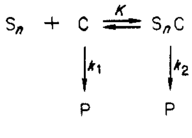


Figure 1. Double-reciprocal plot based on eq 2 used to calculate the micellar reaction rate k_2 and the micelle–carbonate association constant K (see text). Data are taken from entries 16–20 in Table I.

Results and Discussion

Carbonate Hydrolysis. "Water reactions" refer to hydrolyses in which only substrate and water participate.[10] Additional acidic and basic catalysts play no role. We have shown previously[4] (by means of the so-called proton inventory method) that the "water reaction" of bis(4-nitrophenyl) carbonate in 0.01 N HCl entails two water molecules in the transition state leading to the tetrahedral intermediate. As seen from Table I (entries 1–5), 60% dioxane in the water impedes the hydrolysis rate about 5-fold. Furthermore, inert salts KBr, KCl, and Me_4NBr also reduce the hydrolysis rate, with KCl having the least effect (entries 7–12). The rates are given here merely to "calibrate" the micellar data below; attempts to interpret them in terms of structure-making or -breaking activity would have little meaning.

Entries 13–20 show the rates of the carbonate hydrolysis in the presence of varying concentrations of hexadecyltrimethylammonium bromide (HTAB) in aqueous 0.01 M HBr.[11] Cationic surfactant clearly retards the reaction well above the critical micelle concentration. The rate data were analyzed by means of eq 1, a scheme which we proposed years ago[12] and which has survived the test of time.[13]



$$\begin{tikzcd} S_n + C \arrow[r, shift left, "K"] \arrow[d, "k_1"] & S_nC \arrow[l, shift left] \arrow[d, "k_2"] \\ P & P \end{tikzcd} \qquad (1)$$

Micelles S_n bearing n monomers adsorb carbonate C with an association constant K; k_1 and k_2 represent the hydrolysis rate in bulk water and inside the micelle, respectively. Evaluating k_1 is trivial since it equals the rate constant in the absence of surfactant (18.0×10^{-2} min^{-1}, entry 1). Parameters K and k_2 were obtained from eq 2

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(1) Cordes, E., Ed. "Reaction Kinetics in Micelles"; Plenum Press: New York, 1973.

(2) Mittal, K. L., Ed. "Micellization, Solubilization, and Microemulsions"; Plenum Press: New York, 1977; Vol. 1 and 2.

(3) Yatsimirski, A. K.; Martinek, K.; Berezin, I. V. *Tetrahedron* **1971**, *27*, 2855.

(4) Menger, F. M.; Venkatasubban, K. S. *J. Org. Chem.* **1976**, *41*, 1868.

(5) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111.

(6) Menger, F. M.; Jerkunica, J. M.; Johnston, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4676.

(7) Menger, F. M. *J. Phys. Chem.* **1979**, *83*, 893.

(8) Stigter, D. *J. Phys. Chem.* **1974**, *78*, 2480.

(9) Wennerstrom, H., Lindman, B. *J. Phys. Chem.* **1979**, *83*, 2931.

(10) Johnson, S. L. *Adv. Phys. Org. Chem.* **1967**, *5*, 237.

(11) Rate constants are independent of acid concentration from 1×10^{-4} to 1×10^{-2} M.

(12) Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 4698.

(13) Cordes, E. H. *Pure Appl. Chem.* **1978**, *50*, 617.

$$\frac{1}{(k_1 - k_{\mathrm{obsd}})} = \frac{1}{(k_1 - k_2)} + \frac{1}{(k_1 - k_2)K(\mathrm{S}_n)} \qquad (2)$$

by plotting $1/(k_1 - k_{\mathrm{obsd}})$ vs. $1/(\mathrm{S}_n)$. The micelle concentration (S_n) equals $(\mathrm{S_t} - \mathrm{CMC})/n$, where $\mathrm{S_t}$ is the total HTAB concentration in solution; n and the CMC are taken as 105 and 1.0×10^{-3} M, respectively.[14] Throughout the experiments the initial carbonate concentration was kept low (3×10^{-5} M) so as not to perturb the micelles. A plot based on the data in Table I and eq 2 is shown in Figure 1. The intercept provides a k_2 of $9.3 \pm 0.4 \times 10^{-2}$ min^{-1} and the slope of K of $4 \pm 1 \times 10^4$ M^{-1}. Micelles characteristically display such huge association constants for water-insoluble compounds, a fact to which we will return later. An identical analysis of the carbonate hydrolysis in dodecyltrimethylammonium bromide micelles (rate data not listed) gives a $k_2 = 13 \times 10^{-2}$ min^{-1} and a $K = 8 \times 10^3$ M^{-1}.

Despite the obvious affinity for the carbonate by HTAB micelles, their effect on the "water reaction" is small: k_2 for hydrolysis in HTAB micelles equals 9.3×10^{-2} min^{-1} as compared to 18.0×10^{-2} min^{-1} in bulk water. On the other hand, dioxane (60%) reduces the rate to 3.3×10^{-2} min^{-1}, while 1.0 M $\mathrm{Me_4NBr}$ plus 60% dioxane lowers the rate even more (0.7×10^{-2} min^{-1}, entry 6). Clearly, the micellar reaction behaves as if it proceeds in a highly aqueous medium. Assume now that the small rate decrease found for the micellar hydrolysis stems from the ion atmosphere provided by the head groups. If concentrated $\mathrm{Me_4NBr}$ solutions simulate this atmosphere, then the ionic strength at the binding sites of the micelle must average approximately 2.8. This follows from the fact that 2.8 $\mathrm{Me_4NBr}$ gives a hydrolysis rate similar to k_2 (entries 10–12). An ionic strength of 2.8 agrees well with a previously determined theoretical value.[15]

The effect of added inorganic salt on the micellar reaction rates (entries 21–27) supports the ion atmosphere assumption. Although KBr decreases the hydrolysis rate inside the HTAB micelles, KCl increases it. In bulk water, *both* KBr and KCl decrease the reaction rate (entries 7–9), but KBr is the more potent. Thus, excess chloride ion added to the HTAB systems displaces the bromide counterions near the surfactant head groups, enhancing the rate. In summary, the data in Table I can be reasonably explained by substrate adsorption at a highly aqueous region where small rate perturbations originate largely from specific salt effects.

We now turn to the central question: Why does the water-insoluble carbonate adsorb into an aqueous region with such a large association constant? If a micelle were indeed a water-free "oil droplet" surrounded by an ionic shell, as proposed by Hartley,[16] then adsorbed carbonate must be located in the Stern layer consisting of ionic head groups, counterions, and water of solvation. But then it becomes unclear what intermolecular forces bind the carbonate to the Stern layer. Although there is evidence of weak association between cations and aromatics,[17] we can dismiss this as a major source of binding to HTAB for the following reasons. (1) Aromatics frequently associate with anionic micelles as tightly as they do with cationic ones.[18] (2) Nonaromatics such as tetranitromethane can also bind to HTAB with constants in the 10^4–10^5 M^{-1} range.[19] (3) There exist nonaromatic ketones that are both salted out from water at high ionic strengths and solubilized in water by cationic micelles.[20]

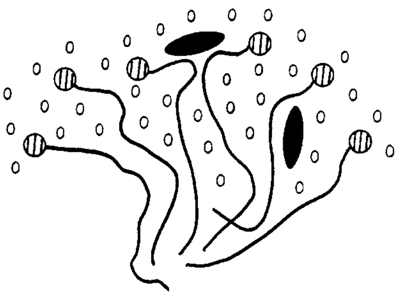

Figure 2. Schematically represented section of a "porous cluster" micelle showing two possible sites for hydrophobic bonding of a guest molecule (black ovals). Water molecules (small ovals) are found near the guests and deep within the micelle. See ref 5 for photographs of molecular models of this micelle.

Table II. Solvolysis of *p*-Chlorobenzhydryl Chloride at 25.0 °C in Water[a]

entry	additive	k_{obsd}, min^{-1}
1	30% dioxane[b]	6.0
2	40% dioxane	1.1
3	60% dioxane	0.028
4	80% dioxane	0.00045
5	30% dioxane + 0.10 M $\mathrm{NaClO_4}$	7.3
6	30% dioxane + 0.50 M $\mathrm{NaClO_4}$	10
7	30% dioxane + 0.10 M NaCl	5.5
8	30% dioxane + 0.50 M NaCl	4.1
9	30% dioxane + 1.0 M NaCl	2.8
10	30% dioxane + 0.20 M $\mathrm{Na_2SO_4}$	4.3
11	0.0050 M HTAC[c]	5.4
12	0.010 M HTAC	2.2
13	0.020 M HTAC	1.0
14	0.050 M HTAC	0.36
15	0.10 M HTAC	0.17
16	0.15 M HTAC	0.11
17	0.20 M HTAC	0.077[d]
18	0.10 M HTAC + 0.01 M NaOH	0.17
19	0.10 M HTAC + 0.01 M HCl	0.17
20	0.10 M HTAC + 0.07 M NaCl	0.14
21	0.10 M HTAC + 0.32 M NaCl	0.085
22	0.10 M HTAC + 0.62 M NaCl	0.057
23	0.10 M HTAC + 1.0 M $\mathrm{Na_2SO_4}$	0.030
24	0.20 M HTAC + 30% dioxane	0.095

[a] Runs used 2.51×10^{-4} M chloride. [b] v/v. [c] Hexadecyltrimethylammonium chloride. [d] Rate constant was independent of *p*-chlorobenzhydryl chloride concentration from 8.4×10^{-5} to 1.7×10^{-3} M.

The inability of the Hartley micelle to explain binding data supports the alternative "porous cluster" model described in a recent review article.[5] This model portrays the micelle as a loose assemblage of surfactant molecules bearing water-filled cavities. Aqueous pockets prevail whether the surfactant chains are folded or fully extended. There are undoubtedly a multitude of micellar conformations in equilibrium with each other, but they all possess hydrocarbon chains in contact with water near the micelle surface. Binding of water-insoluble compounds to the chains "releases" frozen water, an entropically favorable process. In other words, micelles are best pictured as having rough surfaces where the carbonate associates hydrophobically. Considerable micellar water remains after adsorption to permit rapid hydrolysis. The binding is represented schematically in Figure 2.

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(14) Wasik, S. P.; Hubbard, W. D. *J. Res. Natl. Bur. Stand., Sec. A* **1964**, *68*, 3590. Runs were carried out at 50.0 °C, but the CMC varies only slightly with temperature: Flockhart, B. D. *J. Colloid Sci.* **1957**, *12*, 557.

(15) Mukerjee, P. *J. Phys. Chem.* **1962**, *66*, 943.

(16) Hartley, G. S. *Trans. Faraday Soc.* **1935**, *31*, 31.

(17) Bunton, C. A.; Minch, M. J. *J. Phys. Chem.* **1974**, *78*, 1490.

(18) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975; pp 92–96.

(19) Fendler, J. H.; Liechti, R. R. *J. Chem. Soc., Perkin Trans. 2*, **1972**, 1041.

(20) Menger, F. M.; Boyer, B. *J. Am. Chem. Soc.* **1980**, *102*, 5936.

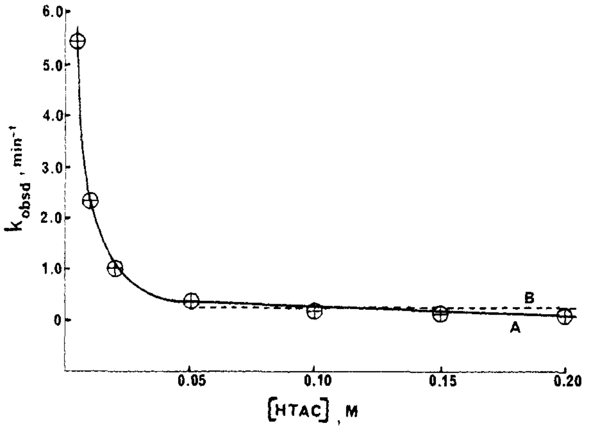
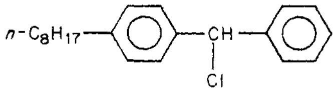


Figure 3. (A) Plot of k_{obsd} at 25.0 °C for solvolysis of *p*-chlorobenzhydryl chloride in HTAC micelles vs. HTAC concentration. (B) Plot of k_{obsd} at 25.0 °C for solvolysis of *p*-octylbenzhydryl chloride in HTAC micelles vs. HTAC concentration.

Benzhydryl Chloride Solvolysis. Solvolysis of *p*-chlorobenzhydryl chloride represents an entirely different type of first-order reaction; its mechanistic simplicity also facilitates micellar investigations. The water-insoluble substrate does not measurably partition from heptane into water. Since the chloride solvolyzes 10^4 times faster in 30% dioxane–water than in 80% dioxane–water (Table II, entries 1–4), the reaction can be used as a sensitive environmental probe. Salt effects on the solvolysis in 30% dioxane (entries 5–10) are relatively small and vary in sign with the salt. Hexadecyltrimethylammonium chloride (HTAC) progressively inhibits the solvolysis with increasing concentration (entries 11–17). This is shown graphically in Figure 3A. The micellar reaction is pH independent (entries 18–19) and manifests a negative salt effect with both sodium chloride and sodium sulfate (entries 20–23).

Quantitative analysis of the micellar solvolysis (as accomplished above for the carbonate reaction) is not feasible owing to an interesting dilemma. Since the bulk water rate greatly exceeds the micellar rate ($k_1 \gg k_2$ in eq 2), a double-reciprocal plot based on eq 2 cannot generate k_2. In effect, the kinetic probe is *too* sensitive to the environment. We can extract k_2 from the kinetic data only by assuming that the rate vs. [HTAC] plot in Figure 3 gravitates toward a finite k_2 as saturation is approached. The following observations support this assumption. (1) Adding 30% dioxane to the HTAC system has only a small effect on the solvolysis rate (compare entries 17 and 24). If k_{obsd} = 0.076 min^{-1} at 0.20 M HTAC represented material reacting *outside* the micelle, then the dioxane should have elevated the rate substantially by solubilizing additional substrate into the bulk medium. A similar insensitivity was observed for the micellar reaction toward 10–30% acetonitrile. (2) *p*-Octylbenzhydryl chloride has



a solvolysis rate which is independent of surfactant in the range of 0.05–0.20 M HTAC (Figure 3B). The compound is totally micellized and displays a k_2 of 0.3 min^{-1}. Judging qualitatively from Figure 3A, the *p*-chloro analogue has a k_2 an order of magnitude smaller than 0.3 min^{-1} (a reasonable value when alkyl vs. chlorine substituent effects are considered).

Although we are unable to define precisely the k_2 for *p*-chlorobenzhydryl chloride, the estimated value of 0.01–0.04 min^{-1} yields useful information. Micellar adsorption subjects the solvolyses to two major environmental changes: a decrease in medium polarity and a high concentration of cationic head groups. Both elevate the energy of the transition state, leading to the carbonium ion intermediate. If we assume that the rate reduction observed in HTAC micelles stems solely from a polarity effect, then k_2 = 0.01–0.04 min^{-1} corresponds to a polarity equivalent to about 60% dioxane (Table II, entries 1–4). In actual fact, the cationic head groups undoubtedly do electrostatically destabilize the transition state. This means that the polarity at the binding sites of the substrate must correspond to a water–dioxane mixture containing considerably *less* than 60% dioxane. In other words, *p*-chlorobenzhydryl chloride (a compound which does not observably partition from heptane into water) preferentially binds to highly aqueous regions of the micelles. Kinetic data from the bis(4-nitrophenyl) carbonate hydrolysis led, of course, to the same conclusion: water-insoluble compounds are surrounded by water inside micelles.

Our "porous cluster" micelle model consists of an outer Stern region and an inner hydrocarbon-like nucleus. The Stern region (comprising well over half the micellar volume) contains ionic head groups, counterions, and water. Water solvates *both* the ions and the chain sections that happen to reside in the Stern region. Solvation of the chains seems no more objectionable than dissolution and hydration of monomeric hexanoate in water. The point is that water *must* fill the spaces which necessarily exist between the chains. When a micelle encounters a hydrophobic guest (such as one of our kinetic probes), the guest enters and displaces water. This is nothing more than hydrophobic association. Contrast the above rationale with one invoking the Hartley micelle. Carbonate and the benzhydryl chloride would have to adsorb, inexplicably, into the Stern layer resembling a concentrated salt solution.

We have referenced above a forceful almost beligerent, opposition to the Menger micelle in favor of the classical Hartley model.[9] Even more recently, Franses et al.[21] *defined* a micelle as "closed". By "closed" they meant that a "closed connected surface can be constructed such that all the hydrophilic surfactant moieties lie on the same side of the surface and all the lipophilic moieties lie on the other side." If one accepts this definition, then in our opinion the aggregates formed by simple surfactants in water are *not* micelles. This is because evidence is amassing from a variety of techniques (kinetics, ^{13}C NMR,[6] gas solubility,[7] ORD,[20] molecular models,[5] etc.) that surfactant aggregates are porous, that water penetrates *into* the micelles to fill the spaces, and that the surfactant monomers are arranged much more randomly than the Hartley micelle implies.

Experimental Section

Materials. Bis(4-nitrophenyl) carbonate was prepared by the method of Fife and McMahon.[22] The carbonate, crystallized twice from benzene, melted at 139–141 °C (lit.[18] mp 138–140 °C). Alkaline hydrolysis of the material produced 2 molar equiv of *p*-nitrophenoxide. Hexadecyltrimethylammonium chloride (Eastman) was crystallized two times from methanol–ether and dried overnight at 80 °C under reduced pressure. Hexadecyltrimethylammonium bromide (Aldrich cetyltrimethylammonium bromide) was crystallized repeatedly from acetone and dried in a vacuum desiccator. *p*-Chlorobenzhydryl chloride, prepared by the method of Nishida,[23] was distilled twice at 1.0 mm (bp 133–135

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[21] Franses, E. I.; Davis, H. T.; Miller, W. G.; Scriven, L. E. *J. Phys. Chem.* **1980**, *84*, 2413.

[22] Fife, T. H.; McMahon, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 7481.

°C). Dioxane was distilled over $LiAlH_4$ immediately prior to use.

The following three paragraphs describe the synthesis of *p*-octylbenzhydryl chloride. A 250-mL three-necked flask containing 14.7 g (0.11 mol) of $AlCl_3$ and 38 mL of carbon disulfide was fitted with a reflux condenser and dropping funnel. A mixture of 19.0 g (0.10 mol) of *p*-octylbenzene and 15.5 g (0.11 mol) of benzoyl chloride in 38 mL of carbon disulfide was added dropwise to the $AlCl_3$ over 90 min with magnetic stirring followed by boiling under reflux for 12 h. The solvent was removed, the residue poured into 250 mL of ice water with stirring, and the organic layer taken up in two 100-mL portions of benzene. After drying the benzene with $MgSO_4$, we removed the solvent and distilled the residue under reduced pressure to give 26.2 g (89% yield) of *p*-octylbenzophenone with the expected spectral properties.

p-Octylbenzophenone (2.62 g, 0.0089 mol), 1.75 g of NaOH, 1.75 g of zinc dust, and 70 mL of 95% ethanol were placed in a 250-mL round-bottomed flask and refluxed for 3 h with stirring. The reaction mixture was cooled and filtered; the filtrate (combined with an ethanol wash) was poured into 500 mL of ice water containing 25 mL of HCl. A benzene extraction (2 × 100 mL) followed by drying of the benzene layer over $MgSO_4$, removal of the solvent, and distillation of the residue at 0.6 mm gave 2.30 g (87% yield) of *p*-octylbenzhydrol (bp 185–186 °C).

p-Octylbenzhydrol (2.30 g, 0.0078 mol) in 70 mL of benzene was subjected to a slow stream of HCl gas while the solution was magnetically stirred over 3.0 g of $MgSO_4$. The mixture was filtered and the benzene removed from the filtrate with the aid of a rotary evaporator. The residue was then chromatographed on a silica column (2 × 35 cm), using pure benzene as the eluant, to give 2.4 g (98% yield) of *p*-octylbenzhydryl chloride. No hydroxyl or carbonyl was evident in the IR spectrum.

Anal. Calcd for $C_{21}H_{27}Cl$: C, 80.0; H, 8.64. Found. C, 80.40; H, 8.89.

Kinetics. Hydrolysis rates of bis(4-nitrophenyl) carbonate were determined by following the appearance of *p*-nitrophenol at 320 nm, using an Acta II spectrophotometer thermostated at 50.0 ± 0.1 °C and set at the 0–0.1 absorbance range. A 3.00-mL aqueous HTAB solution containing 0.01 N HBr (assayed titrimetically) was equilibrated in the cell chamber for greater than 15 min. Reaction was then initiated by adding 20 μL of a concentrated solution of the carbonate in acetonitrile with the aid of a small stirring rod. Concentrations of substrate in the cuvette were approximately 3×10^{-5} M. We followed the reaction to greater than 80% completion and took infinity values at 10 half-lives. First-order rate constants, calculated in the usual manner, were reproducible to within 3% in most cases. Since the rate changes in Table I are small, each run was carried out 3–5 times and the rate constants averaged.

Solvolysis of *p*-chlorobenzhydryl chloride was carried out in much the same manner by following the decrease in absorbance at 245 nm at 25.0 °C.

Acknowledgment. This work was supported by the National Science Foundation, National Institutes of Health, and Petroleum Research Foundation. We also appreciate greatly the collaboration of Professor Junzo Sunamoto, Nagasaki University, whose student (H.Y.) spent a year in these laboratories on an exchange program.

Registry No. Bis(4-nitrophenyl) carbonate, 5070-13-3; *p*-chlorobenzhydryl chloride, 134-83-8; octylbenzene, 2189-60-8; benzoyl chloride, 98-88-4; *p*-octylbenzophenone, 64357-43-3; *p*-octylbenzhydrol, 75812-79-2; *p*-chlorobenzhydryl chloride, 75812-80-5.

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[23] Nishida, S. *J. Org. Chem.* **1967**, *32*, 2692.

Acetal Hydrolysis: The A1 Mechanism[1]

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Received August 13, 1980

The hydrolysis of 5-methyl-7-*exo*-methyl-6,8-dioxabicyclo[3.2.1]octane (**1**) shows no general acid catalysis, with the caveat that general acid catalysis with a Brønsted $\alpha > 0.7$ would probably have escaped detection; k_H/k_D is 0.43; it is not catalyzed by I^-. The rate constant and isotope effect for the H^+-catalyzed hydrolysis of **1** are similar to those for 2-methyl-2-(2-methypropyl)-1,3-dioxolane (**2**) even though, in **1**, steric inhibition to carbon–oxygen cleavage concerted with proton transfer should lead that step to be rate determining if a concerted mechanism were to be used. In fact, both **1** and **2** appear to hydrolyze by a nonconcerted mechanism. Since they are unexceptional acetals, it appears that the concerted mechanism is limited to cases where the A1 mechanism encounters special difficulties and/or the concerted mechanism is especially favorable.

Prior to the late 1960's, general acid catalysis has not been conclusively demonstrated for the hydrolysis of acetals. Ortho esters, on the other hand, were known to be subject to buffer catalysis for quite some time.[2] Due to the structural similarity of these compounds, a considerable amount of effort went into putting their hydrolyses into the same mechanistic scheme. Interest in the mechanism of catalysis by the enzyme lysozyme[3] also led to a search for structural features that would give rise to general acid catalysis in acetal hydrolysis. Considering the accepted A1 mechanism for acetal hydrolysis (eq 1–3), the likeliest modification leading to buffer catalysis would involve coupling of proton transfer and carbon–oxygen cleavage into a single concerted process.[4,5] In this paper the terms "concerted process" and "concerted mechanism" refer to the mechanism ascribed to ortho ester hydrolysis by Eliason and Kreevoy,[4] possibly modified by the admixture of a little hydrogenic motion to the reaction co-

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[1] This work was supported in part by the U.S. National Science Foundation through Grants CHE76-01181 and CHE79-25990. We are also grateful to Professor J. L. Jensen of Long Beach State University for very helpful comments on the manuscript.

[2] For recent reviews see: (a) Cordes, E. H.; Bull, H. G. *Chem. Rev.* **1974**, *74*, 581–603; (b) Fife, T. H. *Acc. Chem. Res.* **1972**, *5*, 264–272 and references contained therein.

[3] Dunn, B. M.; Bruice, T. C. *Adv. Enzymol.* **1973**, *37*, 1–60.

[4] Eliason, R.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 7037–7041.

[5] Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705–718.