Irradiation of Cholan-24-yl 5-(*p*-Benzoyl)phenylpentanoate (V). Irradiation of 475 mg (0.78 mmol) of this ester in 900 ml of benzene for 2 hr and standard work-up (lead tetraacetate, hydrolysis, chromatography) afforded 48 mg (17%) of cholan-24-ol and 59 mg (22%) of chol-14-en-ol (XX). A similar irradiation of 1.150 g (1.72 mmol) of this ester in 1800 ml of benzene and oxidative work-up (acetylation, dehydration, and ruthenium tetroxide oxidation, as in the case of the irradiation of the cholestan-3α-yl propionate ester in carbon tetrachloride) afforded 51 mg (8%) of cholan-24-ol-15-one (XXI).

Control Irradiations. Irradiation under our standard conditions of 602 mg (3.32 mmol) of resublimed benzophenone in 150 ml of 1,1,2-trichlorotrifluoroethane for 15.5 hr caused the disappearance of *ca.* 50% of the benzophenone carbonyl chromophore.

Benzophenone (612 mg, 3.40 mmol) and 3α-cholestanyl acetate (594 mg, 1.40 mmol) in 150 ml of 1,1,2-trichlorotrifluoroethane were irradiated for 12 hr. Roughly half of the benzophenone carbonyl chromophore had disappeared at this time. Lead tetraacetate oxidation, base hydrolysis, and silver nitrate–silica gel chromatography afforded 41 mg of steroidal olefin alcohol. Nmr analysis of this material showed it to be a 1:2 mixture of the cholest-9(11)-en-3α-ol and cholest-14-en-3α-ol (XVI) in a yield of 7.7%.

Irradiation of a 10^{-3} *M* benzene solution of 3α-cholestanyl acetate also 10^{-3} *M* in benzophenone or methyl *p*-benzoylbenzoate brought about rapid (2 hr) disappearance of the benzophenone carbonyl chromophore but no detectable modification of the steroid component.

Preparative Irradiation of 5α-Cholestan-3α-yl (*p*-Benzoyl)phenylacetate (Ib). Irradiation of a combined total of 11.296 g (18.5 mmol) of the ester in three equal batches each in 5.0 l. of benzene, each for 10 hr, and base hydrolysis of the combined photoproduct mixture afforded 4.911 g of neutral steroid mixture and 6.041 g of acidic material, chiefly, benzhydrol-4-acetic acid. The nmr of the neutral material contained no aromatic signals, and indicated a mixture of 5α-cholestan-3α-ol and 5α-cholest-14-en-3α-ol. Chromatography of the mixture on 20% silver nitrate–silica gel afforded 1.549 g of 5α-cholestan-3α-ol and 2.483 g (44% isolated yield) of 5α-cholest-14-en-3α-ol (XVI).

Phosphorescence Lifetimes.[1b] All esters were given a final purification by passage through an alumina column, eluted with carbon tetrachloride. The solvent, 1,1,2-trichlorotrifluoroethane, was distilled and passed through an alumina column. All glassware was cleaned with chromic acid, then 10% sodium hydroxide solution, and finally rinsed 4 times with distilled water and dried at 50° in a stream of nitrogen. Benzophenone, methyl *p*-benzoylbenzoate, and 3α-cholestanyl acetate were further purified by sublimation.

The 5-ml samples in Pyrex tubes were degassed by 8–11 cycles of the freeze–pump–thaw routine and sealed frozen under vacuum. The flash was a Xenon Corp. nanolamp with a decay lifetime of 5 μsec under the conditions used. The lamp light was filtered free of visible light and the phototube filters removed light of $\lambda < 480$ nm. The fast-rise-time oscilloscope was self-triggered by the signal and this signal recorded using a polaroid camera. Emission spectra from the same samples were obtained on a Hitachi spectrophosphorimeter with excitation at 350 nm.

Circular Dichroism Spectra. The spectra were recorded on a Cary Model 60 instrument with each component at 10^{-3} *M* in purified solvents. The instrument calibration was checked with 5α-cholestan-3-one in dioxane, $\Delta\epsilon$ +1.095 at 280 nm (lit.[42] $\Delta\epsilon$ +1.132 at 280 nm). Temperature control was accomplished using a jacketed 1-cm cell through the jacket of which was circulated methanol from a thermostatic bath and pump with electronic-temperature controller.

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Electrolyte Effects on the Cationic Micelle Catalyzed Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate Anion[1,2]

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Abstract: The unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion is strongly catalyzed by micelles of cationic and nonionic surfactants. The catalysis by cationic micelles can be enhanced by adding some electrolytes or nonionic surfactants or by using dicationic surfactants, indicating that the catalysis is sensitive to changes in micellar structure and charge density. The mode of incorporation of aromatic sulfonate and carboxylate anions into cationic micelles has been investigated by nmr spectroscopy and by electrochemical and viscosity measurements, and the effects of such incorporated anions on micellar catalysis and structure are discussed. It appears that the anions insert into the micelle with the aryl groups fitting between the ammonium head groups of the surfactant.

Micellar catalysis is observed when reactants are taken into the micellar pseudophase and there have a greater reactivity than in the bulk solution.[5–10] Analogies between enzyme and micellar catalysis have been widely discussed,[6–10] but are discounted[8] because micellar catalysis generally lacks the substrate specificity and high catalytic activity of enzymes. Reactions occurring on micelles are akin to those occurring on lipid–protein interfaces, especially because micelles, like lipid bilayers, are easily structurally altered by

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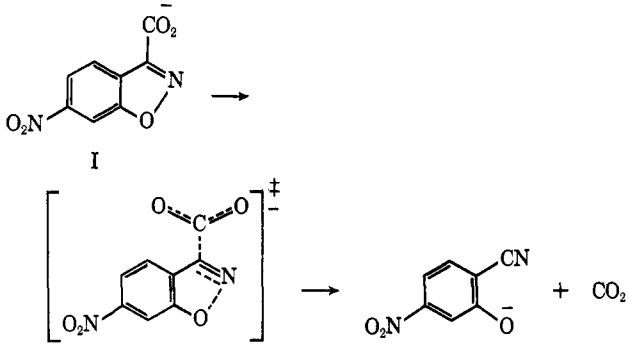
added solutes,[11-15] with changes in reaction rate. Because these structural modifications alter the reactivity of adsorbed substrates, they may serve a biochemical regulatory role.

Micelle-catalyzed reactions as models for electrostatic and hydrophobic interaction in biological systems should provide information regarding the mechanism of regulation of reactions occurring on membranes because micelles are structurally simpler and more easily modified than complex biological interfaces. For this purpose, it is desirable to use a unimolecular rather than a bimolecular reaction to avoid complications due to the incorporation of more than one reactant into the micelle.

Few unimolecular micellar-catalyzed reactions have been examined, but the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion (I) is strongly catalyzed by cationic and nonionic micelles,[16] and unexpectedly, the catalysis by cationic micelles is enhanced by some added electrolytes.[17] Some salts speed the decarboxylation of 2-phenyl-2-cyanoacetate ion in cationic detergents, but only salts which absorb weakly at 235 nm could be studied.[18] These salt enhancements of micellar-catalyzed reactions are significant exceptions to the generalization that added salts always inhibit micellar catalysis by excluding ionic reagents from the



I

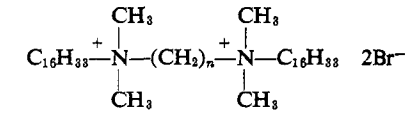
micellar pseudophase and increasing the aggregation number of the micelle.[6,7,9] For this reason, and also because the decarboxylation of I has a very large solvent effect,[19] we have studied its micelle-catalyzed decarboxylation using several surfactants and in the presence of a wide variety of salts and organic additives to determine the relation between reaction rate and micellar structure. Electrochemical and viscosity measurements and nmr spectral evidence also reveal the effects of additives on the micelle–solute interactions. The nmr spectral evidence will be treated in greater detail in a later paper.

The decarboxylation of I provides a simple chemical model for biologically important decarboxylations[19,20] because it is unimolecular and is not catalyzed by acids or bases.

Experimental Section

Materials. The methyl ester of 6-nitrobenzisoxazole-3-carboxylic acid was prepared by the reaction of methyl 2,4-dinitrophenylacetate with NaOMe and isoamyl nitrite in MeOH,[21] and was recrystallized from methanol. 6-Nitrobenzisoxazole-3-carboxylic acid was prepared by heating the methyl ester in slightly aqueous sulfuric acid on a steam bath for 20 min and then pouring the reaction mixture onto ice.[22] The white crystals, after drying *in vacuo* over P_2O_5, had mp 167–169° [lit.[22] 167–169° (monohydrate)].

The preparation and purification of cetyltrimethylammonium bromide (CTABr),[5] sodium lauryl sulfate (NaLS),[5] and the dicationic detergents (IIa, b) have been described.[23] *N*-Cetylpyridinium



IIa, $n = 4$
b, $n = 6$

bromide was prepared from pyridine and 1-bromohexadecane[24] and was recrystallized three times from EtOH–petroleum ether, mp 64–67° (lit.[24] 56–59°), and had the predicted nmr spectrum.

All samples of CTABr were repurified until they gave the same concentration–surface tension profile. The nonionic detergent Igepal DM-730, a poly(oxyethylene(24)–nonylphenol), and bis(2-ethoxyethyl) ether were used without further purification. Sodium tosylate (NaOTos), benzenesulfonate, and 2-naphthalenesulfonate were recrystallized from alcohol and dried under reduced pressure. Sodium *p*-isopropylbenzenesulfonate, *p-tert*-butylbenzenesulfonate, and *p*-phenylbenzenesulfonate were made by sulfonation of the parent hydrocarbon with sulfuric acid, followed by neutralization in concentrated NaOH–NaCl solution.[25] Recrystallization from EtOH gave products with the predicted nmr spectra. Sodium *p*-trifluoromethylbenzenesulfonate was prepared following the method of Yale and Sowinski;[26] nmr and ir spectra were consistent with the assigned structure.

Viscosity Measurements. The viscosities were measured at 25° using Ostwald viscometers, which were calibrated using water (for flow times > 50 sec) or sucrose solutions. The flow times for water varied between 58 and 0.5 sec (the viscometers with the longer flow times were used for CTABr solutions of low viscosity).

The flow was Newtonian except for the most viscous solutions containing sodium toluate, tosylate, and *p*-isopropylbenzenesulfonate. Our data for these solutions are merely comparative and refer only to the conditions used. The whole range of concentrations of CTABr and sodium *p*-isopropylbenzenesulfonate could not be examined because, under some conditions, fine crystals of CTA^+-p-$C_3H_7C_6H_4SO_3^-$ separated out when the concentrations of surfactant and added salt were similar.

Conductivity. The conductivities were measured at 25° using a Wayne Kerr B 221 bridge. Two conductivity cells with constants of 5.85 and 0.1 cm^{-1} were used.

Transport Numbers. The transport numbers for mixtures of CTABr and sodium tosylate were determined at 25° using a cell with compartments divided by a porous disk; general methods were followed.[27] A current of 0.8–1.3 mA was used for 3–4 hr, and the concentrations of tosylate ion in the two compartments were measured spectrophotometrically (using extinction coefficients of tosylate ion in the presence of CTABr), and those of CTA^+ by the usual dichromate method.[28]

Kinetics. The reaction at 25.0 ± 0.1° was followed spectro-

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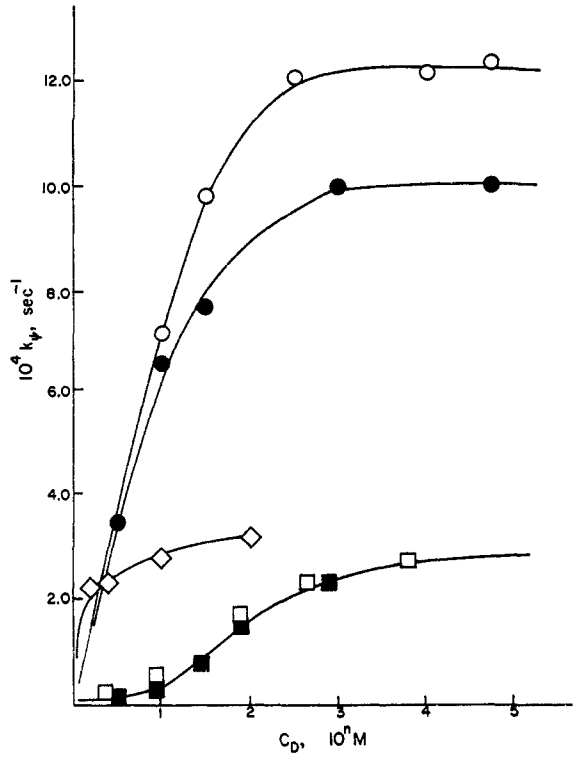

Figure 1. Micellar catalysis of the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate at 25.0°: (□) CTABr in 0.002 *M* NaOH, $n = 3$; (■) CTABr in 0.002 NH_3 buffer (pH 9), $n = 3$; (◇) *N*-cetylpyridinium bromide in 0.002 *M* NH_3 buffer, $n = 2$; dicationic surfactants IIb (●) and IIc (○) in 0.002 *M* NH_3, $n = 4$.

photometrically at 410 nm using a Gilford spectrophotometer with a water-jacketed cell compartment. At higher temperatures, we used a Cary 11 recording spectrometer with a water-jacketed cell compartment. The integrated first-order rate constants, k_ψ, were calculated graphically with linear plots for up to 3 half-lives. The substrate concentration was varied from 1 to 5 × 10^{-4} *M* with only a small change in first-order rate constant, but generally we used 1–2 × 10^{-4} *M* substrate. The substrate was added as an aliquot of stock solution (usually 50 μl). Two buffers were used: a 0.002 *M* NaOH solution (pH 11.1–11.2) and a 0.002 *M* HCl solution containing enough NH_3 to give a pH of 8.9. Both solutions were stored in air-tight polyethylene containers. Distilled deionized water was used throughout. Changes in the buffer did not markedly change the first-order rate constant, k_ψ (sec^{-1}).

Nmr Spectra. Changes in the nmr spectra of mixtures of CTABr with various sodium arenesulfonates and arenecarboxylates in 90% (v/v) D_2O–H_2O were determined as a function of relative concentrations on an HA-100 nmr spectrometer (probe temperature 31 ± 1°). The concentration of organic salts and surfactant was low (<0.03 *M*), and for some solutions a Varian 1024 channel computer of average transients was used. The HA-100 was locked on water (frequency sweep mode), and all chemical shifts (relative to water) for any one series of samples were recorded as close together in time as possible to avoid changes in the chemical shift of water resulting from temperature fluctuations; for the same reason, the lock was maintained continuously throughout any one series of samples. The reproducibility of chemical shifts was within 0.01 ppm.

Changes in the chemical shift of the ortho and meta protons of NaOTos in D_2O–acetonitrile and D_2O–dioxane mixtures, as the concentration of the organic solvent component was increased, were determined at 50-Hz sweep width on a Varian T-60 nmr spectrometer. The deviation between duplicate measurements was 0.05 ppm.

Results

Kinetics in Various Surfactants. The decarboxylation of I is catalyzed by both cationic and nonionic micelles.[16] Plots of k_ψ against surfactant concentration, C_D, give plateaux for concentrations of cationic detergents well above their critical micelle concentrations (cmc)[23] (Figure 1) rather than the rate maxima generally observed for ion–molecule reactions. These plateaux appear to be typical of micellar catalyzed spontaneous reactions.[29–31]

The value of $k_\psi = 2.95 \times 10^{-4}$ sec^{-1} for reaction in the presence of CTABr is constant for surfactant concentrations up to 2 × 10^{-2} *M*. The maximum catalysis by CTABr is 95-fold; by *N*-cetylpyridinium bromide, 100-fold; and the dicationic detergents (IIa and IIb) give 330- and 400-fold catalysis, respectively, at 25°. The nonionic detergent Igepal gives a reaction rate *vs.* concentration profile which rises at all concentrations examined; the maximum observed catalysis is 65-fold at 0.10 *M* Igepal.[16] Mixtures of CTABr and Igepal are better catalysts than either alone, but Igepal–IIb mixtures are poorer catalysts than the dicationic surfactant alone (Table I). Micelles of dicationic surfactants are typically better catalysts than monocationic surfactants of the same chain length[23] (Figure 1), probably because aggregation is assisted by linkage between the cationic head groups so that micellar incorporation of initial and transition states is more effective.

Table I. Rates in Mixed Micelles of Igepal–CTABr and IIb–Igepal[a]

$10^2 C_{Igepal}$, *M*	$10^2 C_{CTABr}$, *M*	$10^4 C_{IIb}$, *M*	$10^4 k_\psi$, sec^{-1}
0.00	1.95		2.95
0.15	1.95		3.16
0.17	1.95		3.18
0.18	1.95		3.37
0.24	1.95		3.59
0.30	1.95		3.25
0.76	1.95		3.72
0.98	1.95		3.53
1.02	1.95		3.42
5.06	1.95		3.71
2.70	0.0143		1.06
2.70	0.0572		1.41
2.70	0.143		2.08
2.70	0.285		3.72
2.70	0.475		4.17
0.27	0.474		2.86
0.54	0.951		3.35
0.68	1.19		3.25
1.35	2.37		3.53
0.00		8.0	15.7
0.03		8.0	14.2
0.07		8.0	13.4
0.19		8.0	12.3
0.95		8.0	14.0
1.11		8.0	7.04

[a] Rate constants in 0.002 *M* NH_4^+–NH_3 buffer (pH 9) at 25°; IIb is 1,6-bis(*N*-cetyl-*N*,*N*-dimethylamino)hexane dibromide.

The Arrhenius plots are linear for both the spontaneous reaction and that in CTABr in 0.01 *M* NH_4^+–NH_3 buffer, pH 9.4. The rate constants, $10^6 k_\psi$ (sec^{-1}), for the spontaneous reactions at 25.0, 50.1, and 68.0° are 3.0, 18.0, and 220, respectively, and the rate constants, 10^4 k_ψ (sec^{-1}), for reaction in 0.017 *M* CTABr

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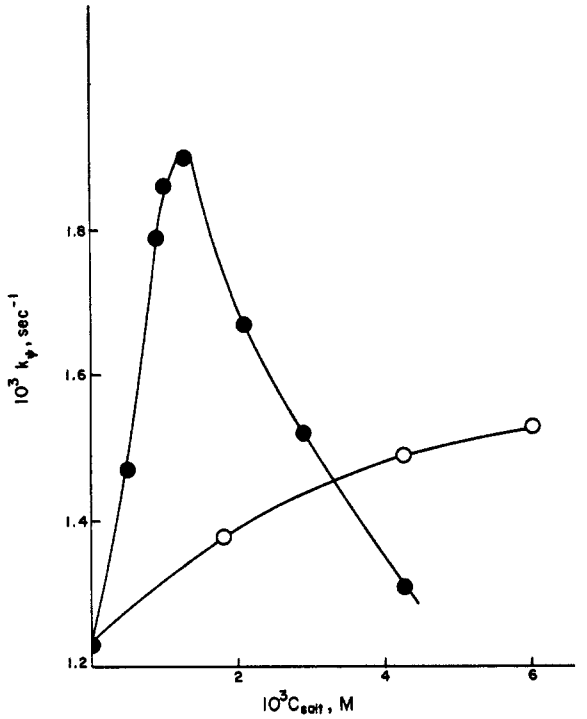

Figure 2. The effect of NaOTos (●) and Na_2SO_4 (○) on the micellar catalysis by 4.0×10^{-4} *M* IIb in 0.002 *M* NH_3 buffer (pH 9), 25.0°.

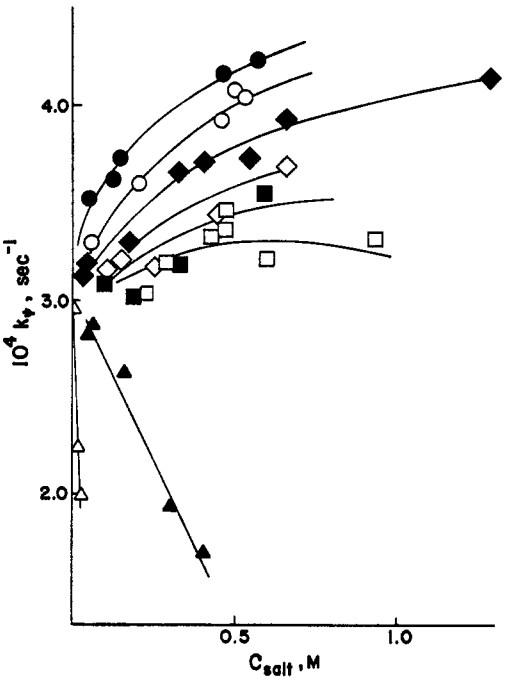

Figure 3. The effect of salts on the catalysis by 2×10^{-2} *M* CTABr in 0.002 *M* NH_3 buffer, 25°: (●) Na_2SO_4; (○) NaBr; (◆) MCl (M = Li, Na, Me_4N); (◇) NaF; (■) NaOAc; (□) NaOH; (▲) sodium pivalate; (△) NaCNS.

at 24.9, 34.6, 39.9, 44.3, and 54.3° are 3.87, 10.6, 20.3, 35.0, and 100, respectively (the difference between this value at 24.9° and that given in Table I is caused by differences in the buffer concentration). The rate increase in the presence of CTABr micelles is the net result of a decrease in $\Delta H^{\ddagger}$ (29.4 for the uncatalyzed and 21.3 kcal mol^{-1} for the catalyzed reaction) and a decrease in $\Delta S^{\ddagger}$ from 15 eu for the uncatalyzed to −2.7 eu for the catalyzed reactions. This result is similar to the decrease in both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the CTABr micelle-catalyzed decarboxylation of 2-cyanophenylacetic acid,[18] and is readily understandable in terms of the interactions of the initial and transition states with the micelles. The reaction rate is unaffected by anionic micelles of NaLS (Table II).

Table II. Effect of Salts and Anionic Surfactant in the Absence of Cationic Surfactant[a]

Sodium salt	$10^2 C_s$, *M*	$10^5 k_\psi$, sec^{-1}
		3.0
Lauryl sulfate	1.3	3.0
Lauryl sulfate	2.3	3.0
Benzoate	4.9	2.8
Benzoate	12.5	2.9
Sulfate	28.2	3.0
Chloride	38.8	3.0

[a] At 25.0° in aqueous solution with 0.002 *M* NH_3 buffer, pH 9.

Kinetic Salt Effects. The rate in the absence of surfactants is insensitive to added electrolytes[19] (Table II), and that in CTABr is relatively insensitive to changes in pH and buffer, provided that the substrate is fully ionized and the buffer concentration is low ($\leq$0.002 *M*) (Table III). However, the micellar-catalyzed process is profoundly influenced by higher concentrations of

Table III. Effect of CTABr upon the Decarboxylation[a]

$10^4 C_D$, *M*	$10^4 C_{substrate}$, *M*	$10^5 k_\psi$, sec^{-1}
	1.0	0.30
4.75	0.5	1.47
9.51	0.5	3.32
14.2	0.5	7.67
19.0	0.5	15.1
28.6	0.5	24.1
195	1.0	29.5
3.60[b]	3.0	1.37
7.61[b]	1.5	3.58
9.51[b]	1.5	7.3
19.0[b]	1.5	18
26.6[b]	1.0	23.3
38.0[b]	1.0	27.2
95.1[b]	1.0	27.2
190[b]	1.0	27.0

[a] At 25.0° and in 0.002 *M* NH_3 buffer (pH 9) unless specified. [b] In 0.002 *M* NaOH (pH 11.1).

electrolytes. Addition of most simple hydrophilic salts to CTABr and IIb (Figures 2 and 3) speeds the reaction at all concentrations, the only exceptions being sodium thiocyanate which retards the CTABr catalyzed reaction.[32] The choice of cation is not critical because the rate increases by tetramethylammonium, sodium and lithium chloride are the same. The choice of anion is all important; for CTABr catalysis, the rate enhancements are in the order $CNS^- <$ pivalate < no salt < $OH^- < AcO^- \approx F^- < Cl^- < Br^- < SO_4^{2-}$ (Figure 3). The more hydrophobic sodium salts of aliphatic carboxylic acids have no large effect on the CTABr catalysis (Table IV), sodium butyrate slightly increas-

(32) Solutions of CTABr containing less than 1 equiv of NaCNS are very viscous and precipitation occurs with higher NaCNS concentrations. The CNS^- anion apparently reorganizes the cationic micelle differently than other inorganic anions examined, even at concentrations well below the solubility limit.

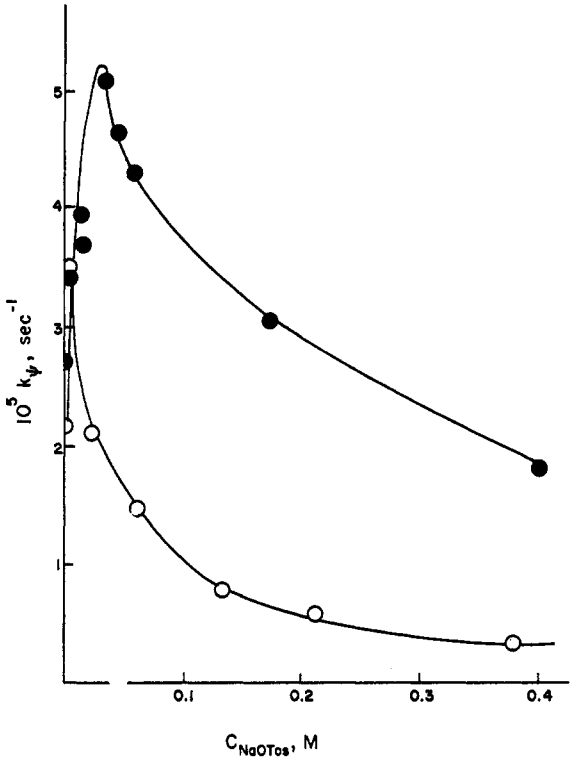

Figure 4. The effect of NaOTos on the catalysis by CTABr in 0.002 M NH_3 buffer, 25°: (○) 2.4 × 10^{-3} M CTABr; (●) 1.9 × 10^{-2} M CTABr.

Table IV. Effect of Aliphatic Carboxylate Anions on the CTABr Catalyzed Reaction[a]

Sodium salt	$10^2 C_{salt}$, M	$10^4 k_\psi$, sec^{-1}
		2.95
Acetate	9.9	3.09
	18.2	3.01
	32.8	3.18
	58.5	3.55
n-Butyrate	3.4	3.10
	4.3	3.19
	7.9	3.10
	16.2	3.16
Phenylacetate	1.4	3.01
	1.8	3.03
	4.9	2.94
	9.5	3.06
Pivalate	0.4	3.18
	4.4	2.83
	5.9	2.89
	15.7	2.63
	29.9	1.94
	40.6	1.71

[a] At 25.0° in aqueous 2 × 10^{-2} M CTABr, pH 9.0; in the absence of surfactant $10^6 k_\psi$ = 3.0 sec^{-1}.

ing, phenylacetate having little effect, and pivalate slightly decreasing catalysis. Such hydrophobic anions as arenesulfonates, arenecarboxylates, and aryl phosphates give marked enhancements at low concentrations, but there is a rate maximum peculiar to each anion, and at higher concentrations the rate is less than that in the presence of surfactant alone (Table V and Figure 4). The anion concentration corresponding to the rate maximum depends upon both the concentration of the cationic surfactant and the structure of the anion, but the maximum is generally observed when the

Table V. Effect of Aromatic Hydrophobic Anions on the CTABr Catalyzed Reaction[a]

Sodium salt	$10^2 C_{salt}$, M	$10^4 k_\psi$, sec^{-1}
		2.95
$C_6H_5CO_2^-$	0.7	2.88
	1.8	3.00
	6.7	3.33
	8.4	3.28
	29.1	1.68
	52.1	0.78
$C_6H_5SO_3^-$	0.8	3.08
	1.4	4.42
	1.7	3.15
	2.0	3.33
	2.7	4.53
$C_6H_5PO_4^{2-}$	1.0	4.43
	3.9	4.08
	4.5	4.35
	14.4	4.37
	23.3	4.91
p-$(CH_3)_2CHC_6H_4SO_3^-$	0.2	3.18
	0.4	2.91
	0.6	3.30
	1.3	4.00
p-$CF_3C_6H_4SO_3^-$	0.3	2.22
	0.8	2.38
2-Naphthalenesulfonate	0.17	2.96
	0.34	3.22
	0.55	3.50
	1.11	4.65
	1.52	3.72
	1.66	2.50

[a] At 25.0° in aqueous 2 × 10^{-2} M CTABr, pH 9; the values of k_ψ at higher salt concentrations are given in Figure 4.

concentration of aromatic anion and surfactant are approximately equal (Table V) unless the surfactant concentration is near the cmc, in which case inhibition occurs (Figure 4). Arenesulfonates with para substituents larger than methyl gave such viscous mixtures with CTABr that mixing problems interfered with rate measurements except at very low anion concentrations. For the same reason, rate constants in CTABr–sodium toluate mixtures could not be accurately measured although the rapid formation of yellow product (probably the 2-cyano-4-nitrophenoxide ion) suggests that such mixtures are strongly catalytic.

Addition of the very large hydrophobic salt, sodium cholate, inhibits catalysis even when its concentration is much less than that of CTABr, but the anion of estrone (pH 12.5) has little kinetic effect at such concentrations (Table VI). A neutral steroid, testosterone, also inhibits catalysis even at low concentrations, but smaller neutral organic molecules have little effect. Urea and dioxane retard catalysis only at high concentrations (>0.5 M), and benzene has no effect on the catalysis by CTABr (Table VI).

Viscosity Measurements. The addition of sodium arenecarboxylates and -sulfonates to a solution of CTABr causes a marked increase in viscosity, and enhancements of both rate and viscosity are largest when the concentrations of surfactant and tosylate are approximately equal (Figure 5). (The rate and viscosity were not measured at precisely the same concentration in these experiments). The values of the viscosities, η (centistokes), relative to water, are plotted against salt concentration for 0.02 M CTABr in Figure 6, and the maximum values of η are given in Table VII. Forma-

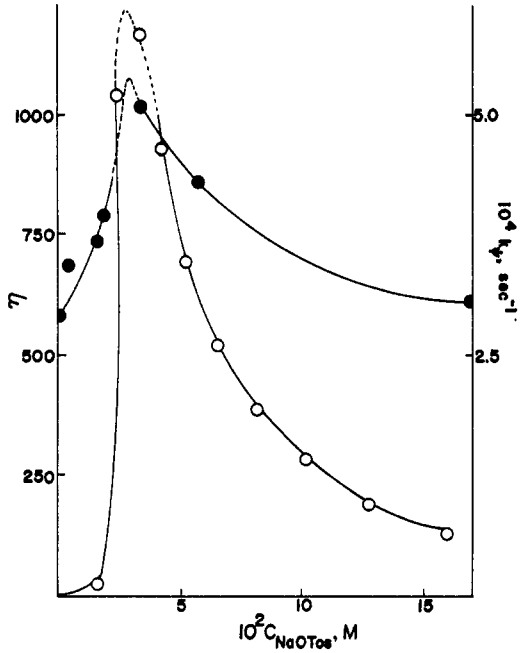

Figure 5. Comparison of the effect of NaOTos on the catalysis by CTABr and on CTABr solution viscosity at 25°: (○) viscosity for 2.5×10^{-2} *M* CTABr; (●) k_ψ in 1.9×10^{-2} *M* CTABr.

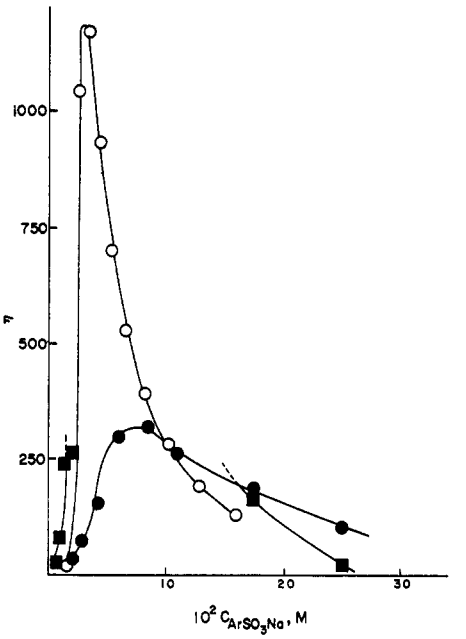

Figure 6. The effect of sodium arenesulfonates on the viscosity of 0.025 *M* CTABr, 25°: (●) $NaC_6H_5SO_3$; (○) NaOTos; (■) Na-*p*-$(CH_3)_2CHC_6H_4SO_3$.

Table VI. Effect of Organic Solutes on the CTABr Catalyzed Reaction[a]

Additive	$10^3C_{additive}$	10^4k_ψ, sec^{-1}
		2.95
Sodium cholate	1.19	2.73
	3.17	2.45
	6.33	1.80
Estrone	4.45	3.43[b]
	6.80	3.15[b]
Testosterone	1.28[c]	2.50
	2.57[c]	2.20
Urea	161	2.84
	321	2.71
	535	2.24
Dioxane	133	3.07
	1785	2.65
	2300	2.20
Benzene	21.1	2.99
	35.7	2.96
	44.7	3.08

[a] At 25° in aqueous 2×10^{-2} *M* CTABr, pH 9 except where specified. [b] At pH 12. [c] With 10 *M* equiv of dioxane to testosterone.

Table VII. Values of Maximum Viscosity in Mixtures of CTABr and Sodium Salts[a]

10^2C_{CTABr}, *M*	$C_6H_5SO_3Na$		*p*-$CH_3C_6H_4$-SO_3Na		*p*-$CH_3C_6H_4$-CO_2Na	
	η_{max}	10^2C_s	η_{max}	10^2C_s	η_{max}	10^2C_s
0.75	3.4	8	33	1.7	25	4.5
1.00	44	8			80	4.7
1.50			127	2.9		
2.50	32	8	1170	3.3	6200	7
4.00			6000	4.2		

[a] Values of η_{max} at 25°.

tion of a 1:1 salt prevented our examining a wide range of concentrations of the *p*-isopropylbenzenesulfonate ion. Added sodium benzoate has little effect on the viscosity of CTABr, and the values in Table VII show the importance of a *p*-methyl group on the viscosity.

Conductivity. When NaOTos is added to a solution of CTABr, the specific conductance, λ, increases linearly with tosylate concentration with an abrupt change of slope when the concentrations of surfactant and tosylate ions are approximately equal. The tosylate concentration at the change of slope is given in Table VIII together with the parameters in eq 1 which relate

Table VIII. Effect of Sodium Tosylate on the Parameters for the Specific Conductivity of CTABr[a]

10^3C_{CTABr}, *M*	*a*	*b*	10^3C_{NaOTos},[d] *M*
1.0	0.104[b]	39.5[b]	0.61
	0.087[c]	65[c]	
5.0	0.26[b]	80[b]	5.2
	0.34[c]	65[c]	
8.0	0.34[b]	86[b]	6.3
	0.47[c]	74[c]	

[a] Parameters defined by the expression $\lambda = a + bC_{NaOTos}$ at 25°. [b] Below the breakpoint. [c] Above the breakpoint. [d] At the breakpoint.

$$\lambda = a + b[\text{NaTos}] \quad (1)$$

λ to tosylate concentration. With 10^{-3} *M* CTABr, the slope of the plot of λ against C_{NaOTos} increases above the break point. For higher concentrations of CTABr, the slope of such plots decreases above the break point. These differences are not surprising because added sodium tosylate may affect the conductivity in a number of different ways; *e.g.*, it could decrease it by increasing the viscosity of the solution and increase it by the addition of ions and by displacing bromide ions from the Stern layer of the micelles of CTABr. These conductivity experiments are merely intended to demonstrate the interactions between CTA and tosylate ions.

Transport Numbers. The transport numbers for

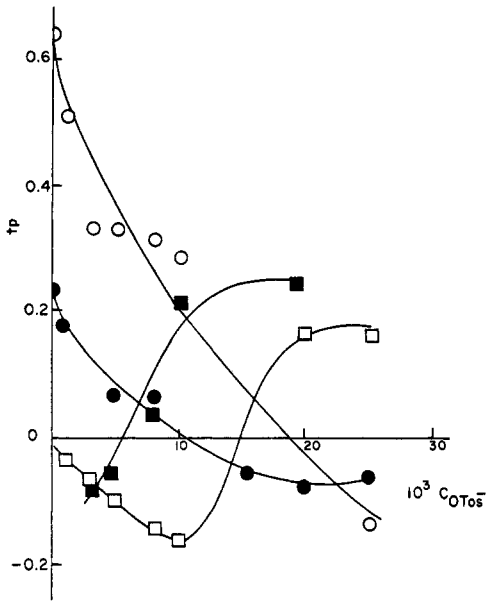

Figure 7. Transport numbers of CTA^+ (circles) and $OTos^-$ (squares) in CTABr–NaOTos mixtures. Solid symbols for 5×10^{-3} *M* CTABr and open symbols for 15×10^{-3} *M* CTABr, 25°.

mixtures of CTABr and NaOTos (Figure 7) show that with excess CTA^+ the tosylate anion is transported to the cathode, whereas, with excess tosylate, the CTA^+ cation is transported to the anode. The actual points are scattered, probably because of diffusion through the porous disk, but the results confirm the conductivity data and indicate that there are strong interactions between the CTA^+ and tosylate ions which change the net charge on the micelle.

Nmr Experiments. The strong interaction between CTABr and various arene sulfonates is shown by changes in the nmr spectra of mixtures of the surfactant and the organic salts. As the concentration of $NaArSO_3$ is increased relative to CTABr, the *N*-methyl proton signal of CTABr shifts upfield (Tables IX and X) and broadens. The broadening (but not the shift) increases as the hydrophobicity of the para substituent in $ArSO_3^-$ is increased, so much so that when it is isopropyl or *tert*-butyl the signals are too broad for accurate chemical shift determinations. The changes in the proton signal of the carbon chain methylenes of CTABr also depend on this para substituent. In the presence of sodium benzenesulfonate, these protons give a single, unsymmetrical peak which shifts downfield (Table X) and broadens considerably, but in the presence of NaOTos these *C*-methylenes give two partially resolved peaks: one shifts downfield (0.05 ppm) and the second upfield (the upfield peak becomes too broad for accurate measurement of the chemical shift, Figure 8). The C-terminal methyl proton signal of CTABr is not noticeably affected when $ArSO_3^-$ is added to CTABr. For the CTABr concentrations examined (<0.03 *M*), the *N*-methylene proton signal of CTABr is too weak to allow accurate chemical shift measurements, even in the absence of salt.

When the concentration of CTABr is increased relative to that of $NaArSO_3$, the aryl ortho-proton signals move slightly upfield (0.01–0.02 ppm) while under the

Table IX. Effect of Sodium Tosylate on the Chemical Shift of the $-N^+(CH_3)_3$ Protons of CTABr[a]

$10^2 C_{NaOTos}$, *M*	*R*[b]	δ_{HOD}^{NMe}, ppm[c]	$10^2 W_{1/2}$, ppm[d]
		1.488	1.1
0.58	0.22	1.549	1.3
1.16	0.43	1.584	1.3
1.74	0.65	1.614	3.2
2.32	0.86	1.648	7.3
2.90	1.08	1.665	7.0
3.48	1.29	1.700	9.5
4.06	1.51	1.682	9.5
4.64	1.72	1.701	10.0
5.22	1.94	1.703	10.0
5.80	2.16	1.707	10.5

[a] At 31°, chemical shifts upfield from water signal in 90% (v/v) D_2O–H_2O containing 0.0269 *M* CTABr. [b] $R = C_{NaOTos}/C_{CTABr}$. [c] Chemical shift. [d] $W_{1/2}$ = peak width at half-height.

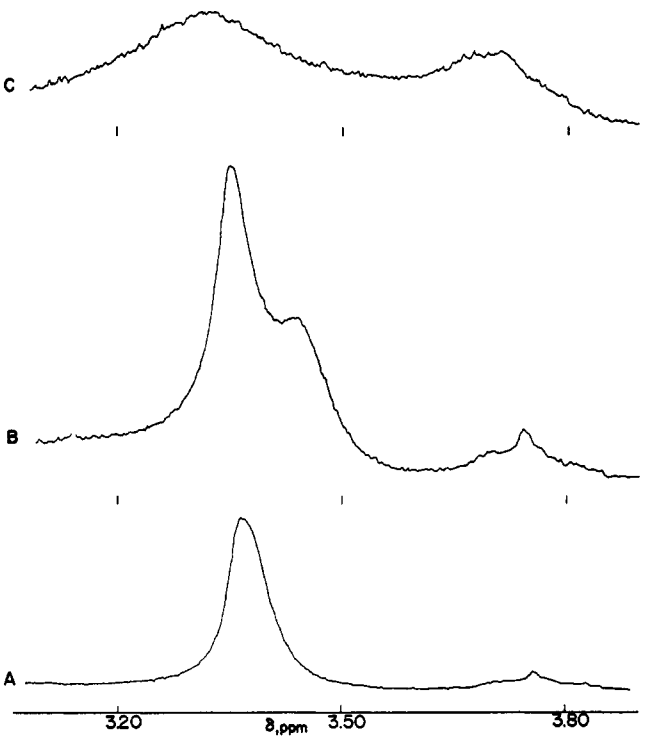

Figure 8. Nmr spectra of the methylene and *C*-methyl protons of 0.027 *M* CTABr with added NaOTos: (A) no CTABr; (B) 0.006 *M* NaOTos; (C) 0.029 *M* NaOTos. Spectra recorded at different amplitudes and after different periods of time averaging.

Table X. Effect of Sodium Benzenesulfonate on the Nmr Spectra of CTABr[a]

$10^2 C_{CTABr}$, *M*	*R*[b]	$\delta_{HOD}^{N\text{-}Me}$, ppm[c]	$\delta_{HOD}^{C\text{-}CH_2}$, ppm[d]
2.86	0.57	1.65	3.34
2.54	0.64	1.65	3.33
2.23	0.73	1.66	3.33
1.91	0.85	1.67	3.33
1.59	1.03	1.68	3.31
1.27	1.28	1.69	3.320
0.95	1.72	1.686	3.294
0.64	2.55	1.702	3.300
0.32	5.09	1.708	3.299

[a] At 31°, chemical shifts upfield from water signal in 90% (v/v) D_2O–H_2O containing 0.0163 *M* sodium benzenesulfonate. [b] $R = C_{Na\ salt}/C_{CTABr}$. [c] Chemical shift of CTABr *N*-methyl protons. [d] Chemical shift of CTABr *C*-methylene protons.

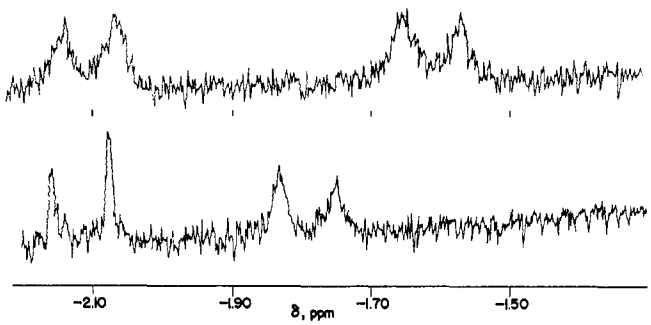

Figure 9. Nmr spectra of the aromatic protons of 0.015 *M* NaOTos with 0.024 *M* CTABr (upper spectrum) and without CTABr (lower spectrum). Chemical shifts in ppm downfield from HOD signal.

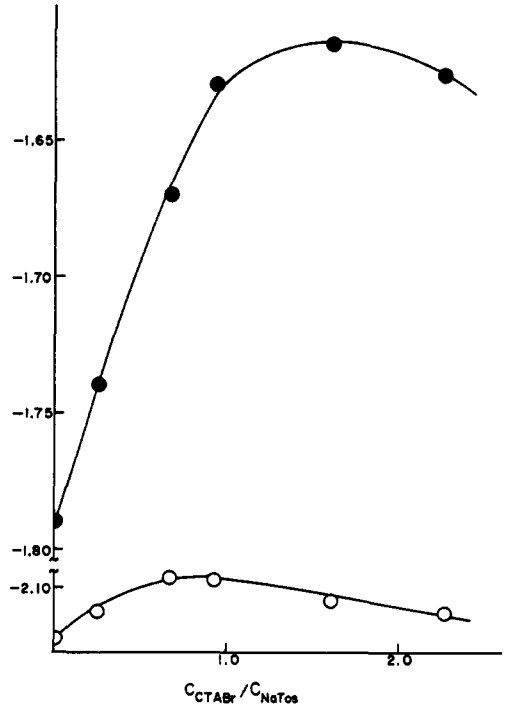

Figure 10. The chemical shift (downfield from HOD signal) of the meta (●) and ortho protons (○) of 0.015 *M* NaOTos with added CTABr.

same conditions the meta- (and para-) proton signals shift appreciably upfield (0.17 ppm for the meta protons of NaOTos) as do the proton signals of any *p*-alkyl substituents. The maximum shift occurs when the concentration of the aromatic anion and the surfactant are approximately equal; at higher concentrations of CTABr, the shift decreases (Figures 9 and 10). The aromatic peaks broaden when the surfactant and aromatic anion concentrations are similar, the broadening increasing with the hydrophobicity of the para substituent.

The chemical shift of the $C^{19}F_3$ signal of sodium *p*-trifluoromethylbenzenesulfonate was determined relative to trifluoracetic acid (internal capillary). Although the salt is water soluble, addition of less than 1 molar equiv of CTABr gives a precipitate which dissolves only in excess CTABr. In the latter solutions, the ^{19}F signal shifts downfield with increasing CTABr concentration as does the aryl-CH_3 proton signals of CTABr–NaOTos mixtures containing excess CTABr (Figure 11).

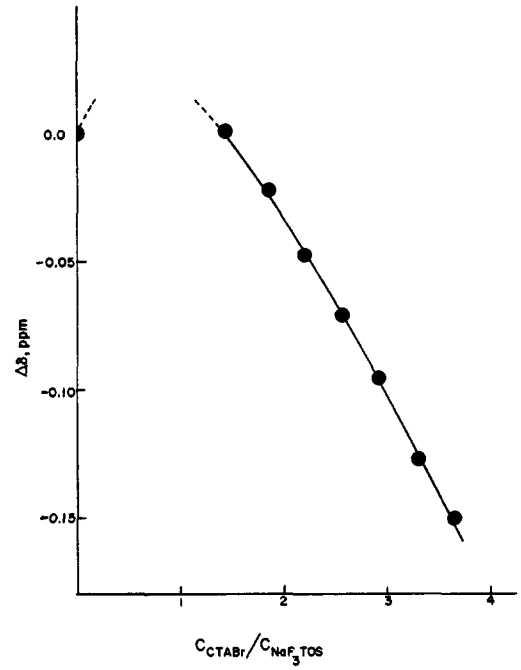

Figure 11. The change in the ^{19}F chemical shift of $NaCF_3C_6H_4SO_3$ with added CTABr.

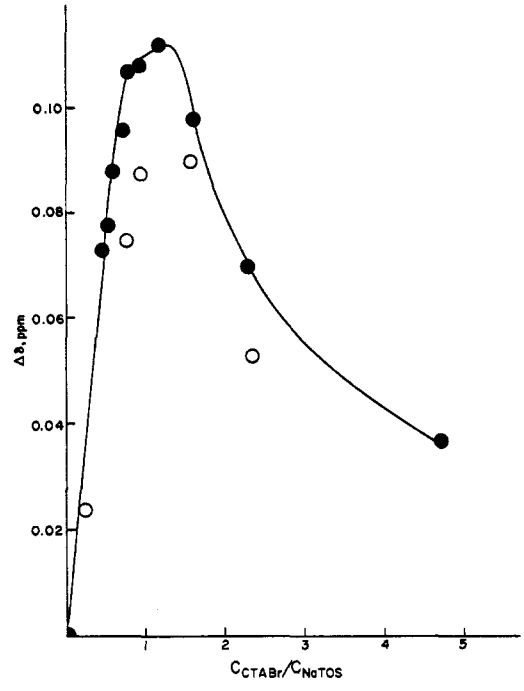

Figure 12. The change in the chemical shift of the *p*-methyl protons of NaOTos with added CTABr: (○) NaOTos constant (0.015 *M*); (●) CTABr constant (0.027 *M*).

These spectral changes depend only on the relative amounts of CTABr and $NaArSO_3$. The same pattern is obtained whether the $NaArSO_3$ concentration is varied or *vice versa*. For example, the change in the chemical shift of the *p*-methyl protons of NaOTos with added CTABr was determined both ways and this change is shown in Figure 12 where all chemical shifts are reported relative to that of 0.015 *M* NaOTos in the absence of CTABr (2.278 ppm upfield from water); the small difference between the two sets of data is prob-

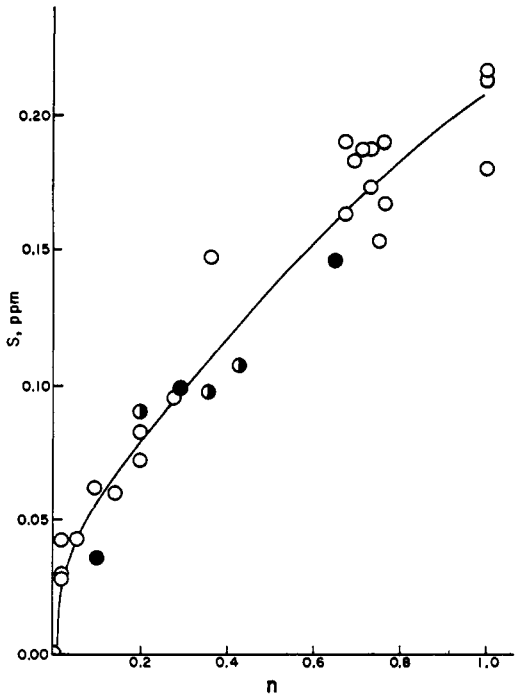

Figure 13. The change in the separation of the ortho- and meta-proton signals of NaOTos as a function of the mole fraction of the solvent organic component: (○) 0.335 *M* NaOTos in D_2O–CH_3CN; (half-shaded circles) 0.168 *M* NaOTos in D_2O–CH_3CN; (●) 0.051 *M* NaOTos in D_2O–dioxane.

ably due to a difference in the chemical shift of water for these two sets of solutions.

Because all the chemical shifts discussed above were recorded relative to water as the internal standard, there will be some contribution due to changes in the water signal, but such changes are probably negligible for any one set of solutions because the concentrations of added salt and surfactant are much lower than that of water, and by itself CTABr does not change the chemical shift of water.[33] In any event, changes in the internal standard cannot cause changes in the relative chemical shifts of different protons of the same molecule and it is on these relative changes that our discussion of the interaction between CTA^+ and $ArSO_3^-$ ions is based.

The micellar effects on the chemical shift of the aromatic protons of NaOTos can be compared with solvent effects. In D_2O–acetonitrile and D_2O–dioxane mixtures, the meta protons of NaOTos are shifted upfield relative to the ortho protons as the concentration of organic solvent is increased. The change in separation of the ortho and meta protons of NaOTos is plotted as a function of the mole fraction, *n*, of the organic components in Figure 13, where the parameter *S* is equal to $(\Delta\delta_{org} - \Delta\delta_{D_2O})$ with $\Delta\delta_{org}$, the chemical shift difference between the ortho and meta protons in the aqueous organic solvent, and $\Delta\delta_{D_2O}$, that difference in 90% D_2O–H_2O (v/v) at 25°. The general trend in upfield shift does not depend markedly upon the concentration of NaOTos or the nature of the organic component; *e.g.*, the changes in separation all fit, within experimental error, on the same curve. The maximum separation in mixed aqueous organic solvents is greater than that observed in D_2O–CTABr mixtures, but unlike the D_2O–CTABr case, there is no leveling off or decline in shift at the higher concentrations of the organic component.

The addition of simple hydrophilic salts to CTABr solutions causes a broadening of both the *N*-methyl and *C*-methylene proton signals, as well as substantial changes in the chemical shift of the former at high electrolyte concentrations (~1 *M*).[34] However, the salt order for the enhancement of catalysis is not the same as the nmr shift order, *i.e.*, Na_2SO_4 > NaBr > NaCl > NaOAc (kinetic order) and NaBr > NaCl > Na_2SO_4 > NaOAc (order of nmr shifts, downfield to upfield), but the line broadening probably reflects increased micellar aggregation, and this effect may be closely related to the catalytic efficiency of the micelle.

Discussion

In bimolecular micellar catalyzed reactions, the rate increase can be due to changes in environment reducing the free energy difference between the initial and transition state, and also to an increase in the frequency of molecular collisions as a consequence of the close association of the two reacting species at the micellar interface. Micellar catalysis is often rationalized in terms of a bringing together of reactants on the micelle or in its Stern layer, and salt inhibition is rationalized in terms of their ions displacing the reactant ions from the micelle even though the importance of such "concentration effects" relative to factors affecting the free energy difference between the absorbed initial and transition states cannot be evaluated unambiguously. It is not at all inconceivable that they work against each other.

In principle, unimolecular reactions are better than bimolecular reaction as probes of the electrostatic and hydrophobic forces operating on individual incorporated molecules. If the surfactant concentration is high enough for all the substrate to be incorporated into micelles, then changing the concentration of ions or other solutes in the Stern layer can influence the reaction rate only by changing the structure of the micelle and its water interface, and therefore changing the interactions of the initial and transition states with the medium.

For reactions with anionic initial and transition states, if the charge is more delocalized in the transition state than in the initial state then (all else being equal) the rate should be increased by transfer from water to a less polar solvent,[19,36,37] Because the nature of the environment within a micelle is intermediate between that of water and a saturated hydrocarbon,[38] incorporation of a carboxylate anion into a micelle should accelerate its decarboxylation with electrostatic and hydrophobic effects on both $\Delta H^{\pm}$ and $\Delta S^{\pm}$. The decrease in free energy upon incorporation into the micelle should be less for the carboxylate anion than for the more delocalized anionic transition state because carboxylate anions are less stable, relative to more de-

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(34) These shifts may be caused in part by a shift of the water peak which also shifts at high electrolyte concentrations.[35] A more complete discussion of changes in the nmr spectra of a quaternary ammonium salt with added electrolytes will be forthcoming.

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localized anions (*e.g.*, phenolate anions) in dipolar aprotic than in protic solvents.[39] Because this difference in stability can be attributed partially to electrostatic interactions, which are reflected in the enthalpy, $\Delta H^{\ddagger}$ should be less for the micelle-catalyzed process. The interaction between the cationic surfactant head groups and the incorporated anionic substrate should increase as the negative charge is delocalized with closer association and loss of freedom so that $\Delta S^{\ddagger}$ also decreases. In addition, the entropic and enthalpic consequences of the desolvation of the CO_2^- group may be different for the micelle-catalyzed process and contribute to the catalysis. This catalysis is markedly sensitive to changes in surfactant structure as demonstrated by the increased catalytic efficiency of the dicationic surfactants; but its relation to micellar structure and micelle–substrate interactions cannot be explained until the structure of micelles of IIa and IIb is known.[23]

The increased catalysis with added inorganic salts can be more easily rationalized. The addition of small hydrophilic electrolytes increases the catalysis because these salts increase micellar size,[40,41] forcing a closer association of the cationic head groups and increasing their association with an incorporated substrate molecule. This increased beneficial association[42] must be reflected in a lowering of the free energies of both the initial and transition states, but the latter is stabilized more because it has a partial negative charge delocalized into the ring. Consistent with this argument is the observation that the salt order for increasing micellar size, $HCO_2^- < F^- < Cl^- < Br^-$, is that for enhancing micellar catalysis, $CH_3CO_2^- \approx F^- < Cl^- < Br^-$. In addition, initial-state repulsions between the substrate carboxylate ions and the added anions will be relieved in the transition state.

The perturbation of micellar structure by incorporation of aromatic hydrophobic anions is much greater than that caused by simpler salts. Micellar interactions are dynamic and the aromatic ions are probably freely moving in and out of the micelle; however, the most reasonable time-average location would be between the cationic heads of adjacent surfactant ions so that the $-SO_3^-$ groups are protruding well into the water-rich Stern layer. This arrangement permits solvation by water of the hydrophilic $-SO_3^-$ group, as well as "solvation" by the electron rich aromatic ring for the hydrophobic $-N^+(CH_3)_3$ group and van der Waals' interaction between the surfactant chains and the para substituent. Association between quaternary ammonium compounds and aromatic systems is well established[44,45] and nmr work[33] suggests that polar aromatic compounds are held at the surface of cationic micelles. The viscosities of mixtures of CTABr and benzene (or other nonionic aromatic compounds) go through maxima at approximately equal concentrations of cation and aromatic compound[33] and the nmr line widths of the CTABr proton signals also show this pattern,[33] indicating that there is an interaction between quaternary nitrogen and the aromatic ring even in the absence of a charged substituent. An estimation of the extent of van der Waals' interactions between the surfactant chains and the para substituent of the aromatic anion can be based on measured dissociation constants of *n*-alkyltrimethylammonium arylsulfonate "ion pairs" in aqueous solutions,[46] which indicate that the association increases with the length of the "overlapping organic portions."

The changes in the nmr spectra, viscosities, and conductivity are all consistent with such a mobile CTA^+ $ArSO_3^-$ CTA^+ sandwich structure. The CTABr *N*-methyl proton signals are shifted upfield either because of the ring current of the incorporated aromatic group or because of some medium effect, *e.g.*, exclusion of solvent, induced by close association with the hydrophobic anion.[47] The insertion of either tosylate or benzenesulfonate ions between adjacent surfactant molecules forces the micelle to change from a spherical aggregate to a sheet, rod, or other laminar array with increased distances between methylene groups on adjacent surfactant molecules. With either ion, this increased distance leads to a downfield shift of some of the CTABr *C*-methylene proton signals, but because the more hydrophobic tosylate ion is inserted further into the space between adjacent chains, some of the *C*-methylene proton signals are also shifted upfield by the ring current of the tosylate ring. The viscosity results suggest that the elongation of the micelles is much greater when tosylate rather than benzenesulfonate ions is incorporated, and the electrochemical experiments provide additional evidence for the strong interactions between CTA^+ and tosylate ions. The increased line broadening observed with the more hydrophobic anions is probably a consequence of a reduction in molecular motion because of tighter association. Because the C-terminal methyl protons of CTABr remain in essentially an organic solvent environment, there is no change in their freedom to rotate and no broadening of their nmr signal.

The changes in the chemical shift of the aromatic anion are also consistent with this mode of association. With increasing CTABr concentration, the meta protons of $OTos^-$ undergo a more pronounced change in

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(42) The addition of salts to aqueous mixtures of R_4N^+ and an aromatic solubilisate enhances the solubilization of the latter; *cf.* ref 43.
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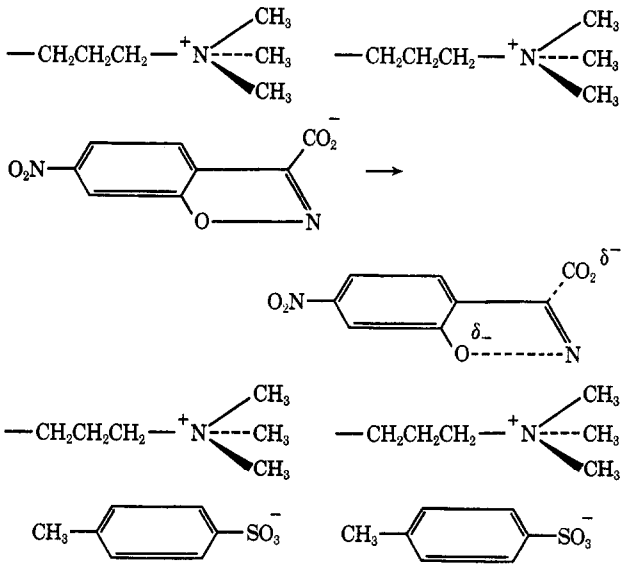
(47) However, added carboxylate ions cause greater upfield shifts in the CTABr *N*-methyl proton signal than do aliphatic carboxylate anions so that ring current effects are probably the principal factor.

chemical shift than the ortho protons (Figure 10), but this difference is smaller than that observed when NaOTos is transferred from water to an organic solvent (Figure 13), indicating that this anion never penetrates very deeply into the micelle.

The observation that the changes in chemical shift, line broadening, viscosity, and reaction rates go through maxima at roughly equal concentrations of aromatic anion and surfactant suggests that the association between CTA^+ and $ArSO_3^-$ ions is most extensive when there is a one-to-one ion pairing, probably because this arrangement allows the closest and most symmetrical packing[48] and the most effective charge neutralization. The substrate would be incorporated into this CTA^+ $ArSO_3^-$ CTA^+ sandwich structure where it would be held between two CTA^+ cationic head groups. This



incorporation should destabilize the initial state relative to the transition state because the neighboring $-SO_3^-$ and $-CO_2^-$ groups would compete for the available water and suffer unfavorable interactions, whereas the transition state would be stabilized because of interaction between the cationic head groups and the ring with its partially delocalized negative charge. The decreased catalysis observed at high concentration ratios of added anion to CTABr molecules is a consequence of a breakdown of this sandwich structure and the formation of more spherical, partially anionic, micelles which do not take up the anionic substrates. Our kinetic and structural evidence suggests that a *p*-alkylphenyl group fits very easily into the micelle. The rate enhancements by NaOTos are greater than those by the more hydrophobic 2-naphthalenesulfonate ion (Table V) suggesting that the naphthyl group may not fit as easily into the micelle as does a substituted phenyl group.

The addition of a wide variety of additives leads to changes in micellar structure which, in turn, result in wide variations in the catalytic efficiency of the micelle, and for hydrophobic sufonates and carboxylates and some simple hydrophilic salts can be related to changes in substrate–micelle interactions which have been investigated by nmr. The changes in the structure of cationic micelles upon the incorporation of the nonionic surfactant Igepal (which leads to increased catalysis) or upon the incorporation of neutral and negatively charged steroids (which lead to decreased catalysis) have not yet been investigated by nmr, but the changes in catalytic efficiency suggest that Igepal promotes catalysis, probably by forming mixed micelles with lower charge density, and the steroids retard catalysis by profoundly changing the structure of CTABr micelles, possibly by forming structures akin to the phospholipid–steroid aggregates in biological membranes.[13,15]

Micellar effects upon bimolecular reactions depend upon changes in local reactant concentrations and interactions with the micelle,[5-10,49] but the unimolecular decarboxylation of aromatic carboxylate ions is favored by factors which relatively stabilize the transition state by increasing $R_4N^+ \cdots$ aryl interactions and which selectively destabilize the initial state by increasing unfavorable dipolar interactions with the $-CO_2^-$ group. These results strongly suggest that synthetic modifications of surfactant structure will provide micelles of greater catalytic efficiency than those now available.

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(48) The incorporation of more than 1 equiv of $ArSO_3^-$ disrupts this symmetry, but the transport of CTA^+ to the anode in the presence of excess NaOTos shows that anionic aggregates can form, although the low viscosity of the solutions suggests that these aggregates are not linear nor of very high molecular weight.

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