70-8; **9**, 762-63-0; **10**, 692-47-7; **11**, 692-48-8; **12**, 598-96-9; **13**, 107-40-4; **14**, 28923-90-2; **15**, 34235-29-5; **16**, 34235-30-8; $Me_2C{=}CH_2$, 115-11-7; $MeCH{=}CMe_2$, 513-35-9; cyclohexane, 110-82-7.

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Micellar Effects upon the Reaction of the Tri-*p*-anisyl Carbonium Ion with Nucleophiles[1]

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Anionic micelles of sodium lauryl sulfate (NaLS) strongly catalyze the acid heterolysis of tri-*p*-anisylmethanol but do not affect the rate of attack of water upon the carbonium ion. Cationic micelles of cetyltrimethylammonium bromide (CTABr) and nonionic micelles of Igepal strongly inhibit the acid heterolysis but also do not affect the rate of attack of water upon the carbonium ion. Micelles of NaLS strongly inhibit the attack of hydroxide or azide ions upon the carbonium ion, and micelles of CTABr and Igepal weakly catalyze these reactions. Igepal decreases acidity as measured by H_0' and H_R.

One of the first kinetic studies of micellar catalysis and inhibition was that carried out by Duynstee and Grunwald on the alkaline fading of stable triphenylmethyl dye cations, *e.g.*, crystal violet.[2] Attack of the hydroxide ion upon the carbonium ion was inhibited by anionic and catalyzed by cationic micelles. These kinetic effects are readily explicable in terms of electrostatic interactions between the micelles and the initial and transition states.[3]

The equilibrium constant for carbonium ion formation from tri-*p*-anisylmethanol (ROH) in dilute acid is markedly increased by anionic micelles of sodium lauryl sulfate (NaLS) and decreased by cationic micelles of cetyltrimethylammonium bromide (CTABr),[8] and it was of interest to examine the forward and back reactions.

We have recently examined the kinetic salt effects upon the reaction of the tri-*p*-anisyl carbonium ion with water and related them to salt effects upon the H_R scale.[9,10] Our aim in the present work was to examine micellar effects upon the reactions shown in eq 1.

$$R^+ + H_2O \underset{k_b}{\overset{k_f}{\rightleftarrows}} ROH + H^+ \qquad (1)$$

This investigation cannot be carried out using the triphenylmethyl dye cations because they are stable in water and hydroxylic solvents in the absence of added nucleophiles.[2,11] We were also interested in examining micellar effects upon the reactions of the relatively reactive tri-*p*-anisyl carbonium ion with hydroxide and azide ion for comparison with results obtained using the stable dyestuff cations in which the positive charge is delocalized into the amino-substituted aryl groups.[2]

Only ionic surfactants were used in the original work on micellar effects on acidity functions.[8] We have now extended these measurements to the uncharged micelles of Igepal, which is a nonylphenyl polyethylene oxide (mol wt 1403) and also measured the effects of Igepal upon the rates of nucleophilic attack upon the tri-*p*-anisyl carbonium ion.

Experimental Section

Materials.—The purification of the ionic surfactants has been described.[8] Igepal was kindly supplied by GAF Corp. and was used without purification. The carbonium ion was introduced as a solution of tri-*p*-anisylmethyl chloride (Aldrich) in dilute HCl. All solutions were made up using distilled deionized water, and were degassed before use.[9]

Kinetics.—The reactions with water were followed at 25.0° using a Durrum–Gibson stopped flow apparatus. A solution of the carbonium ion, R^+, in dilute HCl in one drive syringe was rapidly mixed with excess NaOAc in the other drive syringe.[9] The first-order rate constant, k_ψ, for attack of water upon R^+ was found to be 12.4 sec^{-1}, in good agreement with our earlier results.[9]

For experiments with hydroxide ion a slight excess of NaOH was used in one drive syringe, and for experiments with azide ion the acid was neutralized by a slight excess of hydroxide ion.[9]

Indicator Measurements.—The ionizations of tri-*p*-anisylmethanol and *p*-nitroaniline in Igepal were measured following general methods.[8,12]

Results

Indicator Measurements.—The ability of nonionic micelles of Igepal to reduce $-H_0'$ and $-H_R$ (Tables I and II) suggests that the base rather than the anilinium or carbonium ion is taken up by the micelles which protect it from the hydronium ion; and nonpolar organic solvents (except at high concentration) decrease acidity functions, in part by stabilizing the organic base.[11] Igepal has a terminal hydroxyl group which could react with the carbonium ion and thereby further reduce $-H_R$, but this reaction is probably not important because the rate of attack of water upon the carbonium ion is unaffected by Igepal (and the ionic micelles). How-

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(1) Support of this work by the National Science Foundation is gratefully acknowledged.

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(3) For general reviews of micellar effects see ref 4–7.

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(9) C. A. Bunton and S. K. Huang, *J. Amer. Chem. Soc.*, **94**, 3536 (1972).

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(12) For a general review of acidity functions see R. H. Boyd in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 3.

TABLE I

EFFECT OF IGEPAL ON H_R

$10^4 c_D$, *M*	$\Delta H_R{}^a$
0.125	0.05
0.25	0.24
0.50	0.39
1.00	1.52

[a] Values relative to H_R in 0.05 *M* HCl at 25.0°.

TABLE II

EFFECT OF IGEPAL ON H_0'

$10^4 c_D$, *M*	$\Delta H_0'{}^a$
6.25	0.02
12.5	0.04
25	0.08
50	0.18

[a] Values relative to H_0' in 0.1 *M* HCl at 25.0°.

TABLE III

EFFECT OF NaLS UPON THE WATER REACTION[a]

$10^3 c_D$, *M*	c_{OAc^-}, *M*	k_ψ, sec^{-1}
2.5	0.025	11.5
2.5	0.075	12.2
2.5	0.125	12.7
2.5	0.225	12.9
5.0	0.025	11.7[b]
5.0	0.075	12.0[b]
5.0	0.125	12.4[b]
5.0	0.225	12.2[b]

[a] At 25.0° with R^+ and NaLS and 0.05 *M* HCl quenched with NaOAc unless specified. [b] With 5.0×10^{-3} *M* NaLS in each drive syringe.

TABLE IV

EFFECT OF CTABr ON THE WATER REACTION[a]

$10^4 c_D$, *M*	c_{OAc^-}, *M*	k_ψ, sec^{-1}
2.5	0.075	11.7
2.5	0.125	11.5
2.5	0.225	11.5
2.5	0.475	12.7
5.0	0.075	13.6[b]
5.0	0.125	13.2[b]
5.0	0.225	14.0[b]

[a] At 25.0° with R^+ and CTABr and 0.05 *M* HCl quenched with NaOAc unless specified. [b] With 5×10^{-4} *M* CTABr in each drive syringe.

TABLE V

EFFECT OF IGEPAL ON THE WATER REACTION[a]

c_{OAc^-}, *M*	k_ψ, sec^{-1}
0.45	12.4[b]
0.013	12.7
0.065	11.5
0.20	12.7
0.45	12.7

[a] At 25.0° and 10^{-4} *M* Igepal with R^+, 0.05 *M* HCl and 2×10^{-4} *M* in one syringe and sodium acetate in the other. [b] In the absence of Igepal.

ever, Igepal is even more effective than CTABr at inhibiting the ionization of tri-*p*-anisylmethanol; *e.g.*, $\Delta H_R = 1.10$ in 7.5×10^{-4} *M* CTABr,[8] whereas it is 1.52 in 10^{-4} *M* Igepal (Table I). The effect of Igepal upon H_0' (Table II) is slightly smaller than that of CTABr for which $\Delta H_0' = 0.23$ in 5×10^{-3} *M* CTABr.[8]

Water Reaction.—Micelles do not affect the rate of attack of water upon the carbonium ion (Tables III–V). The rate constants are approximately, the same whether the surfactant was in one or both drive syringes, suggesting that the reaction is much slower than the formation and disruption of the micelles and solute incorporation in them. As expected, acetate ion had little effect on k_ψ.[9,13] The ionization of the alcohol is markedly decreased by both Igepal and CTABr (Table I and ref 8) and we were forced to use them in low concentration ($2.5-5 \times 10^{-4}$ *M*) and even then the low concentration of carbonium ion reduced the accuracy of the rate measurements. Nonetheless the mean values in the presence of CTABr, $k_\psi = 12.8$ sec^{-1}, of Igepal, $k_\psi = 12.4$ sec^{-1}, and of NaLS, $k_\psi = 12.3$ sec^{-1}, are in good agreement with $k_\psi = 12.4$ sec^{-1} obtained in the absence of surfactant.

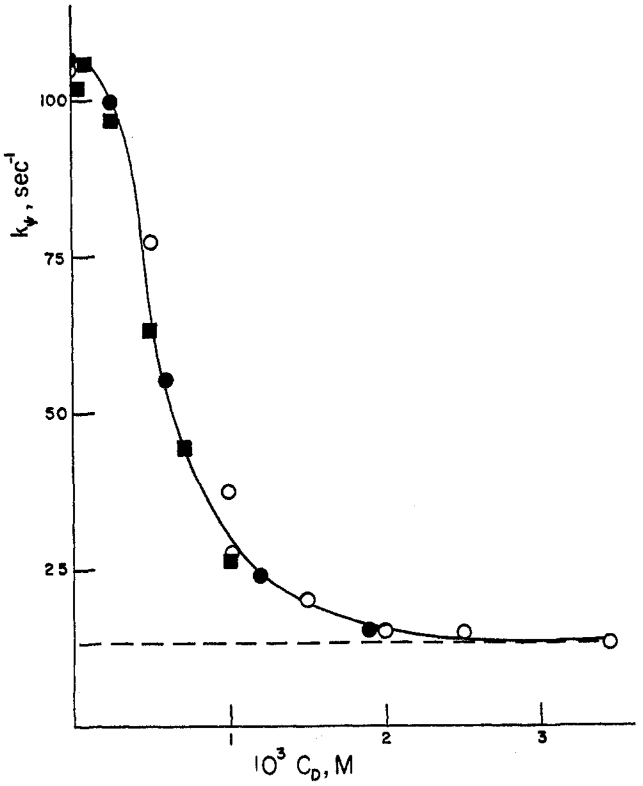

Figure 1.—Effect of NaLS upon the attack of 0.0145 *M* hydroxide ion on the tri-*p*-anisyl carbonium ion. The broken line is for reaction in the absence of hydroxide ion; ■, NaLS, R^+ and 0.1 *M* HCl in one drive syringe; ●, NaLS and OH^- in one drive syringe; ○, NaLS in both drive syringes.

Reaction with Hydroxide Ion.—As expected, anionic micelles of NaLS protect the carbonium ion from attack by hydroxide ion. In the absence of surfactant, reaction with hydroxide ion is rapid,[9] but high concentrations of hydroxide ion have to be used to increase the reaction rate in the presence of 2.5–5 m*M* NaLS (Tables VI and VII and Figure 1). For concentrations of hydroxide ion below 0.03 *M* the value of k_ψ in 2.5–5 m*M* NaLS is very close to that of the spontaneous reaction of the carbonium ion with water (Tables III and VI and ref 9), and the rate enhancement at higher concentrations is probably caused by attack of hydroxide ion upon that small amount of carbonium ion which is not bound to the micelle. [The values of k_ψ in the absence of surfactant (Table VI) are calculated using $k_2 = 8200$ l. mol^{-1} sec^{-1}, for attack of OH^- upon the carbonium ion[9].]

This inhibition is observed at concentrations of

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(13) E. A. Hill and W. J. Mueller, *Tetrahedron Lett.*, 2565 (1968).

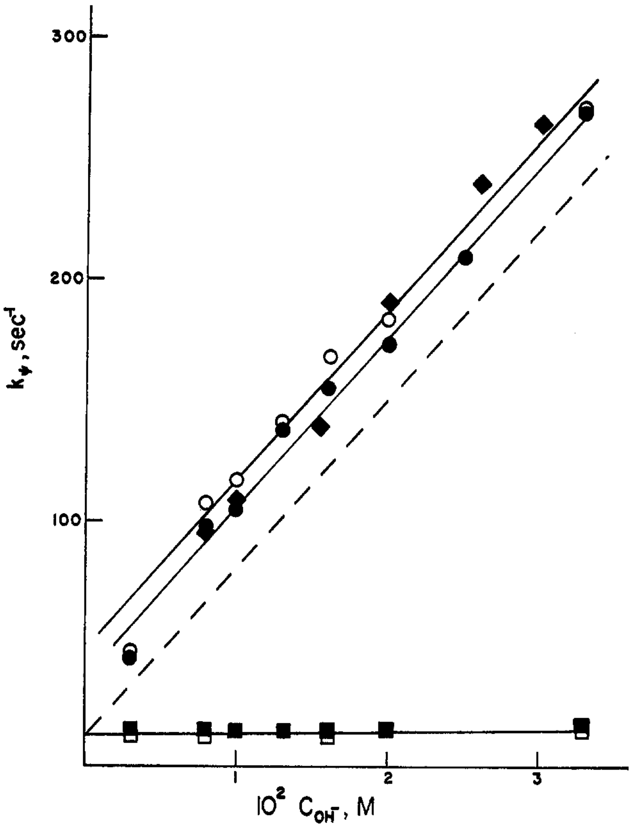

Figure 2.—Effect of surfactants on the reaction with hydroxide ion. The broken line is for reaction in the absence of surfactant; ■, 2.5 × 10^{-3} *M*; □, 5 × 10^{-3} *M* NaLS; ●, 5 × 10^{-4} *M*, ○, 10^{-3} *M* CTABr; ◆, 2 × 10^{-4} *M* Igepal.

TABLE VI

EFFECT OF HYDROXIDE ION UPON THE REACTION IN NaLS[a]

	$10^3 c_D$, *M*		
c_{OH^-}, *M*	0	2.5[b]	5.0[c]
0.003	37	15.4	12.9
0.008	79	15.0	13.1
0.010	95	15.2	
0.013	119	15.2	
0.016	145	15.2	14.0
0.020	177	15.4	
0.033	283	16.8	15.9
0.091	756	28.8	
0.100	833		27.6
0.225	1950	71.3	57.7
0.475	3900	198	

[a] Values of k_ψ, sec^{-1} at 25.0°; in the absence of OH$^-$ k_ψ = 12.3 sec^{-1} in NaLS; values in the absence of NaLS are calculated.[9] [b] NaLS with NaOH. [c] NaLS in each syringe.

TABLE VII

EFFECT OF NaLS IN LOW CONCENTRATIONS ON THE HYDROXIDE ION REACTION[a]

$10^4 c_D$, *M*	k_ψ, sec^{-1}
	107
0.025	106
0.25	101
1.0	106[c]
2.5	96.9[b]
2.5	100
5.0	63.4[b]
5.0	77.0[c]

[a] At 25.0° in 1.45 × 10^{-2} *M* NaOH, R^+ in 0.05 *M* HCl in one syringe, NaOH + NaLS in the other. [b] R^+ and NaLS in one syringe. [c] NaLS in both syringes.

NaLS below the critical micelle concentration (cmc), but it is possible that micellization is induced by the carbonium ion.[14]

Equilibration of the carbonium ion with the anionic micelle must be relatively fast because k_ψ depends only slightly upon the way in which the solutions in the drive syringe are made up.

It was difficult to follow this reaction in the presence of CTABr and Igepal, which depress the acid ionization of the alcohol, but the kinetic effects of these surfactants are small (Figure 2). It is possible that we would have seen larger rate enhancements had we been able to use greater than 10^{-3} *M* CTABr. We note that Duynstee and Grunwald observed relatively large rate enhancements of the reaction of hydroxide ion with a number of stable triphenylmethyl dye cations by cationic micelles, but they were able to use relatively high surfactant concentrations.[2] The relatively small rate enhancements which we observe are understandable because electrostatic repulsions between a carbonium ion and a cationic micelle should oppose hydrophobic binding to the micelle and therefore hinder incorporation of the carbonium ion in the micellar pseudophase.

The small rate enhancement by Igepal (Figure 2) suggests that there is a small interaction between the carbonium ion and the nonionic micelles, possibly involving a base-catalyzed attack of the hydroxyl head groups of Igepal.

Reaction with Azide Ion.—Micellar effects upon the attack of azide ion upon the carbonium ion follow the pattern observed for the hydroxide ion reaction. Anionic micelles of NaLS suppress the reaction completely, but cationic micelles of CTABr and nonionic micelles of Igepal have little effect and the rate constants are similar to those found in water (Table VIII).

TABLE VIII

EFFECT OF SURFACTANTS UPON REACTION WITH AZIDE ION[a]

$10^5 c_{N_3^-}$, *M*	Surfactant			
	NaLS[b]	CTABr[c]	Igepal[c]	None[d]
1.25	14.3			180
1.55			159	200
2.35			210	240
2.5	13.7	267		250
2.5		292		
3.1			238	280
4.7			315	380
5.0	13.8	405		395
6.25			450	470
9.4			650	650
10.0	13.8	725		680
12.5			850	825

[a] Values of k_ψ, sec^{-1}, at 25.0° and 10^{-3} *M* NaOH and 0.025 *M* NaCl. [b] 5 × 10^{-3} *M* NaLS. [c] 5 × 10^{-4} *M* CTABr and Igepal. [d] Values of k_ψ in the absence of surfactant are from ref 9.

In water initial attack of azide ion gives an equilibrium mixture of the alkyl azide and the carbonium ion, and is followed by a slow conversion to the thermodynamically more stable tri-*p*-anisylmethanol.[9] The difference between the absorbance after the initial reaction is complete and that at time infinity gives the

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[14] For NaLS, cmc = 6–9 × 10^{-3} *M* depending upon the method used.[15]

[15] P. Mukerjee and K. J. Mysels, "Critical Micelle Concentrations of Aqueous Surfactant Solutions," NSRDS-NBS, Washington, D. C., 1971.

amount of carbonium ion at the initial equilibrium, and $K_N \approx 7 \times 10^4$ l. mol^{-1} in water.[9]

$$\mathrm{ROH} \xleftarrow[\text{slow}]{\mathrm{H_2O}} \mathrm{R^+} + \mathrm{N_3^-} \overset{K_N}{\rightleftarrows} \mathrm{RN_3}$$

A similar phenomenon is observed in CTABr, and the association constant, K_N, is slightly larger than in water (Table IX). (There is considerable uncertainty in these values of K_N because of the low initial concentration of R^+ in the presence of CTABr.)

TABLE IX

EQUILIBRIUM CONSTANT FOR THE FORMATION OF ALKYL AZIDE IN CTABr[a]

$10^5\ c_{NaN_3}$, *M*	Absorbance	K_N, l. mol^{-1}
2.5	0.022	1.5×10^5
2.5	0.026	1.3×10^5
5.0	0.019	1.0×10^5
5.0	0.019	1.0×10^5
10.0	0.010	1.0×10^5
10.0	0.009	1.1×10^5

[a] At 25.0°. [b] At the initial "equilibrium;" the absorbance of R^+ before reaction is 0.108.

Igepal has little effect upon the rate constant for attack of azide ion (Table VIII) and in this system the initial reaction leads to complete disappearance of the carbonium ion. *i.e.*, K_N is very large. Nonionic micelles of Igepal should stabilize the alkyl azide relative to the carbonium and azide ions. Simple electrostatic considerations suggest that a cationic micelle should have little effect upon the equilibrium between the alkyl azide and the carbonium and azide ions, as is observed.

Discussion

Formation and Reaction of the Carbonium Ion.—For reaction 1, $K_a = k^f/k^b$, and, because K_a, as measured by ΔH_R (the change in H_R) is very sensitive to added micelles (Table I and ref 8) whereas k^f is not (Tables III–V), the rate constant for the acid heterolysis of the alcohol is sharply increased by micelles of NaLS and decreased by micelles of CTABr and Igepal. These rate effects are shown in Table X calculated from k^f and k^b in water[9] and ΔH_R, for surfactant concentrations which are convenient for the measurement of ΔH_R (Table I). These micellar effects are in the direction generally observed for acid-catalyzed reactions.[5,6,16]

TABLE X

MICELLAR EFFECTS UPON FORMATION OF THE CARBONIUM ION[a]

Surfactant	c_D, *M*	k_b, l. mol^{-1} sec^{-1}
NaLS	5×10^{-3}	1.8×10^5
CTABr	10^{-3}	3
Igepal	10^{-4}	3.8

[a] At 25.0°; in the absence of surfactant k^b = 79 l. mol^{-1} sec^{-1}; see ref 9.

Micelles of both CTABr and NaLS solubilize tri-*p*-anisylmethanol,[8] and this stabilization of the initial state should, of itself, reduce k^b. However, these initial state effects upon the alcohol are small compared with the overall effects upon k^b.

The absence of any effect of cationic micelles of CTABr upon k^f (the first-order rate constant for attack of water upon R^+) is readily understandable if most of the carbonium ion is in the aqueous phase rather than in the micellar pseudophase (but see ref 2). Igepal behaves similarly to CTABr in having no effect on k^f and decreasing k^b, suggesting that the alcohol can enter the nonionic micelle which protects it from the hydronium ion. There are a number of ion–molecule reactions which are inhibited by nonionic micelles.[6,17] The carbonium ion, on the other hand, must be in the aqueous phase or in the exterior of the nonionic micelle where it can be attacked by water.

Inhibition of anionic attack and analogy with other systems show that the tri-*p*-anisyl carbonium ion is taken up strongly by anionic micelles of NaLS, even though there is no effect upon k^f. If the bulk of R^+ is in the micellar pseudophase the relative stabilities of R^+ and the transition state are unaffected by incorporation in the micelles, suggesting that the carbonium ion is close to the water-rich micellar surface.

Reactions with Ionic Nucleophiles.—The micellar effects upon the reaction of the tri-*p*-anisyl carbonium ion with anions accord very well with earlier observations and can be rationalized in terms of dominant electrostatic interactions. The very marked inhibition by NaLS of anion attack upon R^+ shows that the carbonium ion must be taken up very strongly by anionic micelles, but into a region of the micelle where it is open to attack of water.

Registry No.—Tri-*p*-anisyl carbonium ion, 28550-87-0; NaLS, 2386-53-0; tri-*p*-anisylmethanol, 3010-81-9; water, 7732-18-5; CTABr, 57-09-0; hydroxide ion, 14280-30-9; azide ion, 14343-69-2.

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(16) M. T. A. Behme and E. H. Cordes, *J. Amer. Chem. Soc.*, **87**, 260 (1965); M. T. A. Behme, J. G. Fullington, R. Noel, and E. H. Cordes, *ibid.*, **87**, 266 (1965); R. B. Dunlap and E. H. Cordes, *ibid.*, **90**, 4395 (1968); C. A. Bunton and L. Robinson, *ibid.*, **91**, 6072 (1969).

(17) C. A. Bunton and L. Robinson, *J. Org. Chem.*, **34**, 773 (1969).