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Micellar Effects on the Hydrolysis of *p*-Nitrobenzoyl Choline and the Related *N*-Hexadecyl Ester[1]

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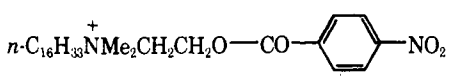
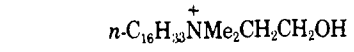
The reaction of hexadecyl(2-hydroxyethyl)dimethylammonium bromide *p*-nitrobenzoyl ester (n-$C_{16}H_{33}N^+Me_2CH_2CH_2OCOC_6H_4NO_2Br^-$, I) with hydroxide ion is catalyzed to similar extents by cationic micelles of hexadecyltrimethylammonium bromide (CTABr) or hexadecyl(2-hydroxyethyl)dimethylammonium bromide (n-$C_{16}H_{33}NMe_2CH_2CH_2OHBr^-$, II), suggesting that the greater catalytic efficiency of II in other reactions is due to nucleophilic attack by the zwitterion generated by II at high pH. Saponification of the more hydrophilic *p*-nitrobenzoyl choline (III) is not micellarly catalyzed. In the absence of surfactant I is slightly more reactive than III in aqueous dioxane and the reactions slow as the solvent becomes more aqueous, but there is a rate minimum in reactions of I at ca. 95 mol % water, and the rate increases in more aqueous solvents owing to association of I.

The biological importance of acetyl choline makes choline esters interesting substrates for mechanistic work[2] and a systematic study has been made of substituent effects upon reactions of hydroxide ion with benzoyl cholines.[3] We have kinetic evidence for the intermediacy of a related ester, hexadecyl(2-hydroxyethyl)dimethylammonium bromide *p*-nitrobenzoyl ester (I), in reactions of *p*-nitrobenzoyl phosphate in dilute alkali catalyzed by micelles of the choline derivative (II),[4] and we were therefore interested in the hydrolysis of I.



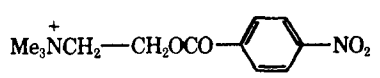
I



II

Micelles of II are effective catalysts of phosphate ester hydrolysis,[9] and of SN2 and E2 reactions at saturated carbon, and of reactions of carboxylic esters and amides.[10]

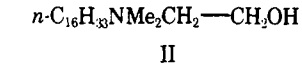
We also compared the reactivity of I with that of *p*-nitrobenzoyl choline (III), because self-micellization of I could make it more reactive than III toward anionic nucleophiles.



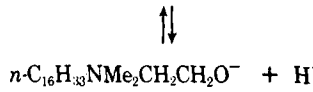
III

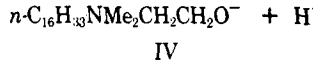
There has been considerable work on the reactions of esters of long-chain n-alkane carboxylic acids with n-alkyl amines and related compounds.[11-14] Comicellization has been shown to be of great importance in many of these reactions, and both the overall reaction rate and the kinetic form changes when the reactants are micellized.[11,12] Substrate micellization is also of great importance in hydrolysis of monoalkyl sulfates in both acidic and basic media.[15] Many biological reactions occur at interfaces, and the use of chemically inert micelles and micellized reactants can give evidence on the role of these microscopic medium effects;[5-8,16] for example, the hydroxyethyl head group of II can be regarded as a model for the corresponding group in serine which is implicated as a nucleophile in many enzymic reactions.[17]

In this work we compare reactivities of I and III in the presence of micelles of the cationic surfactants (detergents), hexadecyltrimethylammonium bromide (CTABr) and II. At high pH micelles of the choline-derived surfactant II are effective reagents for the decomposition of di- and trisubstituted phosphate esters, and it was suggested that the alkoxide moiety of the zwitterion IV attacked the phosphoryl group.[9b]



II





IV

Although in nucleophilic reactions involving II[10,18] the alkoxide moiety could act as a nucleophile, other reasonable mechanisms can be postulated.[9,10] For example, the hydroxyl moiety could act as a general acid and assist attack of hydroxide ion, or the alkoxide moiety in IV could act as a general base and activate a water molecule (cf. ref 19), and it has also been suggested that micelles of II activate hydroxide ions.[10] The kinetic form of the reaction and its pH–rate profile do not distinguish between these possibilities.

Nucleophilic attack by IV upon I gives no chemical change, and in that event micelles of II should be no better catalysts than micellized CTABr. However, if II is more ef-

Table I
Reaction of p-Nitrobenzoyl Choline Iodide[a]

H_2O, wt %	H_2O, mol %	k_ψ, sec^{-1}
100	100	0.126
95	98.9	0.133
90	97.8	0.167
80	95.1	0.229
70	91.9	0.341
60	88.0	0.576
50	83.0	0.931

[a] At 25.0° and 0.01 M NaOH.

fective than CTABr, it would appear that it is acting in some other way than as a nucleophile; cf. ref 9, 10.

Experimental Section

Materials. p-Nitrobenzoyl choline (III) was prepared as the iodide from MeI and 2-dimethylaminoethyl p-nitrobenzoate,[3] and was recrystallized from 85% EtOH–H_2O. It had mp 238–239° dec (lit.[3] 238–239° dec). It was bright yellow as a solid or in Me_2SO, but it was colorless in H_2O, EtOH, and Me_2CO. However, this difference may be due in part to its low solubility in some of these solvents. It was converted into its nitrate by treatment with $AgNO_3$ in MeOH, which after recrystallization (95% EtOH), gave fine, colorless needles, mp 211–213° dec.

The NMR spectra (60 MHz) of the iodide and nitrate were very similar in Me_2SO-d_6, as was that of the nitrate in Me_2CO-d_6 or D_2O. Because of low solubility only a poor NMR spectrum was obtained in D_2O, and Me_2SO was the only solvent which could be used with the iodide. The NMR spectra in Me_2SO-d_6 (60 MHz) had the following τ values: 1.76, partially resolved pair of doublets (4); 5.27, multiplet (2); 6.13, multiplet (2); 7.66 (9). The relative peak areas are in parentheses.

The uv and visible spectra were examined in Me_2SO. For both the iodide and the nitrate λ_{max} 260 nm [ϵ 11200 (nitrate) and 11500 (iodide)]. There was no maximum in the visible region, but when the spectra were measured using 0.027 M ester in 0.1-mm cells, the absorbance of the iodide was considerably higher than that of the nitrate in the region 280–350 nm. This difference disappeared when the concentration was reduced to 10^{-2} M, so that the color apparently depends on an interaction between p-nitrobenzoyl choline and iodide ions in the solid or in relatively concentrated solution.

Hexadecyl(2-hydroxyethyl)dimethylammonium bromide p-nitrobenzoyl ester (I) was prepared by reaction of p-nitrobenzoyl chloride with II in dry pyridine for 12 hr (cf. ref 14a). The pyridine was removed in vacuo, and recrystallization (twice) from CCl_4–$CHCl_3$ removed the pyridine salts; I was obtained largely as the bromide, but slightly contaminated with the chloride. Another sample prepared from 1-bromohexadecane and 2-(dimethylamino)ethyl p-nitrobenzoate in refluxing $CHCl_3$ for 24 hr had mp 122–124° after recrystallization from $CHCl_3$–CCl_4. (Anal. Calcd: C, 59.6; H, 8.7; N, 5.2; Br, 14.7. Found: C, 59.3; H, 9.0; N, 5.3; Br, 14.5.) The samples had the same chemical properties.

The NMR spectrum of I at 60 MHz in $CDCl_3$ had the following τ values: 1.79, singlet (4); 5.10, multiplet (2); 5.67, multiplet (2), 6.30, multiplet (2); 5.67 multiplet (2); 6.30, multiplet (2); 6.47, singlet (6); 8.78 (31). The relative peak areas are in parentheses.

The preparation and purification of the surfactants have been described.[9] A purified sample of 8-anilinonaphthalenesulfonic acid (ANSA) was provided by Professor H. W. Offen and Mr. C. Mastrangelo. Dioxane was refluxed over Na and redistilled under N_2. The mixed solvents were made up by weight using redistilled deionized water.

Critical Micelle Concentration. The critical micelle concentration (cmc) of I in neutral water–dioxane (95:5 w/w) was determined using a fluorescent dye, and by light scattering.[20] The fluorescence spectra of 10^{-6} M ANSA were measured over a range of concentrations of I in a Perkin-Elmer MPF3 spectrometer, with excitation at 365 nm. There was a sharp increase in the intensity of the fluorescence emission beginning at 2×10^{-5} M I.[20a,b] This method tends to give low cmc values because the hydrophobic dye can induce micellization,[20c] and light scattering from I was measured on a Sofica Photo Goniodiffusometer, Model 42000 using incident light at 546 nm for solutions of I. The solutions were centrifuged before measurement to remove dust particles, and there was a sharp increase in the 90° scattering (and at 45° and 60°) at 3.5×10^{-5} M I, and the scattering became constant at concentrations > 4×10^{-5} M. [We could not obtain transparent solutions of I greater than 6×10^{-5} M, because of its low solubility in water–dioxane (95:5 w/w).]

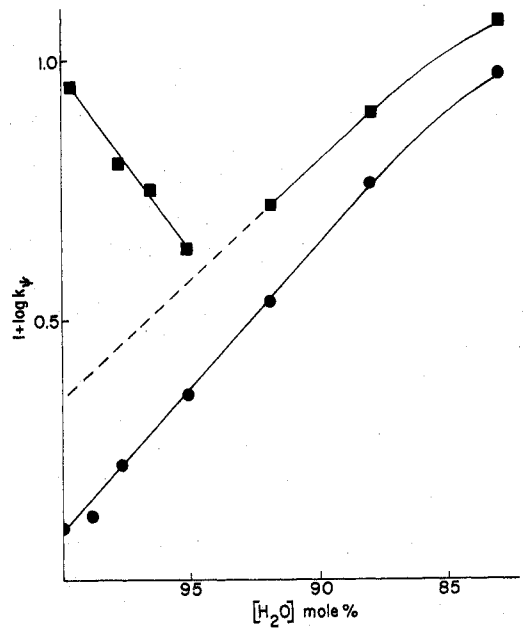


Figure 1. Reaction of p-nitrobenzoyl choline (●) and hexadecyl(2-hydroxyethyl)dimethylammonium bromide p-nitrobenzoyl ester (I) (■) with 10^{-2} M NaOH in aqueous dioxane at 25.0°.

Kinetics. The slower reactions were followed at 262 nm using a Gilford spectrophotometer with water-jacketed cells at 25.0°. The faster reactions were followed at 25.0° on a Durrum stopped flow spectrophotometer with a logarithmic amplifier and a Biomation 805 Waveform recorder for data acquisition. This equipment allowed us to follow the small changes in absorbance during reaction with low substrate concentrations. In the absence of surfactant we generally used 3×10^{-5} M substrate and obtained an absorbance change of ca. 0.3, and in some of these experiments we deliberately used higher concentrations of the ester I in order to observe effects due to its association. Surfactants were in at least 50-fold excess over substrate. The first-order rate constants, k_ψ, are in sec^{-1}, and the surfactant concentration is designated C_D. All reactions of I in the absence of surfactant were in aqueous dioxane because of its very low solubility in water.

Good first-order rate plots were obtained over about 3 half-lives except for some of the reactions of I in solvents of high water content in the absence of surfactant for which the plots were curved. We believe that this curvature is due to substrate association, which is discussed in the Results and Discussion section, and we quote initial rate constants for these reactions.

Most of the reactions were followed in 10^{-2} M NaOH, but more dilute alkali was used in a few experiments with I in water–dioxane (95:5 w/w) and in the presence of surfactant. We did not use buffers, because of their possible effects as electrolytes. In comparing the two sets of results we calculated the second-order rate constants as $k_\psi/[OH]$ with [OH] being calculated from the pH of the more dilute alkali.

Results and Discussion

Reactions with Hydroxide Ion in the Absence of Added Surfactant. The rate constants for reaction of p-nitrobenzoyl choline iodide (III) in 0.01 M NaOH increase steadily with decreasing water content of the solvent (Table I) and a plot of log k_ψ against the mole percent of water is approximately linear (Figure 1). This solvent effect is consistent with the qualitative solvent theory of Hughes and Ingold,[21] but increased hydration of hydroxide ion in the more aqueous solvents is almost certainly important (cf. ref 22).

The solvent effect upon reaction of the hexadecyl derivative I is more complex. In solvents of relatively low water content the rate constant increases with dioxane content of

Table II
Reaction of I in the Absence of Added Surfactant[a]

H_2O, wt %	H_2O, mol %	k_ψ, sec^{-1}
80	95.1	0.43
75	93.6	0.47
70	91.9	0.53
60	88.0	0.79
50	83.0	1.18

[a] At 25.0° with 0.01 *M* NaOH.

the solvent (Table II and Figure 1), as for hydrolysis of *p*-nitrobenzoyl choline, but there is a minimum in a plot of log k_ψ against solvent composition (Figure 1). This figure only qualitatively represents the relation between rate constant for reaction of I and solvent composition, because for the four most aqueous solvents the concentrations of I differed slightly and were 0.026, 0.037, 0.040, and 0.035 m*M* for 95, 90, 85, and 80 wt % water, respectively. With the more aqueous solvents the first-order rate constants increase with increasing substrate concentration, but this dependence of rate on substrate concentration disappears as the water content of the solvent decreases (Figure 2). Therefore the rate minimum at water–dioxane (80:20 w/w) (95 mol % of water) in reactions of I probably arises from substrate self-association which should markedly assist attack of hydroxide ion (cf. ref 15), but even at relatively high dioxane concentrations I is slightly more reactive than *p*-nitrobenzoyl choline (by a factor of ca. 1.25). A hydrophobic solute such as I should micellize in solvents of high water content, although addition of solvents such as dioxane increases the cmc of cationic surfactants, and normal micelles do not form in solvents of high dioxane content.[20a,23] The rate increase with increasing [I] begins at concentrations well below the cmc (Experimental Section), suggesting that the substrate is forming submicellar aggregates which are more reactive than monomeric substrate. There is extensive kinetic and other evidence for the formation of submicellar aggregates, usually between solute and surfactant.[5-7,24]

Most of the runs with I were done using 0.01 *M* NaOH, but with this concentration the faster runs were in the range requiring use of a stopped flow spectrometer. The maximum usable concentration of I was then halved during mixing and because of the low solubility of I we could not use a large concentration range. Therefore some experiments were done with more dilute alkali using a Gilford spectrometer and we then were able to use a concentration of I large enough to observe a considerable rate enhancement, but we did not reach a concentration high enough to give the rate plateau which should be found when a substrate is wholly micellized (Figure 2).

One consequence of substrate association is that the reactions of I are not first order under all conditions. If an associated substrate reacts more rapidly than monomeric substrate, the instantaneous first-order rate constants will decrease during reaction because the relative amount of self-associated substrate will decrease as the total substrate concentration decreases. To avoid this difficulty we estimated initial first-order rate constants for the reactions of I in the more aqueous solvents where we found curved first-order rate plots, i.e., for the reactions in 95 wt % water. There was no curvature of the first-order rate plots for reactions of *p*-nitrobenzoyl choline (III) or for reactions of I in the less aqueous solvents or when the substrate concentration was low.

The self-association of I and its low solubility prevents our measuring directly the first-order rate constant for reaction of monomeric I in aqueous alkali, but we estimate it

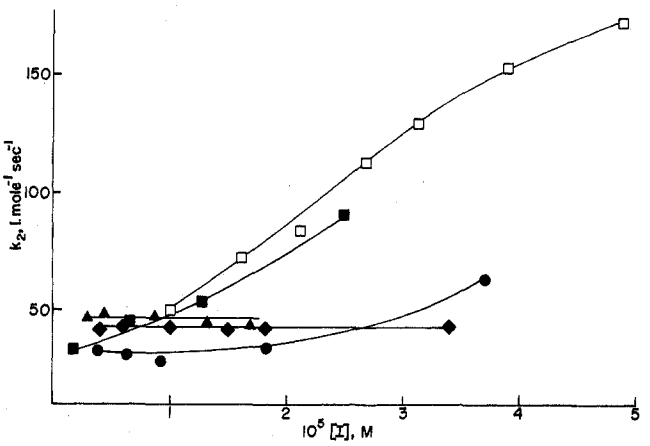


Figure 2. Variation of second-order rate constant for reaction of I in alkaline aqueous dioxane. Solid points, 10^{-2} *M* NaOH; open points, pH 11. □ ■, 95; ●, 90; ◆, 80; ▲, 75 wt % water.

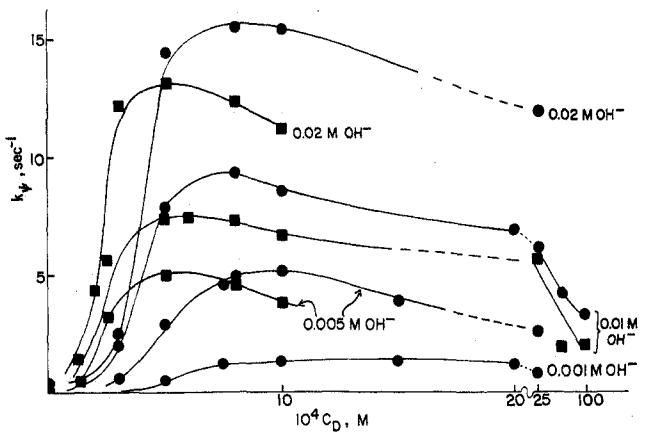


Figure 3. Reactions of I in CTABr (●), and in hexadecyl(2-hydroxyethyl)dimethylammonium bromide (II) (■) in aqueous alkali at 25.0°.

in two ways. (1) If the relative reactivities of *p*-nitrobenzoyl choline (III) and the analogous (monomeric) hexadecyl derivative I are approximately the same in water and 95 mol % water, we can correct the value of k_ψ = 0.43 sec^{-1} (Table II) by the factor of 0.12/0.23, which is given by the relative rates of reaction of *p*-nitrobenzoyl choline in the two solvents (Table I), giving $k_\psi \sim 0.24$ sec^{-1} for reaction of monomeric I in 10^{-2} *M* NaOH in water; or (2) we can extrapolate log k_ψ to zero dioxane (Figure 1), also giving $k_\psi \sim 0.23$ sec^{-1}. There is considerable uncertainty in this value because of the nature of the extrapolations.

Reactions with Hydroxide Ion in the Presence of Added Surfactant. Cationic micelles of either CTABr or the choline derivative II do not catalyze the reaction of *p*-nitrobenzoyl choline (III) with hydroxide ion, almost certainly because this cationic substrate is insufficiently hydrophobic to be incorporated into the cationic micelles and in aqueous 0.01 *M* sodium hydroxide k_ψ = 0.126 sec^{-1}, and 0.118 sec^{-1} with 10^{-3} *M* CTABr and 0.132 sec^{-1} with 10^{-3} *M* II. However the reaction of the hexadecyl derivative I in water is catalyzed by micelles of CTABr and of II (Figure 3). The plots of k_ψ against surfactant concentration show the maxima typical of bimolecular micellar-catalyzed reactions.[5-8,25] There was no curvature in the first-order rate plots when surfactant was present.

The micellar catalyses (k_{rel}) given in Table III are calculated using the estimated value of k_ψ = 0.23 sec^{-1} for reaction in water. These rate enhancements are similar to those found for micellar-catalyzed hydrolyses of esters of aliphat-

Table III
Micellar Rate Enhancements of Reaction of I[a]

	Surfactant	
$[\overline{OH}]$, M	CTABr	n-$C_{16}H_{33}\overset{+}{N}Me_2CH_2CH_2OH$ Br^-
0.005	45 (10)	43 (5)
0.01	41 (8)	33 (5)
0.02	34 (8)	29 (5)

[a] At 25.0°; and calculated using k_ψ = 0.23 for reaction in 10^{-2} M NaOH in water. The values in parentheses are the concentrations (mM) of surfactant at the rate maxima.

ic alcohols,[5-8,26] and they decrease slightly with increasing hydroxide ion concentration as is often found for bimolecular micellar-catalyzed reactions.

The key point is that micellized II is no more effective than CTABr in catalyzing the hydrolysis of the hexadecyl derivative I, although in bimolecular reactions of phosphate esters,[9] acyl phosphates,[27] and alkyl halides, carboxylic esters, and amides[10] micellized surfactants carrying a choline-related head group are much better catalysts than the corresponding tetraalkylammonium ions. We therefore conclude that micelles of I are not acting as general acids or bases and are not activating hydroxide ions, and therefore by inference the high reaction rates in the presence of I involve nucleophile attack upon the substrate by the alkoxide moiety of the zwitterion IV. This conclusion is supported by observation of formation of an intermediate in reactions of 2,4-dinitrochloro- and fluorobenzene in the presence of II.[28]

The simplest explanation of all the high reaction rates is in terms of nucleophilic attack by the alkoxide moiety. We could also assume that attack is by the hydroxyl group of I with IV or hydroxide ion acting as a general base. All these mechanisms lead to the same rate dependence on pH, but those involving proton transfer to a general base should generate a kinetic solvent deuterium isotope effect which is not observed in phosphate ester reactions in the presence of I.[29]

Cationic micelles increase the nucleophilicity of amines toward halonitrobenzenes and the 2,4-dinitrophenyl phosphate dianion,[30] but addition of 10^{-4} M dodecylamine to 1.5×10^{-3} M CTABr reduces the rate of reaction of I with 10^{-3} M hydroxide ion by 30%, presumably because the amine behaves as an inert organic solute in reducing the catalytic efficiency of the micelle (cf. ref 5b and 31), and there is no indication of any concerted action of hydroxide ion and the amine under these conditions.

Registry No.—I, 57016-81-6; II, 20317-32-2; III iodide, 28080-49-1; III nitrate, 57016-82-7; $AgNO_3$, 7761-88-8; p-nitrobenzoyl chloride, 122-04-3; 1-bromohexadecane, 122-82-3; 2-(dimethylamino)ethyl p-nitrobenzoate, 38152-22-6.

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