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Micellar Effects upon Spontaneous and Alkaline Hydrolysis of *t*-Butyl Phenyl Carbonate

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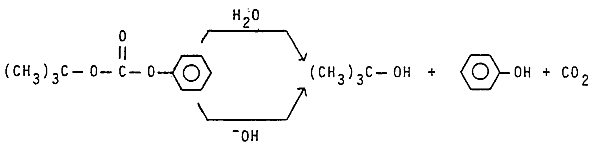
Cationic micelles of hexadecyltrimethylammonium ion HTAX (X=Cl$^-$ and OH$^-$) catalyzes the reactions of *t*-butyl phenyl carbonate with OH$^-$ and k_ψ goes through maximum with increasing [HTACl] but it continues to increase with increasing [HTAOH]. Spontaneous hydrolysis of *t*-butyl phenyl carbonate is inhibited by both cationic and anionic micelles. The second-order rate constant in micelles is smaller than that in water.

Effects of cationic micelles upon rates of bimolecular reactions have been extensively studied[1-4] and the variation in pseudo-first-order rate constants with [surfactant] has been explained quantitatively by considering the distrubution of both reagents between aqueous and micellar pseudophase and the second-order rate constant in each pseudophase.[1-7] *t*-Butyl phenyl carbonate is a convenient substrate for a study of micellar effects on the hydrolysis rate because the reaction can be easily followed spectrophotometrically in a dilute solution and its mechanism is well understood.[8-12] We studied the micellar effects upon both spontaneous hydrolysis of *t*-butyl phenyl carbonate and its reactions with hydroxide ion (Scheme 1).



Scheme 1.

The spontaneous hydrolysis was carried out in aqueous solution of hexadecyltrimethylammonium chloride (HTACl) or sodium dodecyl sulfate (SDS) while the reaction with hydroxide ion were carried out in HTACl and HTAOH, respectively.

Typically the rate constants for bimolecular reactions go through maxima with increasing [surfactant] and with constant [nucleophile] in the presence of inert surfactant counter ion.[1-8]

In the deacylation by OH$^-$ in HTACl or HTABr the rate-maxima can be ascribed to a combination of competition between OH$^-$ and the halide ion for micelle and distribution of the substrate between aqueous and micellar pseudophases.

However, if the solution contains only reactive counter ion the rate constants should become constant once all the substrate is micellar bound provided that β is constant. This behavior has been observed for reactions of hydrogen ions in micellized alkanesulfonic acids,[14] and of *N*-alkylpyridinium ions in micellized HTACN.[15] Nucleophilic reactions in the presence of HTAOH and HTAF do not fit this pattern.[5,16-18]

The aim of the present work was to study reactions of other substrates in the micellized reactive ion surfactant where the nucleophile was OH$^-$ and in HTACl with added inert counter ions.

Experimental

Material. The substrate *t*-butyl phenyl carbonate and surfactants of HTACl, SDS, and HTAOH were prepared or purified by the standard methods.[2,9,11,14] The preparation and manipulation of HTAOH were done under N_2 in the absence of CO_2.

Kinetics. The reactions were followed spectrophotometrically by using a Perkin Elmer spectrophotometer at 234 nm. All reactions were followed in water at 25.0 °C using 5×10^{-5} M substrate. The first-order rate constants, k_ψ, are in reciprocal seconds. Reactions in the absence of surfactant were carried out in a dilute solution of the nucleophile (<0.04 M) to minimize kinetic salt effects (M=mol dm^{-3}).

Results

Reactions in the Absence of Surfactant: The second-order rate constant, k_W, for the reaction of *t*-butyl phenyl carbonate with OH$^-$ at 25.0 °C was 0.013 M^{-1} s^{-1}. Added electolyte slowed down the reaction as it is expected for the reaction between ions of opposite charge (Table 1).

Reaction in the Presence of HTACl: Cationic micelles of HTACl inhibited the spontaneous hydrolysis of *t*-butyl phenyl carbonate to a large degree (Table 2), but it catalyzed the reaction with OH$^-$ and the psuedo-first-order rate constant, k_ψ, goes through maximum with increasing [HTACl] and constant [nucleophile] (Fig. 1). Added inert anions inhibited

Table 1. Salt Effects upon the Reaction of *t*-Butyl Phenyl Carbonate with Hydroxide Ion[a)]

[Salt]/M	NaCl	NaBr	KBr
0.004	1.31	1.28	1.27
0.007	1.29	1.22	1.21
0.01	1.25	1.20	1.20
0.03	1.20	1.15	1.15
0.06	1.15	1.11	1.0
0.1	1.11	0.9	0.88
0.15	1.0	0.92	0.90
0.2	0.98	0.83	0.90

a) Values of $10^4\,k_\psi$/s^{-1}, in 0.01 M NaOH at 25.0 °C and 5×10^{-5} M substrate.

Table 2. Micellar Effects upon the Spontaneous Hydrolysis of *t*-Butyl Phenyl Carbonate[a]

[surfactant]/M	HTACl	SDS
0.0	4.6	4.6
0.002	2.3(0.50)[b]	2.0(0.43)
0.004	1.85(0.4)	1.22(0.27)
0.007	1.27(0.27)	1.0(0.21)
0.01	0.97(0.21)	0.70(0.15)
0.03	0.60(0.13)	0.20(0.04)
0.06	0.20(0.043)	—

a) Values of $10^5\,k_\psi/\mathrm{s}^{-1}$, at 25.0 °C. b) Values in parenthesis are k_{rel}.

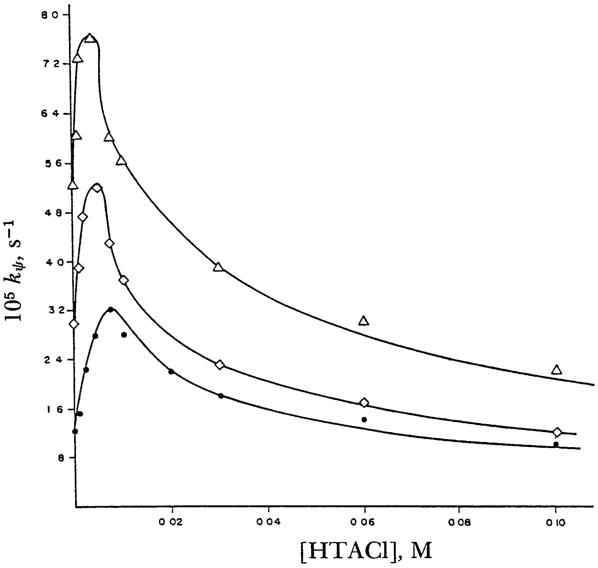


Fig. 1. Reaction of *t*-butyl phenyl carbonate with NaOH in the presence of HTACl (●) 0.01 M NaOH, (◇) 0.03 M NaOH, (△) 0.06 M NaOH.

Table 3. Effect of NaCl on the Reaction of *t*-Butyl Phenyl Carbonate with Hydroxide Ion in the Presence of HTACl[a]

[NaCl]/M	k_ψ/s^{-1}	[NaCl]/M	k_ψ/s^{-1}
0.004	44	0.06	29
0.007	40	0.1	26
0.01	36	0.15	24
0.03	32	0.2	21

a) Values of $10^5\,k_\psi/\mathrm{s}^{-1}$ in 0.03 M NaOH at 25.0 °C and 5×10^{-5} M substrate, in the presence of 0.002 M HTACl.

the reaction because they compete with the reactive anions for the positive site in the micelle[2,5,9,19] (Table 3).

Reaction in the Presence of SDS: Anionic micelles of (SDS) inhibited the spontaneous hydrolysis of *t*-butyl phenyl carbonate drastically and almost stopped the reaction. This result is similar to the effects of SDS upon the spontaneous hydrolysis of substituted benzoic anhydride[20] (Table 2).

Reaction in the Presence of HTAOH: When only reactive anions were present, k_ψ increased steadily with increasing [surfactant], added hydroxide ion increases k_ψ but only to a small extent at higher [surfactant], and at high [surfactant] or [nucleophile], k_ψ tended towards limiting values (Fig. 2). However, *t*-butyl phenyl carbonate is hydrophobic enough to be fully micellar bound at a surfactant concentration well below those corresponding to limiting values of k_ψ, and this was confirmed by HTACl effects upon the spontaneous hydrolysis of *t*-butyl phenyl carbonate (Table 2).

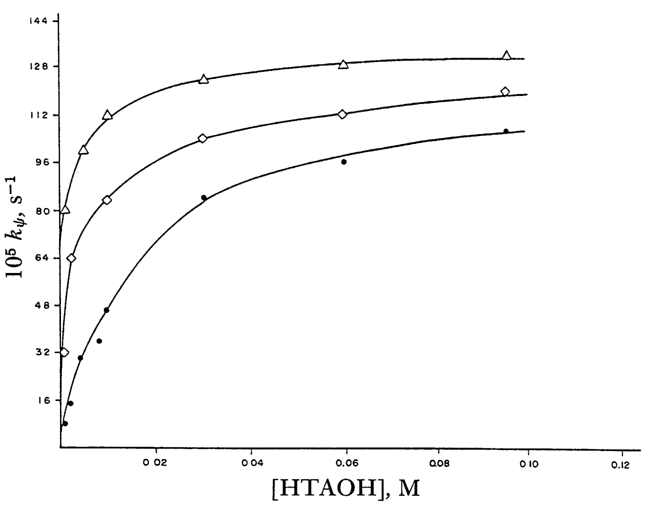
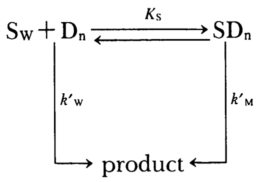


Fig. 2. Variation of the pseudo first-order rate constant, k_ψ, for reaction of *t*-butyl phenyl carbonate in HTAOH. (●) in the absence of NaOH, (◇) with added 0.01 mol dm^{-3} NaOH, (△) with added 0.02 mol dm^{-3} NaOH.

Discussion

Micelles of HTACl and SDS inhibit the spontaneous hydrolysis of *t*-butyl phenyl carbonate and the variations of rate constants with the nature and concentration of the surfactants are illustrated by values of k_{rel} which is the ratio of the rate constant in the micellar solution to that in water which is <1 (Table 2). The effect of micellar charge is given by k^+/k^-, where k^+ is the rate constant in the cationic micelle of HTACl and k^- is that in the anionic micelles of SDS for fully micellar bound substrate, the ratio=4. In considering micellar effects upon reactions of hydroxide ion with *t*-butyl phenyl carbonate one finds it necessary to take into account posible competition



Scheme 2.

between Cl^- and OH^- for the micelle. It is the simplest therefore to consider first reactions in the absence of Cl^- i.e. in HTAOH.

The kinetic analysis follows Scheme 2[21] where S is the substrate, D_n is the micellized surfactant, K_S is the binding constant of S to the micelle written in terms of micellized surfactant,[22] and k'_W and k'_M are first-order rate constants in aqueous and micellar pseudophase, respectively, given by[23,24]

$$k'_W = k_W[OH^-_W] \tag{1}$$

$$k'_M = k_M m^S_{OH} = k_M[OH_M]/[D_n]. \tag{2}$$

In Eqs. 1 and 2, k_W and k_M are second-order rate constants but k_M is defined in terms of the mole ratio of bound OH^- to micellized surfactant.[23,24] These equations give Eq. 3 for the first-order rate constant k_ψ.[23]

$$k_\psi = k_W[OH^-_W] + k_M K_S[OH^-_M]/(1+K_S[D_n]). \tag{3}$$

The quantities in squared brackets are molarities in terms of solution volume.

For mixtures of NaOH and HTACl we write the distribution of OH^- between water and micelles in terms of Eq. 4.[2,19,23,24]

$$K^{OH}_{Cl} = [OH^-_W][Cl^-_M]/[OH^-_M][Cl^-_W]. \tag{4}$$

Equation 4 predicts that the fraction β of micellar head groups neutralized by counter ions is constant, i.e. it could be described in terms of ion-exchange model.[2] The parameter in Eqs. 3 and 4 can be estimated by fitting experimental rate constant surfactant-profiles to these equations (Fig. 1) (Table 4).[24] However, the assumption of constant β fails when the reactive counter ions are small and of high charge density, e.g., OH^- or F^-. So the distribution of counter ion OH^- between aqueous and micellar pseudophases in the reactive counter ions surfactant can be fitted by Eq. 5, i.e. to a mass action model.[9,18,25]

$$K'_{OH} = [OH^-_M]/[OH^-_W]([D_n]-[OH^-_M]). \tag{5}$$

Equation 5 predicts that fraction β will increase with increasing [surfactant]. Equations 3 and 5 were combined by a single computer program which allowed us to simulate the variation of k_ψ with [HTAOH] or [NaOH] and we were able to fit all the rate data for reactions in the surfactants, and with added salt (Fig. 2) using the parameters given in Table 4.

Table 4. Rate and Equilibrium Constants for Reactions in the Presence of HTACl or HTAOH[a]

Medium	$10^4\ k_M/s^{-1}$	K_s(M)	K^{OH}_{Cl}	K_{OH}
HTACl+0.01 M NaOH	4.8	830	4	
HTACl+0.03 M NaOH	4.9	860	4	
HTACl+0.06 M NaOH	5.0	860	4	
HTAOH	6.3	800		60
HTAOH+0.01 M NaOH	6.5	860		60
HTAOH+0.02 M NaOH	6.7	860		60

a) At 25.0 °C and cmc=3×10^{-3} and 7×10^{-4} M for HTACl and HTAOH, respectively. Added NaOH might lower the cmc.

The rate constants k_M and k_W have different dimensions but we convert k_M, s^{-1} into k^m_2, $M^{-1}s^{-1}$ assuming that the reaction occurs in the micellar Stern layer whose molar volume is 0.14 L. So that,[2,26,27]

$$k^m_2 = 0.14\ k_M. \tag{6}$$

Figure 1 illustrates the fit of experimental and calculated data for the reactions of hydroxide ion with *t*-butyl phenyl carbonate in HTACl and the second-order rate constant k^m_2 is 7.4×10^{-5} $M^{-1}s^{-1}$. Figure 2 illustrates the fit for the reaction in HTAOH in the absence of inert counter ions and with added NaOH, i.e. with no ionic competition for the cationic micelles.[14,15,25] Under these conditions k_ψ increases steadily to a constant value as substrate becomes fully micellar bound, and the values of k^m_2 is 8.5×10^{-5} $M^{-1}s^{-1}$.

Calculated k^m_2 from these experiments are similar to those in mixture of HTACl and NaOH. The (small) difference between k^m_2 in the different surfactants are probably due to our assuming the same volume element of the reaction for each surfactant. The second-order rate constant in the micellar pseudophase k^m_2 is smaller than that in water k_W by a factor of 160.

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