Effect of Cationic Micelles on the *ElcB* Mechanism of the Hydrolysis of Substituted *p*-Nitrophenyl Acetate

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Summary The hydrolysis of $XCH_2CO_2C_6H_4NO_2$-*p* catalysed by cetyltrimethylammonium bromide experiences a much larger micellar effect with $X=O_2NC_6H_4$ and PhS than with $MeOC_6H_4$ and PhO, in accord with the change in acidity of CH_2 group and suggesting a change of mechanism from ordinary addition–elimination under non-micellar conditions to an *ElcB* mechanism under micellar conditions.

The micellar catalysed reactions of *p*-nitrophenyl esters of carboxylic acids with hydroxide ion have been extensively investigated.[1] All the evidence so far available seems to be consistent with a mechanism of fast incorporation of ester into the micelle followed by slow rate-determining attack of hydroxide ion on the ester carbonyl group. The rate-accelerating micellar effect, however, is rather small for simple cationic surfactants: for example, the cetyltrimethylammonium bromide (CTABr) micelle accelerates the rate 2 fold for acetate and 5 fold for hexanoate.[2] We have now observed unusually large micellar effects of CTABr on the hydrolysis of the substituted *p*-nitrophenyl acetates (**1**)—(**4**) when the substituent X can stabilize an α-carbanion.

$XCH_2CO_2C_6H_4NO_2$-*p*
(**1**), X = *p*-$O_2NC_6H_4$
(**2**), X = *p*-$MeOC_6H_4$
(**3**), X = PhS
(**4**), X = PhO

Plots of pseudo-first order rate constants (k_{obs}) *vs.* CTABr concentration gave the usual saturation kinetics[1] for all the esters examined, to give the non-micellar (k_0) and micellar rates (k_ψ, plateau rate). The substituent effects on these k_0 and k_ψ values were very different, as illustrated by the rates for the four esters (**1**)—(**4**). The k_0 ($\times$ 10^4 s^{-1}) values were 33 (**4**), 14·6 (**3**), 8·33 (**1**), and 1·88 (**2**), in decreasing order of electron-withdrawing effect of X,[3] and the k_ψ ($\times$ 10^4 s^{-1}) values were 2490 (**1**), 287 (**3**), 41·7 (**4**), and 3·33 (**2**) (pH 8·99, 25 °C, [CTABr] = 9×10^{-4}M). Thus the

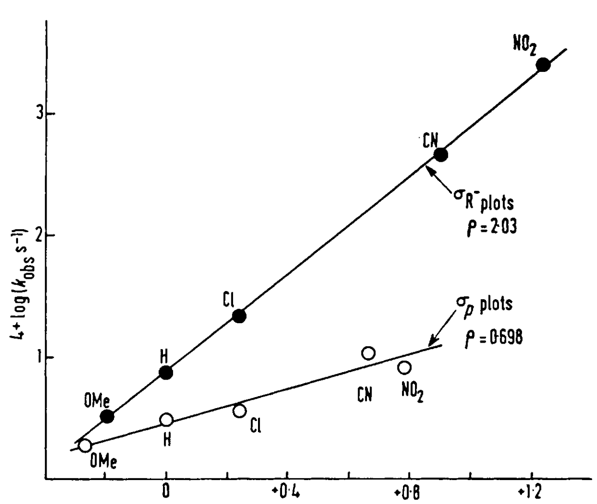

Figure. Hydrolysis of *p*-$XC_6H_4CO_2C_6H_4NO_2$-*p* esters: ○ non-micellar rates (k_0); ● micellar rates (k_ψ); [CTABr] = 9×10^{-4}M; pH 8·99; 25 °C.

micellar effect (k_ψ/k_0) is unusually large for (**1**) and (**3**). It was also found that the pH-log k_ψ profiles for (**1**) and (**3**) indicate rate plateaus at around pH 8 and 10, respectively. The corresponding profiles for (**2**) and (**4**) and the pH–log k_0 profiles for the four esters did not indicate such a rate plateau but showed a linear increase of log k_0 up to pH 11. Such rate plateaus at higher pH may suggest the formation of carbanions.[4] The formation of carbanion at the methylene group with a good leaving *p*-nitrophenoxy group would lead to a change in the mechanism of hydrolysis from an ordinary addition–elimination mechanism under non-micellar conditions to an *E*1*cB* mechanism under micellar conditions.[5] This appears to be further substantiated by different substituent effects on the k_0 and k_ψ rates in the hydrolysis of *p*-substituted benzyl *p*-nitrophenyl esters [including (**1**) and (**2**)] as shown in the Figure; the log k_0 values vary linearly with Hammett σ_p constants[6] to give $\rho(\sigma) = 0{\cdot}698$, while the log k_ψ values vary linearly with σ_R^- constants[7] to give $\rho(\sigma) = 2{\cdot}03$. Thus the micellar reaction seems to take place by an *E*1*cB* mechanism involving carbanion and keten intermediates.[5]

A larger micellar effect for activated esters appears to be consistent with our previous observation that the ionization of the allyl methylene proton of sulphonium salts experiences a much larger micellar effect than that of the corresponding methyl protons.[8] The carbon acidity of 4-nitrophenylacetonitrile has also been shown to experience a large micellar effect in a CTABr micelle.[9] All these facts suggest a more stabilization for a more delocalised carbanion occurring in a micellar phase of cationic surfactant.

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[1] J. H. Fendler and E. J. Fendler, 'Catalysis in Micellar and Macromolecular Systems,' Academic Press, New York, 1975.

[2] L. R. Romsted and E. H. Cordes, *J. Amer. Chem. Soc.*, 1968, **90**, 4404.

[3] S. Oae, W. Tagaki, K. Uneyama, Y. Ikeda, and I. Minamida, *Tetrahedron*, 1968, **24**, 5293.

[4] Both *p*-nitrophenyl and phenylthio groups are known to stabilize α-carbanions: D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1975; S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, 1964, **20**, 417; S. Oae, W. Tagaki, K. Uneyama, and I. Minamida, *ibid.*, 1968, **24**, 5283. Preliminary experiments indicated deuterium incorporation into the starting esters (**1**) and (**3**) under heterogeneous conditions (suspension of ester in D_2O containing CTABr micelle).

[5] An *E*1*cB* mechanism has already been reported for the hydrolysis of some activated esters under non-micellar conditions: A. Williams and K. T. Douglas, *Chem. Rev.*, 1975, **75**, 627; B. Holmquist and T. C. Bruice, *J. Amer. Chem. Soc.*, 1969, **91**, 2993, 3003; R. F. Pratt apd T. C. Bruice, *ibid.*, 1970, **92**, 5956.

[6] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[7] A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 1961, **388**; σ_p was used for Cl.

[8] T. Okonogi, T. Umezawa, and W. Tagaki, *J.C.S. Chem. Comm.*, 1974, **363**.

[9] M. J. Minch, M. Giaccio, and R. Wolff, *J. Amer. Chem. Soc.*, 1975, **97**, 3766.