# Catalysis in Ester Hydrolysis by a Cationic Detergent Containing an Imidazole Group at the Polar Head

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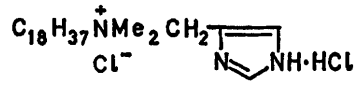
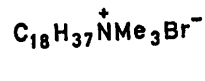
*Summary* 4-(Dimethylstearyl)methylimidazolylammonium chloride (I) was found to be an effective catalyst in the hydrolysis of *p*-nitrophenyl acetate.

MICELLAR catalysis by detergents as a model for enzymatic catalysis has drawn considerable interest in recent years,[1] *e.g.* the catalysis by a mixed micellar system of a 1:1

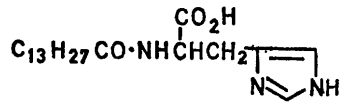
complex of myristoyl histidine and cetyltrimethylammonium bromide of the hydrolysis of *p*-nitrophenyl esters.[2] A characteristic feature of this catalyst is that it gives a faster rate of acylation of imidazole nitrogen than a catalyst containing *N*-acetylhistidine. However, deacylation is so slow that the catalyst is no longer effective in the presence of an excess of substrate.



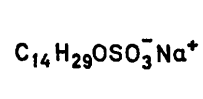
(I)



(III)



(II)

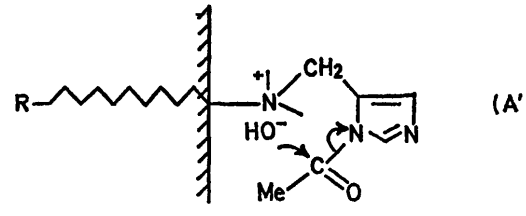


(IV)

A=(I) B=(II)+(III) C=(I)+(IV)

We report that deacylation is accelerated when the imidazole group is a part of the polar head groups of a cationic detergent. Systems A—C have been examined for the hydrolysis of *p*-nitrophenyl acetate (PNPA). Compound (I) was prepared by treating 4-chloromethylimidazole with dimethylstearylamine in benzene, to yield an amorphous powder which melts at 65° forming liquid crystals which decompose at 178°; elemental analysis and the n.m.r. spectrum ($D_2O$) confirmed the structure. It is stable during the hydrolysis although it was decomposed by a hot alkaline solution. The critical micellar concentration of (I) under the kinetic conditions (Figure) was $1\cdot9 \times 10^{-5}$ M.[3]

The formation of *p*-nitrophenol was initially rapid, then slow, with system B[2] (with an excess of substrate[3,4]), whereas with system A the same pseudo first-order rate constant was observed throughout the whole reaction period. The initial rate was *ca.* 3 times slower for A than for B at pH 7. However, when the pH was raised to 8, an eightfold increase of the rate was observed for A while only a 1·2 fold increase was observed for B. The pH–rate profile for the initial reaction was a sigmoid curve for B,[3] while for A the reaction was first-order with respect to [OH⁻]. Representative rate data with† [Im] = $5 \times 10^{-4}$M [PNPA] = $1 \times 10^{-4}$M, at 25° are as follows: $k_{obs} \times 10^3$ s$^{-1}$; A, 1·10 (pH 7), 8·8 (pH 8); B, 3·00 (pH 7), 3·70 (pH 8); imidazole, 0·25 (pH 8).



(A')

Micellar surface

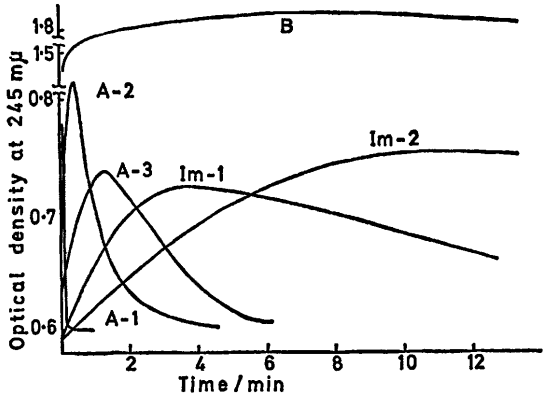



FIGURE. *Formation and the decomposition of acylimidazole intermediate in the hydrolysis of* p-*nitrophenyl acetate* (PNPA) *with phosphate buffer* 0·05 M, [PNPA] $1\cdot58 \times 10^{-4}$ M [Imidazole] $5 \times 10^{-3}$ M and at 25°. pH *values for the systems are:* A-1, A-2, A-3 = 9, 8, 7; B(III/II = 10) = 8; Im-1, Im-2 = 8, 7.

The Figure shows the formation of an acylimidazole intermediate ($\lambda_{max}$ 245 nm)[5,6] in each of the hydrolyses catalysed by A, B, and imidazole. The catalysis by A has a special feature in that both the formation and the decomposition of acylimidazole intermediate are accelerated by increasing pH. Presumably the positive charge on the micellar surface of A causes the ionization of neutral imidazole to a more nucleophilic imidazole anion, and hydroxide ion concentrated near the positive charge causes a rapid deacylation [as in (A')]. Supporting evidence is the loss of catalytic activity of (I) in system C where charge neutralization may take place. A high hydroxide ion concentration is also expected on a positive micellar surface of B, but not at the active site because of the charge neutralization between the anionic carboxyl and the positive ammonium groups.

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† B: (III/II = 5); for other conditions, see Figure 1.

[1] E. H. Cordes and R. B. Dunlap, *Accounts Chem. Res.*, 1969, **2**, 329.
[2] C. Gitler and A. Ochoa-Solano, *J. Amer. Chem. Soc.*, 1968, **90**, 5004.
[3] Determined by a dye method using eosine as the complexing agent, M. L. Corrin and W. D. Harkins, *J. Amer. Chem. Soc.*, 1947, **69**, 679.
[4] (a) T. Spencer and J. M. Sturtevant, *J. Amer. Chem. Soc.*, 1959, **81**, 1874; (b) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanism," Benjamin, New York, 1966, vol. 1, p. 215.
[5] W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, 1969, ch. 2.
[6] M. L. Bender and V. W. Turnquest, *J. Amer. Chem. Soc.*, 1957, **79**, 1656.