

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

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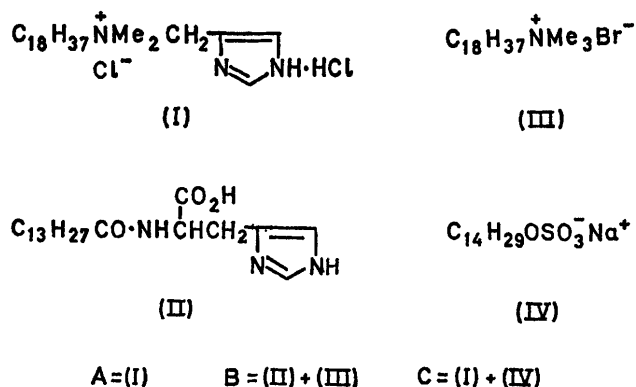
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Summary 4-(Dimethylstearyl)methylimidazolylammonium chloride (I) was found to be an effective catalyst in the hydrolysis of *p*-nitrophenyl acetate. MICELLAR catalysis by detergents as a model for enzymatic catalysis has drawn considerable interest in recent years,¹ *e.g.* the catalysis by a mixed micellar system of a 1:1

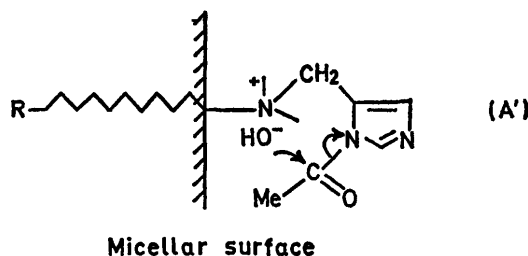
complex of myristoyl histidine and cetyltrimethylammonium bromide of the hydrolysis of *p*-nitrophenyl esters.² A characteristic feature of this catalyst is that it gives a faster rate of acylation of imidazole nitrogen than a catalyst containing *N*-acetylhistidine. However, deacylation is so slow that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

zole 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 (D₂O) 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 1.9×10^{-5} M.³

The formation of *p*-nitrophenol was initially rapid, then slow, with system B² (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] = 5×10^{-4} M [PNPA] = 1×10^{-4} M, at 25° are as follows: $k_{\text{obs}} \times 10^3$ 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).



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-chloromethylimida-



The Figure shows the formation of an acylimidazole intermediate (λ_{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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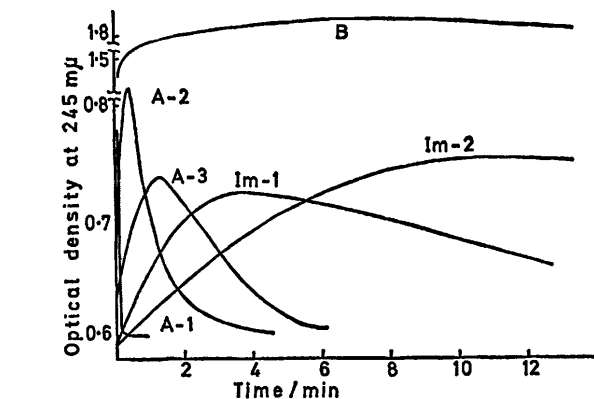


FIGURE. Formation and the decomposition of acylimidazole intermediate in the hydrolysis of *p*-nitrophenyl acetate (PNPA) with phosphate buffer 0.05 M, [PNPA] 1.58×10^{-4} M [Imidazole] 5×10^{-3} M and at 25°. pH values for the systems are: A-1, A-2, A-3 = 9, 8, 7; B(III/II = 10) = 8; Im-1, Im-2 = 8, 7.

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

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⁶ M. L. Bender and V. W. Turnquest, *J. Amer. Chem. Soc.*, 1957, **79**, 1656.