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STRUCTURAL EFFECT OF MIXED MICELLES IN THE DEACYLATION OF *p*-NITROPHENYL ESTERS BY SPECIFIC HYDROXAMIC ACIDS

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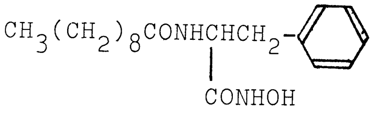
In the presence of cationic surfactants, the deacylation rate of *p*-nitrophenyl esters by 2-hexyldecanohydroxamic acid which possesses the branched alkyl chains was larger than those by decanohydroxamic acid or the hydroxamic acid of N-decanoylphenylalanine which has the straight alkyl chain.

Reactions performed in the presence of ionic micelles are influenced by electrostatic and hydrophobic interactions between a substrate and a surfactant aggregate.$^{1)}$ The catalytic activity of comicelles formed with hydroxamic acids having a hydrophobic alkyl chain and hexadecyltrimethylammonium bromide (CTAB) in the ester deacylation has recently drawn considerable attention.$^{2-4)}$

In this work, the authors carried out systematic experiments to characterize the micellar catalysis by surfactants (CTAB, CEAB, and CBzAC),$^{5)}$ which have alkyl segments of the identical chain length and different head groups, in the deacylations of *p*-nitrophenyl carboxylates (S_n)$^{6)}$ by decanohydroxamic acid (1), hydroxamic-acid of N-decanoylphenylalanine (2),$^{7)}$ and 2-hexyldecanohydroxamic acid (3)$^{8)}$ in alkaline media.

$CH_3(CH_2)_8CONHOH$

1



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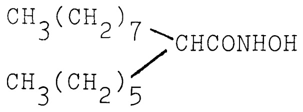

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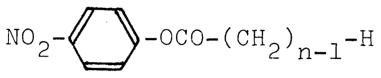


S_n(n=2,4,6,10,12, and 16)

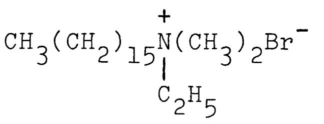
$CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_3Br^-$

CTAB

Table 1. k_{cat}($sec^{-1}M^{-1}$) Values in the Deacylations of S_n by Hydroxamic Acids and Surfactants at pH 9.06[a)]

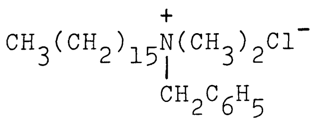
Nucleophile	S_2	S_4	S_6	S_{10}	S_{12}	S_{16}
1 + CTAB	1033	1296	1554	2292	1383	451
1 + CEAB	1364	1368	2129	2322	2419	558
1 + CBzAC	987	1058	1710	2213	1827	1699
2 + CTAB	355	256	331	352	318	254
2 + CEAB	587	408	481	541	495	380
2 + CBzAC	706	486	625	635	636	654
3 + CTAB	1960	2610	3930	3815	3659	1524
3 + CEAB	1720	2106	3487	3207	3043	1885
3 + CBzAC	1647	2039	2954	3206	3068	3379

a) At 31 °C in 0.083 M tris(hydroxylmethyl)aminomethane (Tris) buffer (0.083 M KCl); solvent, (1:9 v/v) CH_3CN-H_2O; 1.0×10^{-4} M of nucleophile, 5.0×10^{-5} M of ester, 5.0×10^{-3} M of CTAB, CEAB, and CBzAC. k_{cat} values were evaluated from $(k_{obs}^{cat}-k_{obs}^{OH})$/[hydroxamic acid unit], where k_{obs}^{cat} and k_{obs}^{OH} denote the rate constants in the presence and absence of the nucleophile, respectively.



$CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_2Br^-$ with C_2H_5 on N

CEAB



$CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_2Cl^-$ with $CH_2C_6H_5$ on N

CBzAC

The pseudo-first-order deacylations were followed spectrophotometrically by taking notice of the phenolate anion formation, and the second-order rate constants, k_{cat}, obtained are summarized in Table 1.

As shown in Table 1, the catalytic constant for the S_n (n=2-12) deacylations by **1** + CEAB was slightly larger than those by **1** + CTAB and **1** + CBzAC. On the other hand, the rate enhancement in the S_n (n=2-16) deacylations by **2** + CBzAC was superior to that by **2** + CTAB (or CEAB). Furthermore, the catalytic activity of **3** + CTAB for the S_n (n=2-12) deacylations was the largest among the comicellar systems of **3** + surfactants. It is deduced, therefore, that the molecular arrangement of **1** + CEAB, **2** + CBzAC, or **3** + CTAB at the micellar surface would be most suitable for the S_n (n=2-12) deacylations in the respective comicellar systems. It is noticeable here that **3** + surfactants offered the largest rate enhancement in the S_n deacylations among the systems of nucleophiles (**1**, **2**, and **3**) + surfactants. These results suggest that the hydrophobic interaction between the branched alkyl chains in nucleophilic **3** and surfactants is somewhat strong in comparison with that between the straight alkyl chain in **1** (or **2**) and surfactants. The selective rate enhancement was observed in the specific S_n deacylations by the respective comicellar catalysts (viz., S_{10} by **1** + CTAB, S_2 by **2** + CBzAC, S_{16} by **3** + CBzAC).

The log k_{cat} values are plotted against pH in Figure 1. As Figure 1 indicates, the $\mathrm{p}K_a$ values of the hydroxamic acids were not influenced by changing S_n species (n=2, 10, and 16). The rate enhancement in the S_n deacylations by **1** in the presence of the surfactants was realized to be more effective than that in the absence of the surfactants (viz., $\mathrm{p}K_a$(**1**)$\geq$10 and $\mathrm{p}K_a$(**1** + surfactants)=9.1-9.2). It is of interest that **3** + CTAB and **2** + CTAB showed lower $\mathrm{p}K_a$ values (8.8 and 8.6, respectively), though the catalytic constants of the former were larger than those of the latter.

In conclusion, the nucleophilic **3**, which has the hydrophilic moiety (hydroxamic acid) bound to the branched hydrophobic portion, in the presence of cationic surfactants was apparently similar to the framework of lecithin, and it is noteworthy that **3** accelerated the deacylation of the specific substrate markedly in the presence of the cationic surfactants (viz., S_6-S_{12} by **3** + CTAB (or CEAB) and S_{16} by **3** + CBzAC). These efficient structural effects of the comicelles are attributable to the hydrophobic interaction and electrostatic charge attraction between the anionic **3** and cationic surfactants and are due to the difference of the arrangement of the reactants on the comicellar surface.

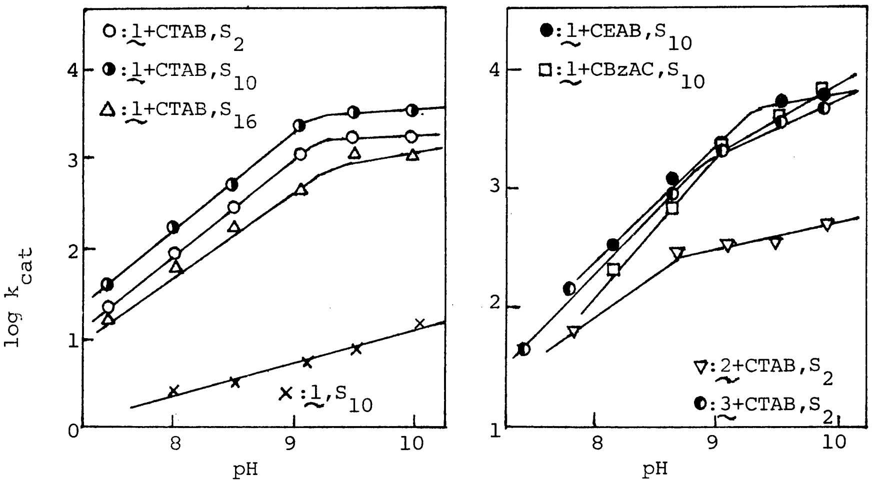


Figure 1 pH Dependence of the k_{cat} value.

References and Notes

1) T. C. Bruice, J. Katzhendler, and Leo R. Fedor, J. Am. Chem. Soc., 90, 1097 (1968).

2) I. Tabushi, Y. Kuroda, and S. Kita, Tetrahedron lett., 1974, 643.

3) T. Kunitake, S. Shinkai, and Y. Okahata, Bull. Chem. Soc. Jpn., 49, 540 (1976).

4) R. Ueoka, K. Shimamoto, Y. Maezato, and K. Ohkubo, J. Org. Chem., 43, 1815 (1978).

5) Commercially available CTAB, CEAB, and CBzAC were used after recrystallizations from anhydrous ethanol-ether, and their critical micelle concentrations were determined by the usual conductivity method under the reaction conditions (31 °C, pH 9.06, 0.083 M Tris-KCl, (1:9 v/v) CH_3CN-H_2O)): CTAB=1.0×10^{-3} M, CEAB=2.0×10^{-4} M, CBzAC=1.1×10^{-4} M.

6) They were prepared by the method described in ref. (4) and satisfactory elemental analyses were obtained.

7) The nucleophile **2** was prepared from N-decanoylphenylalanine and hydroxylamine by the method described in A. Winstein and E. T. Mazza, J. Polym. Sci., Polym. Chem. Ed., 13, 2019 (1975) and satisfactory elemental analyses were obtained.

8) The nucleophile **3** was prepared from 2-hexyldecanoyl chloride and hydroxylamine and satisfactory elemental analyses were obtained.

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