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Micellar Effect of Lauryldimethylsulfonium Halides on the Hydrolysis of *p*-Nitrophenyl Decanoate

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Synopsis. Micellar effects of lauryldimethylsulfonium chloride, bromide, and iodide on the hydrolysis of *p*-nitrophenyldecanoate were found to be very similar to those of the corresponding lauryltrimethylammonium halides.

Ester hydrolysis catalyzed by cationic micelles of quaternary ammonium salts has been extensively investigated in recent years.[1] In most cases, the rate of hydrolysis is first order with respect to hydroxide ion. Meanwhile, we have observed,[2] previously, that the rate of base catalyzed H–D exchange reaction of the methyl group of lauryldimethylsulfonium halides is non-linear with respect to the concentration of hydroxide ion under micellar conditions, but follows to a Michaelis-Menten type saturation kinetics, and we have suggested that the binding of hydroxide ion occurs on a cationic micellar surface prior to the hydrogen abstraction. Although such a difference in the behavior of hydroxide ion between ester hydrolysis and H–D exchange reaction is probably due to different ranges of hydroxide ion concentration which is much higher for the latter than for the former reaction, another possibility is due to some difference in micellar properties between ammonium and sulfonium salts. Incidentally, the micellar effects of sulfonium salts on the ester hydrolysis has little been investigated. Therefore we have compared the micellar effects of lauryltrimethylammonium and lauryldimethylsulfonium halides on the hydrolysis of *p*-nitrophenyl decanoate.

Results and Discussion

The rates of hydrolysis were followed by a conventional spectrophotometric determination of *p*-nitrophenol liberated. The dependency of the rates on detergent concentration is shown in Fig. 1. The Figure indicates typical micellar effects: 1) The rates increase rapidly by increasing detergent concentration near the CMC[1,3] and reach to a maximum, then decrease gradually by further increase of detergent. 2) The rates are affected markedly by the counter anion (X) and increase in the order of X=I<Br<Cl. These two trends are almost the same for each series of sulfonium and ammonium salts. The effects of added salts on the rates are shown in Table 1. The rate of sulfonium chloride observed in the absence of KI was reduced to one fifth by the addition of a half molar amounts of KI over the detergent concentration. The rate of the sulfonium iodide is also reduced by the addition of KCl, but the extent of rate reduction is very small. These salt effects appears to be essentially the same as observed in the micellar effects of quaternary ammonium salts.[4]

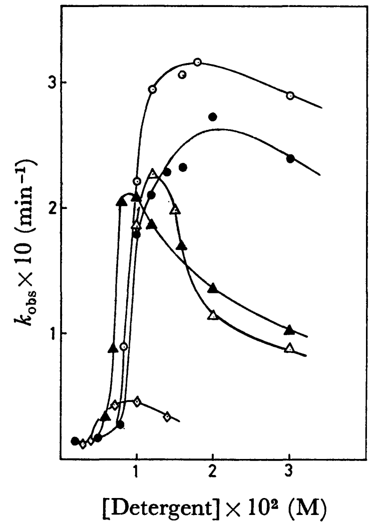

Fig. 1. Plots of k_{obs} *vs.* detergent concentration: Ester, 1×10^{-5}M; pH 10.1 (Na_2CO_3-$NaHCO_3$ buffer, 5×10^{-3}M), 25 °C.
○: n-$C_{12}H_{25}N^+(CH_3)_3Cl^-$, ●: n-$C_{12}H_{25}S^+(CH_3)_2Cl^-$,
△: n-$C_{12}H_{25}N^+(CH_3)_3Br^-$, ▲: n-$C_{12}H_{25}S^+(CH_3)_2Br^-$,
◇: n-$C_{12}H_{25}S^+(CH_3)_2I^-$.

TABLE 1. SALT EFFECT ON THE HYDROLYSIS OF *p*-NITROPHENYL DECANOATE (1×10^{-5}M) CATALYZED BY n-$C_{12}H_{25}S^+(CH_3)_2X^-$ (X=I; 1×10^{-2}M, X=Cl; 2×10^{-2}M): pH 10.1 (Na_2CO_3–$NaHCO_3$ buffer; 5×10^{-3}M), 25°

X=I		X=Cl	
KCl($\times 10^2$M)	k_{obs}(min^{-1})	KI($\times 10^3$M)	k_{obs}(min^{-1})
0	4.57×10^{-2}	0	2.73×10^{-1}
3	3.82×10^{-2}	2	1.90×10^{-1}
5	3.33×10^{-2}	4	1.58×10^{-1}
10	3.01×10^{-2}	10	5.06×10^{-2}

The dependency of the rates on hydroxide ion concentration was also examined. For all the salts shown in Fig. 1, the plots of $\log (k_{obs}-k_o)$ *vs.* $\log [OH^-]$ gave straight lines (slope=1.0) up to $[OH^-]=10^{-2}$ M, and no saturation phenomenon as observed in the H–D exchange reaction was detected. It was difficult to use more higher base concentration as in the H–D exchange reactions ($[OH^-]=0.1$—0.2 M)[2] because the rates become too fast to measure by the present method.

The above results indicate that long chain alkyl sulfonium and ammonium salts behave quite similarly in the hydrolysis of *p*-nitrophenyl decanoate.

Experimental

Materials. *p*-Nitrophenyldecanoate was prepared by the method of Bodansky,[5] mp 35 °C (lit,[6] 35—35.7 °C).

Lauryldimethylsulfonium halides, $n\text{-}C_{12}H_{25}S^{+}(CH_3)_2X^{-}$, were reported previously:[2] iodide, mp 87 °C; bromide, mp 68—70 °C; chloride, mp 64—66 °C.

Lauryltrimethylammonium halides: bromide, mp 243 °C (lit,[7] 243—244 °C); chloride, mp 247 °C (lit,[8] 247 °C).

Kinetics were performed spectrophotometrically with Hitachi 124 spectrophotometer according to our previous method.[9] The pH of the reaction mixture was determined with Hitachi-Horiba pH meter (F-7DE).

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3) The CMC values of $C_{12}H_{25}S^{+}(CH_3)_2X^{-}$ in pure water are; 1.65×10^{-2} M (X=Cl), 1.14×10^{-2} M (X=Br), and 0.689×10^{-2} M (X=I).

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