DAEHAN HWAHAK HWOEJEE
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계면활성제 용액속에서의 화학반응(제 2 보). 카르복시산 에스테르의 가수 분해 반응에 미치는 2-알킬벤즈이미다졸-5-술포네이트의 친핵적 및 미셀효과

洪永錫† · 金政培 · 朴熙鉉 · 李大龍
계명대학교 자연과학대학 화학과

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Chemical Reactions in Surfactant Solutions(II). Nucleophilic and Micellar Catalyses of Sodium 2-Alkylbenzimidazole-5-sulfonates on Hydrolyses of Carboxylic Esters in Aqueous and CTABr Solutions

Young Seuk Hong†, Jeung Bae Kim, Hee Hyun Park, and **Dae Ryong Lee**
Department of Chemistry, College of Natural Science, Keimyung University, Daegu 704-200, Korea

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요 약. CTABr 미셀용액 속에서의 2-alkyl benzimidazole(R-BI) 및 soduim 2-alkylbenzimidazole-5-sulfonate(R-$BISO_3Na$)에 의해 추진되는 p-nitrophenylcarboxylic ester(p-NPCE)들의 가수분해반응에 대한 미셀효과를 다루었다. 이들 반응은 각각 BI 및 $BISO_3Na$에 의해 추진되는 반응의 속도보다 현저히 감소하고, 알킬기가 methyl에서 heptyl로 길어질수록 감소의 정도가 더욱크다. 이것은 CTABr을 포함하지 않는 수용액속에서의 $BISO_3Na$와 R-$BISO_3Na$에 의한 가수분해 반응속도가 별차이가 없음을 감안 할 때, 미셀의사층(micellar pseudophase) 내에서 이들 친핵체의 알킬기가 입체장해(steric hindrance)로 작용하기 때문이다. 이것은 수용액과 미셀용액 속에서의 반응의 측정된 활성화에너지($\Delta H^{\neq}$, $\Delta G^{\neq}$ 및 $\Delta S^{\neq}$)의 값과도 정성적으로 일치하고 있다. 한편, nonyl 기에서 pentadecyl기 까지의 긴 알킬기를 갖고 있는 R-$BISO_3Na$는 그것의 imidazole 부분(BI moiety)이 친핵체로 작용할 뿐 아니라, 이들은 CTABr을 포함하지 않는 수용액속에서 미셀을 형성하고, 그 결과 기질인 p-NPCE를 쉽게 수용하여 반응속도를 촉진시키는 것으로 판단된다. R-$BISO_3Na$에 의한 이들 p-NPCE들의 가수분해반응의 mechanism을 알기 위하여 중수소 동위원소효과(kinetic isotope effect)를 측정하였다. k'_{H_2O}/k'_{D_2O}값이 약 2.5~3.2의 범위로서, 이 값은 R-$BISO_3Na$가 친핵체로만 작용한다고 보기에는 너무 높고, 일반염기로 작용한다고 보기에는 너무 낮다. 따라서 CTABr 미셀용액 속에서의 이 반응은 이 두 mechanism에 의해 동시적으로 진행된다고 생각된다.

ABSTRACT. This study deals with micellar effects on hydrolyses of p-nitrophenyl carboxylic esters (p-NPCE) mediated by 2-alkylbenzimidazole(R-BI) and sodium 2-alkylbenzimidazole-5-sulfonate(R-$BISO_3Na$) in aqueous and CTABr solutions. The reactions mediated by R-BI and R-$BISO_3Na$ in micellar solutions are obviously slower than those by benzimidazole(BI) and sodium benzimidazole-5-sulfonate($BISO_3Na$) respectively, and the reaction rates were decreased with increase of lengths of alkyl groups. This presents a striking contrast to the reactions in aqueous solutions without added CTABr, of which the reaction rates are on approximately same levels. It seems due to steric effect of alkyl groups fo R-BI and R-$BISO_3Na$ in the Stern layer of micelle, and it is supported by measured activation parameters($\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$) of the reactions in aqueous and micellar solutions. In addition to nuc-

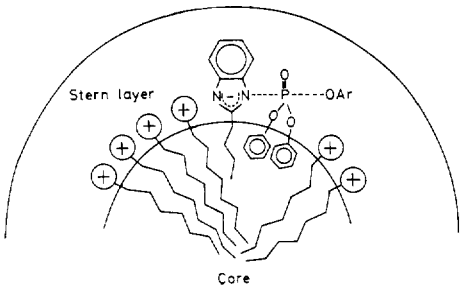
leophilic ability of benzimidazole(BI) moiety of R-BISO$_3$Na on the reactions, these compounds with long alkyl groups(nonyl to pentadecyl) which form a micelle of themselves increase the reaction rates due to their micellar catalyses in aqueous solutions, not including CTABr. We measured the isotope effects to elucidate the mechanism of hydrolyses of p-nitrophenyl carboxylic esters, and the relative first order rate constant(k'_{H_2O}/k'_{D_2O}) are on range of 2.5~3.2. This range is too high to conclude that the hydrolyses of p-NPA mediated by various R-BISO$_3$Na proceed by nucleophilic mechanism. In other words, the reactions are assumed to proceed in part by general basic one, as compared with the reaction catalyzed by imidazole(IM) in aqueous solution.

INTRODUCTION

In 1981, C.A. Bunton and Y.S. Hong et al made studies[1,2] on dephosphorylation of p-nitrophenyldiphenylphosphate(p-NPDPP) mediated by benzimidazolide and naphth- 2, 3-imidazolide ions (BI^- and NI^-) in micellar solution of cetyl trimethyl ammonium bromide(CTABr) and in solutions of the phase transfer catalysts, ethyl tri-n-octyl ammonium bromide and mesylate (TEABr and TEAMs, respectively). In these reaction they gave evidence that the imidazolide ions act as nucleophiles, not as general bases.

Recently the authors discussed depholsphorylation of p-NPDPP mediated by some 2-alkylbenzimidazolide ions(R-BI^-) in CTABr solution[3], in which nucleophilicity and steric effect of R-BI^- were varied by a change of their alkyl groups. In spite of a sharp increase of the binding constants(Ks) of the nonionic nucleophiles(R-BI) with CTABr micelle, with increase of the number of methylene groups, reaction rates mediated by R-BI^- were decreased as compared with those by BI^-, even though both the substrate and nucleophile should be located in the Stern layer of the micelle(*Scheme* 1).

We could not use longer chain alkylbenzimidazoles because they are almost insouluble in water, and in the present work we have synthesized soldium 2-alkylbenzimidazole-5-sulfonates(R-BISO$_3$Na). These compounds are soluble in water very well and we can compare their reactivities towards carboxylic esters in water and cationic micelles of CTABr. And we will discuss micellar property of R-BISO$_3$Na with long alkyl groups and hydrolysis-mechaniam of p-nitrophenylcarboxylic esters.



Scheme 1. The conceptual "anchor effect" proposed, transition state of dephosphorylation mediated by R-BI^- in Stern layer.

EXPERIMENTAL SECTION

Materials. The preparation and purification of CTABr[4] and R-BI have been described[3]. 2-Alkylbenzimidazole-5-sulfonic acids(R-BISO$_3$H) were prepared by the addition of chlorosulfonic acid($ClSO_3H$) to stirred alcoholic solutions of R-BI at 5℃ for 4 hours[5]. The remaining chlorosulfonic acid was decomposed by adding H_2O, and the solutions were heated at 105~110℃ to eliminate HCl, and the product was crystallized on cooling. The crude crystals were neutralized by adding a little excess of dilute $NaHCO_3$ solution, untill red litmus tur-

ned to blue, and after recrystallization from H_2O the products(R-$BISO_3Na$) were identified IR and NMR spectroscopy.

Kinetics The hydrolyses of p-nitrophenyl acetate(p-NPA), propionate(p-NPP) and valerate(p-NPV) by R-BI and R-$BISO_3Na$ were followed in Tris-buffer solution(pH 8.35), in which R-$BISO_3Na$ are not deprotonated.

The formation of p-nitrophenoxide ion was followed spectrometrically on a Beckman DU-8B model in aqueous solution at 30± 0.2℃. The apparent first order rate constants for overall reaction, k_φ, are in reciprocal seconds(sec^{-1}).

Isotope Effect. To identify whether R-$BISO_3Na$ acts as a nucleophile or a general base in hydrolyses of p-nitrophenylacetate(p-NPA) and p-nitrophenylpropionate(p-NPP), the kinetic isotope effect was measured in D_2O.

Activation Parameters. Activation enthalpy (ΔH^*), free energy(ΔG^*) and entropy (ΔS^*) were determined. Experimental temperatures are in the range of 25~45℃[6].

RESULTS AND DISCUSSION

First Order Rate Constants In CTABr Solutions. To minimize pertubation of micellar structures, we used 6.66×10^{-6} M substrates(p-NPCE) and 10^{-4} M R-BI and R-$BISO_3Na$ solutions. And we assumed that the cmc of CTABr in the reaction soutions was 3×10^{-4}M, instead of 8×10^{-4} M which is the cmc in pure water, because it was expected that the hydrophobic solutes decreased the cmc[1,3].

Micellar effects upon the hydrolyses of p-NPCE mediated by R-BI and R-$BISO_3Na$ are shown *Fig.* 1~3 and *Table* 1. The apparent first order rate constants (k_φ) increase with increase of CTABr concentrations, and reach maxima at ca. $5\sim8\times10^{-3}$ M sufactant concentractions, followed by gradual decrease. These rate maxima are characteristic of bimolecular reactions of hydrophobic substrates and follow equation(1), where D_n is concentration of micellized surfactants, Nw and Nm are concentrations of nucleophiles in aqueous and micellar pseudophase respectively, K_S is binding constant of substrate to CTABr, k_w and k_m are second order rate constants and k'_w and k'_m are pseudo first order rate constants in aqueous and micellar pseudophase, respectively.

$$k_\varphi=\frac{k_w[N_w]+k_mK_s[N_m]}{1+K_s[D_n]}=\frac{k'_w+k'_mK_s}{1+K_s[D_n]} \quad (1)$$

Steric Effect of Alkyl Groups of R-BI and R-$BISO_3Na$ on the Reaction Rates. Hydrolyses of p-NPCE mediated by R-BI with R varried from methyl to butyl in CTABr solutions(tris-buffer, pH 8.35) are slower than that mediated by BI by factors ca. 0.03 to 0.08 fold at optimum surfactant concentrations(*Fig.* 1~3).

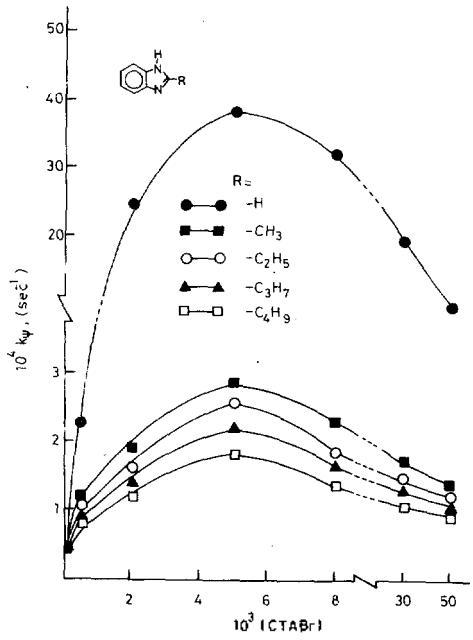
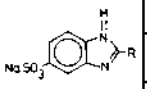


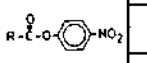
Fig. 1. Micellar effects upon hydrolyses mediated by 2-alkylbenzimidazoles: 6.66×10^{-6}M p-nitrophenylacetate(p-NPA), 10^{-4} M R-BI, Trisbuffer(pH 8.35), 30± 0.2℃.

Table 1. The first order rate constrants of Hydrolysis of p-NPA[a] mediated by sodium 2-alkyl benzimidazole-5-sulfonate in CTABr micellar solution[b]

	rate constant, $10^4 k_\varphi(sec^{-1})$									cmc[d]
	concentration of CTABr(M)									
	0	5×10^{-4}	8×10^{-4}	1×10^{-3}	2×10^{-3}	5×10^{-3}	8×10^{-3}	1×10^{-2}	2×10^{-2}	
R= −H	0.92	34.3	125	274	553	672	427	238	198	
$-CH_3$	0.85	2.73	7.82	17.5	22.4	26.8	21.3	18.3	15.3	
$-C_3H_7$	0.72	2.10	2.67	3.83	5.27	7.76	5.57	4.25	3.62	
$-C_5H_{11}$	0.62	1.98	2.25	3.53	4.72	7.14	5.37	4.02	3.25	
$-C_7H_{15}$	0.57	1.53	2.02	2.98	4.53	5.67	4.25	3.82	2.92	
$-C_9H_{19}$	0.64	1.57	2.23	3.25	5.37	6.87	5.62	4.12	3.85	3.40×10^{-3}M
$-C_{11}H_{23}$	0.92	1.92	2.53	3.72	6.02	7.92	6.12	5.27	4.32	1.95×10^{-4}M
$-C_{13}H_{27}$	1.23	2.25	3.26	4.73	7.25	9.48	7.72	6.56	5.35	1.64×10^{-4}M
$-C_{15}H_{31}$	1.54	2.57	4.73	6.87	9.83	12.37	9.75	7.78	6.63	6.80×10^{-5}M

[a] p-nitrophenyl acetate; 6.66×10^{-6}M, 30± 0.2℃, [b] Tris-buffer;pH 8.35 [c] R-$BISO_3Na$;10^{-4}M, [d] measured by surface tensiometry and conductivity method:The results of these two methods are exactly coincident.

Table 2. The first order rate constrants of Hydrolysis of p-NPA, p-NPP and p-NPV mediated by R-$BISO_3$ Na in 5×10^{-3}M CTABr solution[a]

[b] 	rate constant, $10^4 k_\varphi(sec^{-1})$										[d]
	R-$BISO_3Na$[c]										Ks(M^{-1})
	R× −H	$-CH_3$	$-C_2H_5$	$-C_3H_7$	$-C_5H_{11}$	$-C_5H_{15}$	$-C_9H_{19}$	$-C_{11}H_{23}$	$-C_{13}H_{27}$	$-C_{15}H_{31}$	
R= $-CH_3$ (p-NPA)	672	26.8	9.83	7.76	7.14	5.67	6.89	7.92	9.48	12.4	82.5
$-C_2H_5$ (p-NPP)	1400	57.4	18.4	13.3	12.6	9.31	11.4	14.3	18.7	28.4	150
$-C_4H_9$ (p-NPV)	−	77.2	24.0	17.0	15.7	12.2	13.9	17.8	25.3	45.2	210

[a]Tris buffer;pH 8.35, [b]substrates;6.66×10^{-6}M, 30± 0.2℃, [c]10^{-4}M R-$BISO_3Na$ [d]binding constants of the esters with $C_{15}H_{31}$-$BISO_3Na$ in water.

And same situation appear for those mediated by R-$BISO_3Na$ (*Table* 1 and 2), especially by heptyl-$BISO_3Na$ by farctor ca. 0.008 fold (*Table* 1 and 2). We compared the apparent first order rate constants of hydrolyses of p-NPCE mediated by R-$BISO_3Na$ and $BISO_3Na$ in *Fig.* 4, 5. The relative rate constants($k^{(m)}_{R\text{-}BISO_3Na}/k^{(m)}_{BISO_3Na}$) in micellar solutions are sharply decreased with changing of alkyl groups of R-$BISO_3Na$ from hydrogen to methyl and propyl, and slowly decreased from propyl to heptyl.

The larger binding constants(K_S) of substrated to micelle, generally lead to larger rate constants. However, the rate constants mediated by R-BI and R-$BISO_3Na$ decreased with increasing K_S of the imidazoles(ref. 3 and *Table* 1), as in the previous study of reactions mediated by 2-alkyl benzimidazolide ions($R\text{-}BI^-$)[3]. It seems that these rate-decreases are mainly due to steric effect of alkyl groups of R-$BISO_3$

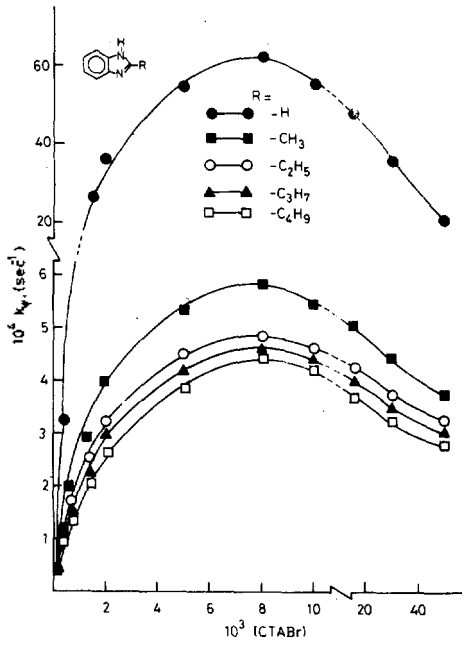


Fig. 2. Micellar effects upon hydrolyses mediated by 2-alkylbenzimidazoles; 6.66×10^{-6}M p-nitrophenyproptonate(p-NPP), 10^{-4} M R-BI, Tris-buffer(pH 8.35), 30 ± 0.2℃.

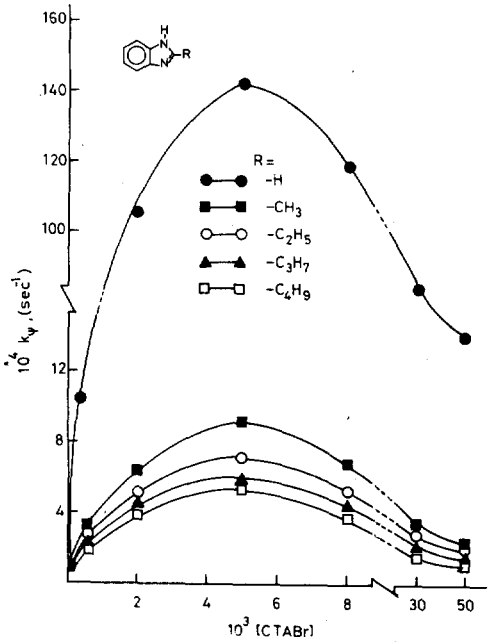


Fig. 3. Micellar effects upon hydrolyses mediated by 2-alkylbenzimidazoles; 6.66×10^{-6}M p-nitrophenylvalerate(p-NPV), 10^{-4} M R-BI, Tris-buffer(pH 8.35), 30 ± 0.2℃.

Na. The alkyl groups may penetrate into the core of micelle due to their hydrophobicity and be relatively fixed at a given position[8]. If this assumption is correct, the ability of R-BI or R-$BISO_3Na$ to attact p-NPCE. as compared with that of BI or $BISO_3Na$, may be decreased due to decrease of mobility of molecules. We refered this steric effect of the alkyl groups of R-BI and R-$BISO_3Na$ as "anchor effect" in previous study[3] on dephosphorylation mediated by R-BI ions. There is another evidence of the anchor effect of alkyl group into micellar core in the study of DeMayo and coworker[9]: in photochemical dimerization of α, β-unsaturated ketone in benzene solvent the product was mainly(90%) head to tail dimer(HT) and in potassium dodecanonate micellar solution the product was quantitatively(100%) head to head dimer(HH).

However, the rate-decrease followed by an increase in the reactions mediated by long alkyl-$BISO_3Na$ (nonyl to pentadecyl). It seems that this rate-increase is due to micellization of these nucleophiles with long alkyl groups of themselves and the micelle can easily accomodate the substrates into, and the reaction is accelerated. To conform this rate-increase by micellization of R-$BISO_3Na$, we observed the rate constants in aqueous solution, not including CTABr(*Fig.* 4,5).

In aqueous solutions the rate constants of hydrolyses mediated by R-$BISO_3Na$, when R is changed from H to heptyl, are not much different(*Table* 1, and *Fig.* 4,5). This means that the inherent reactivities of $BISO_3Na$ and R-$BISO_3Na$ are not much different and probability factor on

steric effect is not important, but in micellar solution collision frequency(due to "anchor" effect) is main effect on the rate-decrease.

We compared the rates of hydrolyses of p-nitrophenylacetate(p-NPA), p-nitrophenypropionate (p-NPP) and p-nitrophenylvalerate(p-NPV) mediated by R-$BISO_3Na$ with long alkyl groups,

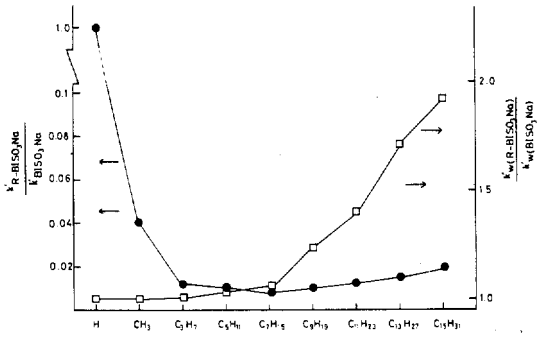


Fig. 4. Relationship between alkyl groups of R-$BISO_3Na$ and relative first order rate constants($k'_{R\text{-}BISO_3Na}/k'_{BISO_3Na}$) on hydrolyses in aqueous (□) and 5×10^{-4}M CTABr solution(●): Tris-buffer(pH 8.35), 6.66×10^{-6} M p-nitrophenylacetate(p-NPA), 10^{-4} M R-$BISO_3Na$, 30± 0.2℃.

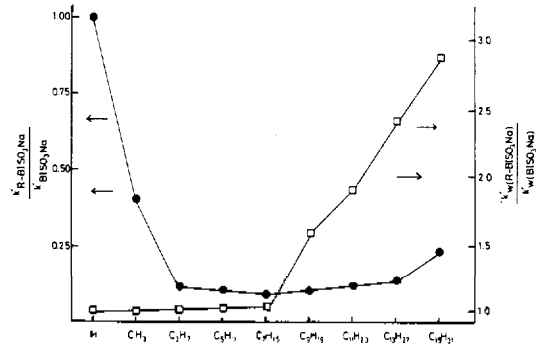


Fig. 5. Relationship between alkyl groups of R-$BISO_3Na$ and relative first order rate constants($k'_{R\text{-}BISO_3Na}/k'_{BISO_3Na}$) on hydrolyses in aqueous (□) and 5×10^{-4}M CTABr solution(●): Tris-buffer(pH 8.35), 6.66×10^{-6} M p-nitrophenylvalerate(p-NPV), 10^{-4} M R-$BISO_3Na$, 30± 0.2℃.

especially pentadecyl-$BISO_3Na$, at the optimum CTABr concentrations(5×10^{-3}M). The binding constants of p-NPA, p-NPP and p-NPV with this nucleophile are quite different(*Table* 2)[10]. And the rate constants of the reactions of p-NPP and p-NPV are sharply increased, as compared with reactions of p-NPA, while the reaction rates of the formers in aqueous solution, not including CTABr, are decreased to some extent, because of larger inductive and steric effect of ethyl and butyl groups than methyl of p-NPA. These rate-increases for reactions with substrates having longer alkyl groups in micellar solutions than p-NPA are mainly due to larger binding constants of the formers having ethyl and butyl groups: it means that carboxyl group of p-NPP and p-NPV are more easily arranged near by BI moiety of R-$BISO_3Na$ micelles and collision frequencies of p-NPP and p-NPV to the nucleophiles are increased as compared with that of p-NPA.

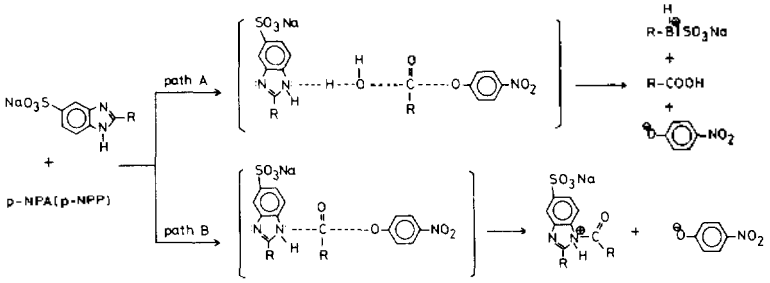
Mecanism of Hydrolyses of p-NPA and p-NPP; Isotofe Effects. We concluded from previous studies[1,3] that dephosphorylations of p-NPDPP mediated by BI^- and R-BI^- in carbonate buffer(pH 10.7) follow the nucleophilic mechanism. However, p-NPA and p-NPV are quite different substrates. To know the mechanism of hydrolyses of these substrates in Tris-buffer(pH 8.35), we measured the first order rates in D_2O solutions(*Table* 3)[11]. If there are large isotope effects, the hydrolyses are predected to go through a general base mechanism(path A in *Scheme* 2), and if not, through nucleophilic attack(path B).

The first order rate constant-ratios in H_2O and D_2O solution, k'_{H_2O}/k'_{D_2O} were on the range of ca. 2.5~3.2, as showm in *Table* 3. Bruice and Benkovic concluded in their study[12] that hydrolysis of p-NPA catalyzed by imidazole(IM) in aqueous solution goes over 90% by forma-

Table 3. The isotope effect(k'_{H_2}/k'_{D_2}) on reaction rates of hydrolysis of p-NPA and p-NPP mediated by R-BI and R-$BISO_3Na$

$R-\overset{O}{\overset{\|}{C}}-O-\langle\bigcirc\rangle-NO_2$ [a]	isotope effect(k'_{H_2O}/k'_{D_2O})[b,c]							
	BI	CH_3-BI	C_3H_7-BI	$BISO_3Na$	CH_3-$BISO_3Na$	C_3H_7-$BISO_3Na$	C_9H_{19}-$BISO_3Na$	$C_{15}H_{31}$-$BISO_3Na$
R= $-CH_3$ (p-NPA)	2.72	2.65	2.76	3.12	3.05	2.80	2.46	2.60
R= $-C_2H_5$ (p-NPP)	2.68	2.74	2.71	3.28	3.12	2.93	2.73	2.83

[a]p-NPA, p-NPP;6.66×10^{-6}M, 30± 0.2℃, [b]Tri-buffer;pD 8.35, DCl solution in D_2O, [c]5×10^{-3}M CTABr solution in D_2O.



Scheme 2.

tion of N-acetyl imidazole(nucleophilic product) and only less 10% by a general base mechanism. Although many reactions exhibit 'normal' kinetic deuterium isotope effects in the range k'_{H_2O}/k'_{D_2O} of about 6 to 10^{13}, the range k'_{H_2O}/k'_{D_2O} of ca. 2.5~3.2 in present study is too high to conclude that the hydrolyses of p-NPA mediated by various R-$BISO_3Na$ proceed by nucleophilic mechanism. In other words, the reactions are assumed to proceed in part by general basic one, as compared with the reaction catalyzed by IM in the aqueous solution. This result seems due to steric effect of alkyl groups of R-$BISO_3Na$ and property of the substrates in micellar pseudophase.

Activation Parameters of the Reactions. We measured activation parameters of reactions in aqueous and micellar solution to compare inherent reactivities of R-BI and R-$BISO_3$Na on hydrolyses of p-NPA and p-NPP.

As shown in *Table* 4, activation enthalpies ($\Delta H^{\neq}$), free energies ($\Delta G^{\neq}$) of the reactions of p-NPA and p-NPP mediated by R-BI and R-$BISO_3Na$ in aqueous solutions, not including surfactant, are quite high. However, the values of the reaction in CTABr micellar solutions are relatively lower than the values in aqueous soloutions. It is consistent with increases of the reaction rates in micellar solutions as compared with the reactions in aqueous solutions.

When we compared the parameters of the reactions mediated by R-BI and R-$BISO_3Na$ in aqueous solutions, there are not much differences between the values of the reactions BI and methyl-BI, and $BISO_3Na$ and methyl-$BISO_3Na$. However, in mecellar solutions there are relatively large difference between the values. It means that the inherent reactivities of BI and R-BI in aqueous solution are almost equal, and the decreases of the reaction rates mediated by

Table 4. Activation Parameters[a,b] of the Hydrolyses of p-NPA and p-NPP mediated by R-BI and R-$BISO_3Na$ in Aqueous and Micellar Solution at 30℃ (A) Hydrolysis of p-NPA in Tris-buffer(pH 8.35), mediated by R-BI or R-$BISO_3Na$[f]

	R-BI					R-$BISO_3Na$					
	R= −H	$-CH_3$	C_2H_5	$-C_3H_7$	$-C_4H_9$	R= −H	$-CH_3$	$-C_5H_{11}$	$-C_9H_{19}$	$-C_{13}H_{27}$	$-C_{15}H_{31}$
ΔH^*	4.56	8.78	9.85	12.0	13.1	6.20	11.3	11.7	12.4	10.2	9.49
	(12.4)	(13.0)	(13.1)	(13.9)	(14.1)	(11.5)	(11.9)	(12.2)	(12.4)	(11.1)	(10.6)
ΔG^*	21.0	22.5	22.5	22.6	22.6	19.4	21.2	22.0	22.0	21.9	21.7
	(23.1)	(23.2)	(23.1)	(23.2)	(23.3)	(23.2)	(23.3)	(23.3)	(23.0)	(23.1)	(23.0)
ΔS^*	−54.3	−45.3	−41.8	−34.8	−31.3	−43.5	−34.1	−34.1	−33.8	−38.4	−40.4
	(−35.4)	(−33.7)	(−33.3)	(−30.9)	(−29.1)	(−35.7)	(−32.6)	(−32.5)	(−32.9)	(−34.3)	(−35.2)

(B) Hydrolysis of p-NPP in Tris-buffer(pH 8.35), mediated by R-BI or R-$BISO_3Na$[f]

	R= −H	$-CH_3$	C_2H_5	$-C_3H_7$	$-C_4H_9$	R= −H	$-CH_3$	$-C_5H_{11}$	$-C_9H_{19}$	$-C_{13}H_{27}$	$-C_{15}H_{31}$
ΔH^*	3.47	7.11	8.76	10.9	11.9	6.57	11.1	11.4	12.2	9.67	9.30
	(14.1)	(14.4)	(14.6)	(14.9)	(15.3)	(11.9)	(12.2)	(12.8)	(13.1)	(11.7)	(11.3)
ΔG^*	20.8	22.2	22.3	22.3	22.4	19.0	20.8	21.7	21.8	21.4	21.2
	(23.2)	(23.2)	(23.2)	(23.2)	(23.2)	(23.3)	(23.3)	(23.3)	(23.4)	(23.1)	(22.9)
ΔS^*	−57.2	−49.8	−44.7	−37.5	−34.8	−41.0	−33.8	−33.6	−33.5	−38.6	−39.3
	(−30.1)	(−28.9)	(−28.4)	(−27.3)	(−26.1)	(−35.6)	(−32.6)	(−32.5)	(−32.1)	(−34.3)	(−35.5)

[a] Temperature ranges of experiment are on 25~45℃, [b] Units of ΔH^* and ΔG^* are Kcal/mole and ΔS^* is e.u., [c] $\Delta H^* = RT^2 \times$slope, [d] $\Delta G^* = -RT \ln K^* = -RT \ln (hk/k_BT)$, where h is plank constant and k_B is Boltzman constant, [e] $\Delta S^* = (\Delta H^* - \Delta G^*)/T$, [f] data are of the reactions in 5×10^{-3}M CTABr solution, data in parentheses are of the reactions in aqueous solution, not including surfactant.

R-BI(or R-$BISO_3Na$) as compared with those by BI(or $BISO_3Na$) are due to an interation of their alkyl groups with micelle, a steric effect.

On the other hand, when we compared the ΔH^* values of the reactions mediated by R-BI and R-$BISO_3Na$ in micellar solutions, ones having longer groups gradually leveled the parameters up. It is consistent with gradual decreases of the reaction rates by changing of R groups of the nucleophiles from methyl to butyl (or pentyl)(*Fig.* 1~5 and *Table* 1 and 2). And ΔS^* values of the reactions by methyl-BI in micellar solutions were sharply increased as compared with those of the reactions by BI, while ΔG^* values were not much increased. The increased ΔS^* values in the micellar reactions indicate that the reactants require more ordering in going to the transition states than they would do in the uncatalyzed reactions, in same way of enzymatic reactions[14]. Thus, the mechanism of the enzymatic[14] and micellar[15] reactions would impose upon the reactants its own orientation and steric requirements, a different means of achieving spatial proximity of the reactants, and its own solvent and concentration effects.

However, in the reactions mediated by R-$BISO_3Na$ with very long alkyl groups, the ΔH^* values are gradually decreased by changing the alkyl groups from nonyl to pentadecyl, and it is

consistent with gradual increases of the reaction rate (*Table* 1 and 2) due to abilities of micellization of R-$BISO_3Na$.

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6. K_a, K_s and cmc values are depending on temperature, although the magnitudes of changes are not generally large. However, acivation parameters of reactions in micellar solutions are usually defined in terms of ΔH^*, ΔG^* and ΔS^* including changes of K_a, K_s and cmc, which should expressed as ΔH_m^*, ΔS_m^*.
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8. Although micelles have fluid structure and monomers migrate from water phase to micelles and move about in the micelles, we assume that micelle structure is wholly not changed, because most monomers stay to form micelle for relatively long time as compared with exchanging velocity of monomers between mice lle and bulky phase.
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10. Binding constant(K_S) of a substrate with micelle can be generally expressed as the equation 2, where D_n is concentration of micellized surfactant concentration (D-cmc), S_W is of substrate in the aqueous phase and Sm is of micelle-substrate complex. If fm is molar fraction of Sm to total substrate concentration[S_T], the equation 2 can be written in the equation 3.

$$D_n + S_W \underset{}{\overset{K_S}{\rightleftharpoons}} S_m : K_S = [S_m]/[D_n][S_W] \quad (2)$$

$$[D_n]K_S = f_m/(1-f_m) = \{[S_m]/[S_T]\}/\{[S_W]/[S_T]\} \quad (3)$$

One can generally get different specific absorptions of substrate, measured in different micellar concentrations, by UV-Visible spectrophotometer. Thus [S_T] and [S_m] and fm can be expressed by the equation 4 and 5, where

$$[S_T] = A_{max} - A_W, \qquad [S_m] = A - A_W \quad (4)$$

$$f_m = [S_m]/[S_T] = (A-A_W)/(A_{max}-A_W) \quad (5)$$

Aw is the absorption of substrate in aqueous phase, Amax in maximum micellar concentraction and A is several given micellar concentrations. Introducing the equation 5 into the equation 3, the equation 6 can be gotten, and Ks value be obtained from slope of a plot of this linear equation (6).

$$(A-A_W)/D_n = -K_S \cdot A_m + \text{constant} \quad (6)$$

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