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계면활성제 용액속에서의 화학반응(제 3보) 유기인산 에스테르의 가수분해반응에 미치는 2-알킬벤즈이미다졸-5-술포네이트의 친핵적 및 미셀 촉매효과

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Chemical Reactions in Surfactant Solutions(III). Nucleophilic and Micellar Catalyses on Hydrolysis of an Organic Phosphate by Sodium 2-Alkylbenzimidazole-5-sulfonates in Aqueous and CTABr Solutions

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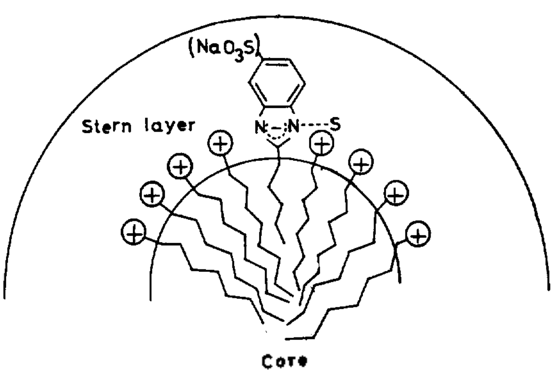
요 약. CTABr 미셀 용액속에서의 sodium 2-alkylbenzimidazole-5-sulfonate(R-BISO_3Na)의 음이온에 의해 추진되는 p-nitrophenyldiphenylphosphate(p-NPDPP)의 탈인산화 반응은 Sodium benzimidazole-5-sulfonate(BISO_3 Na)의 음이온에 의해 추진되는 반응의 반응속도보다 현저히 감소하고, 알킬기의 길이가 methyl기에서 heptyl기로 길어질수록 감소의 정도가 더욱 크다. 이것은 CTABr을 포함하고 있지 않는 수용액속에서의 BI$^-SO_3$Na 및 R-BI$^-SO_3$Na에 의한 탈인산화 반응속도가 별차이가 없음을 감안할 때, 이들 친핵체의 알킬기가 미셀 의사층(micellar pseudophase)내에서 입체장애(steric hinderance)로 작용하기 때문인 것으로 판단된다. 이것은 수용액과 미셀 용액속에서의 반응의 측정된 활성화에너지($\Delta H^{\neq}$, $\Delta G^{\neq}$ 및 $\Delta S^{\neq}$)의 값과도 정성적으로 일치하고 있다. 이러한 입체장애가 반응속도에 미치는 영향을 정량적으로 계산하고자 시도하였다. Nonyl기에서 pentadecyl기까지의 긴 알킬기를 갖고 있는 R-BI$^-SO_3$Na는 그것들의 benzimidazole 부분($\overline{BI}$ moiety)이 친핵체로 작용할 뿐 아니라, 이 분자들은 CTABr을 포함하지 않는 수용액속에서 미셀을 형성하여 반응을 촉진함을 알았다.

ABSTRACT. Dephosphorylation of p-nitrophenyldiphenylphosphate (p-NPDPP) mediated by anions of sodium 2-alkylbenzimidazole-5-sulfonate (R-BI$^-SO_3$Na) in CTABr micellar solutions are obviously slower than that by anion of sodium benzimidazole-5-sulfonate (BI$^-SO_3$Na), 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 of R-BI$^-SO_3$Na 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 nucleophilic ability of benzimidazole moiety of R-BI$^-SO_3$Na on the reactions, these compounds with long alkyl groups (nonyl to pentadecyl) are micellized for themselves, and increase the reaction rates due to their micellar catalyses in aqueous solutions, not including CTABr.

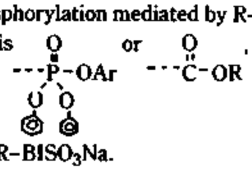
INTRODUCTION

Two studies were made by C.A. Bunton and the author[1, 2] on dephosphorylation of p-nitrophenyldiphenylphosphate (p-NPDPP) mediated by benzimidazolide and naphth-2,3-imidazolide ions (BI^- and NI^-) in micellar solutions 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 reactions evidence that the imidazolide ions act as nucleophiles, not as general bases, was given.

Recently the author also discussed dephosphorylation of p-NPDPP mediated by some 2-alkylbenzimidazolide ions ($R-BI^-$)[3] and hydrolyses of carboxylic esters mediated by sodium 2-alkylbenzimidazole-5-sulfonates ($R-BISO_3Na$)[4] in aqueous and CTABr solutions, in which nucleophilicities and steric effects of $R-BI^-$ and $R-BISO_3Na$ were varied by a change of their alkyl groups. In spite of a sharp increase of the binding constants(K_s) of the nonionic nucleophiles, R-BI, 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). In the latter[4], anions of $R-BISO_3Na$ with long alkyl groups (nonyl to pentedecyl) which form micelles of themselves increase the reaction rates due to their micellar catalyses in aqueous solutions, not including CTABr.



Scheme 1—The conceptual "anchor effect" proposed transition state of dephosphorylation mediated by R-BI⁻ in Stern layer, where S is



nucleophile is $R-BI^-$ or $R-BISO_3Na$.

In the present work we will discuss micellar property of anions of sodium 2-alkylbenzimidazole-5-sulfonates ($R-BI^-SO_3Na$) with long alkyl groups, which are newly prepared, on dephosphorylation of p-nitrophenyldiphenylphosphate (p-NPDPP).

EXPERIMENTAL SECTION

Materials. The preparation and purification of CTABr[5], p-NPDPP[6] and R-BI[3] has been described. 2-Alkylbenzimidazole-5-sulfonic acids ($R-BISO_3H$) were prepared by the addition of chlorosulfonic acid ($ClSO_3H$) to stirred alcoholic solutions of R-BI at 5°C for 4 hours[7]. The remaining chlorosulfonic acid was decomposed by adding H_2O, and the solutions were heated at 105-110 °C to eliminate HCl, and the product was crystallized on cooling. The crude crystals were neutralized by adding $NaHCO_3$, and after recrystallization from H_2O the products ($R-BISO_3Na$) were identified by IR and NMR spectroscopy.

Properties of $R-BISO_3Na$. The apparent acid-dissociation constants(K_a) for deprotonation of $R-BISO_3Na$ in water and micellar solutions were measured by spectral titration[1, 3] monitored at 283 nm (*Table* 1). We calculated the concentration of micellar bound $R-BI^-SO_3Na$ indirectly from the K_a values (we failed in the direct spectral measurement of the concentrations of the materials because of complex shifts of the spectra. If the spectra are simple, they should be usually

Table 1. Ka values of sodium 2-alkylbenzimidazole-5-sulfonate, concentrations of their anions in aqueous and micellar phase and their cmc

$NaSO_3$-BI-R	10^{13} Ka		10^6 [R-BI$^-SO_3$Na]			
	in water	in CTABr	*c*	*d*	*e*	cmc
R=-H	12.3	39.6	16.5	5.79	10.7	
$-CH_3$	3.98	14.8	6.89	1.95	4.94	
$-C_3H_7$	3.83	13.7	6.43	1.88	4.55	
$-C_5H_{11}$	3.77	13.0	6.12	1.85	4.27	
$-C_7H_{15}$	3.61	12.8	6.00	1.77	4.23	
$-C_9H_{19}$	3.42	12.6	5.90	1.68	4.22	$3.40\times10^{-3}M$
$-C_{11}H_{23}$	3.29	12.3	5.77	1.62	4.15	$1.95\times10^{-4}M$
$-C_{13}H_{27}$	3.18	12.0	5.67	1.57	4.10	$1.64\times10^{-4}M$
$-C_{15}H_{31}$	3.07	11.8	5.58	1.51	4.07	$6.80\times10^{-5}M$

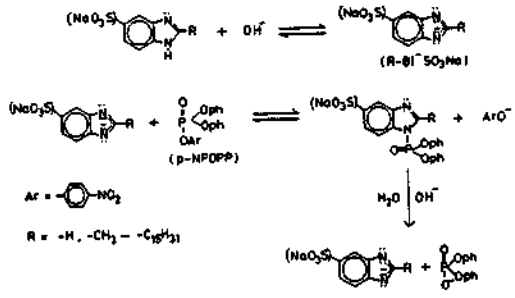
monitored at 283 nm in Beckman DU 8B UV-Visible spectrophotometer. apparent Ka values at optimum concentration of CTABr ($8\times10^{-4}M$) in dephosphorlyation of *p*-NPDPP at 30 ± 0.2 °C. the molar concetration (I^-_{tot}] of R-BI$^-SO_3$Na in $8\times10^{-4}M$ CTABr solution($10^{-2}M$ carbonate buffer, pH 10.7). the molear concentration [I^-_w] of R-BI$^-SO_3$Na in water solution ($10^{-2}M$ carbonate buffer, pH 10.7). the molar concentration [I^-_m] of R-BI$^-SO_3$Na in micellar pseudophase ([I^-_m]=[I^-_{tot}]-[I^-_w]). /measured by surface tensiometry

explained and calculate concentrations of the micellar bound imidazoles from these.).

Determination of cmc of R-BISO_3Na with long alkyl groups was made by surface-tensiometry (*Table* 1).

Kinetics. Dephosphorylations of p-NPDPP mediated by R-BI$^-SO_3$Na and/or OH^- are shown in *Scheme* 2.

The formation of p-nitrophenoxide ion was followed spectrometrically[1, 3] on a Beckman DU-8B model in aqueous solution at 30 ± 0.2 °C. The first order rate constants for overall reaction, k_ψ, are in reciprocal seconds (sec^{-1}). The measured rate constant(k_ψ) include contributions from



Scheme 2.

reactions with OH^- of 0.001 *M* carbonate buffer (pH 10.7) and with deprotonated R-BISO_3Na (R-BI$^-SO_3$Na) (equation 1), where $k'_{R\text{-}I}$, k'_{OH^-} and $k'_{R\text{-}I^-}$ are the first order rate constants with R-BISO_3Na, OH^- and R-BI$^-SO_3$Na, respectively, and we assume that they are independent[1, 3].

$$k\psi = k'_{R\text{-}I} + k'_{OH^-} + k'_{R\text{-}I^-} \quad (1)$$

Activation Parameters. Activation enthalpy (ΔH^*), free energy (ΔG^*) and entropy (ΔS^*) were measured. Experimental temperatures are in the range 25-45 °C.

RESULTS AND DISCUSSION

K_a values of R-BISO_3Na. Measured K_a values of sodium 2-alkylbenzimidazole-5-sulfonates (R-BISO_3Na) in water decreased slightly with increase of length of the alkyl chain, because of inductive or steric effects (*Table* 1). On the other hand overall deprotonations of R-BISO_3Na in micellar solutions gradually increased with increase of CTABr concentrations up to $10^{-2}M$ and was followed by a gradual decrease, as found for BI[1]

and R-BI[3].

Concentrations of R-BISO$_3$Na in Micellar Pseudophase. The concentrations of R-BI$^-$SO$_3$Na in aqueous and micellar solutions (carbonate buffer, pH 10.7) are calculated from their K_a values, and are shown in *Table* 1. Concentrations in micellar pseudophase, $[I_m^-]$, were calculated from equation 2, where $[I_w^-]$ and $[I_{tot}^-]$ are the concentrations of R-BI$^-$SO$_3$Na in aqueous and total reaction solutions, respectively. Values of the calculated $[I_m^-]$ are given in *Table* 1.

$$[I_m^-]=[I^-_{tot}]-[I_w^-] \qquad (2)$$

The concentration ratios of R-BI$^-$SO$_3$Na and BI$^-$SO$_3$Na, [R-BI$^-$SO$_3$Na]/[BI$^-$SO$_3$Na] in *Table* 2b, in the micellar pseudophase are much smaller than unity; for example, in 10^{-4} *M* CH$_3$-BISO$_3$Na solution the ratio is 0.45 and in 10^{-4} *M* heptyl-BISO$_3$Na is 0.39, respectively.

First Order Rate Constants in CTABr Solutions. To minimize perturbation of micellar structures, we used 6.66×10^{-6} *M* p-NPDPP and 10^{-4} *M* R-BISO$_3$Na solutions. And we assumed that the cmc of CTABr in the reaction solutions was 3×10^{-4} *M*, instead of 8×10^{-4} *M* which is the cmc in pure water, because it was expected that the solutes decreased the cmc[1, 3].

The values of $k'_{R\text{-}I}$ for dephosphorylation of p-NPDPP in equation 1 are very small and can be neglected ($k_\psi = k'_{OH^-} + k_{R\text{-}I^-}$). Micellar effect upon the dephosphorylation of p-NPDPP are shown in *Fig.* 1, and the first order rate constants(k_ψ) increase with increase of CTABr concentrations, and reach maxima at ca. 8×10^{-4} *M* surfactant concentration, followed by a gradual decrease. These rate maxima are characteristics of bimolecular reactions of hydrophobic substrates and follow equation 3, where $[D_n]$ is concentration of micellized surfactants, $[N_w]$ and $[N_m]$ are concentrations of nucleophiles in water and in micellar pseudophase, K_s is binding constant to

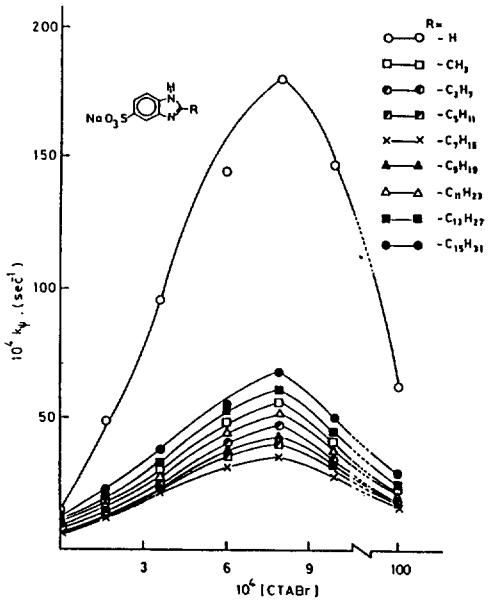


Fig. 1. Micellar effects upon dephosphorylation mediated by R-BISO$_3$Na; 6.66×10^{-6}*M* p-NPDPP, 1×10^{-4}*M* R-BISO$_3$Na, carbonate buffer (pH 10.7), 30 ± 0.2°C.

CTABr, k_w and k_m are second order rate constants, and k'_w and k'_m are first order rate constants in aqueous and micellar pseudophase, respectively[8].

$$k_\psi=\frac{k_w[N_w]+k_mK_s[N_m]}{1+K_s[D_n]}$$

$$=\frac{k'_w+k'_mK_s}{1+K_s[D_n]} \qquad (3)$$

The mechanism of dephosphorylation of p-NPDPP mediated by BI$^-$ and R-BI$^-$ was shown in previous studies[1, 3], and we predict that the reactions mediated by R-BI$^-$SO$_3$Na also follow by this mechanism shown in *Scheme* 2, because the sulfonate group of the nucleophiles should not change the mechanism. However there are increases of overall reactivity of the nucleophiles, because of the negatively charged sulfonate group in positively charged Stern layer of micelle (cf. ref. 3 and *Table* 2).

Table 2. The relationship between concentrations of R-BI$^-$SO$_3$Na and 1st order rate constants of dephosphorylation at optimum micellar concentration ($8\times10^{-4}M$ CTABr)

	$\frac{[R\text{-}BI^-SO_3Na]}{[BI^-SO_3Na]}$	10^3k (sec^{-1})	$10^3k_{OH^-}$	$10^3k_{R\text{-}BI^-SO_3Na}$	$\frac{k_{R\text{-}BI^-SO_3Na}}{k_{BI\text{-}SO_3Na}}$	steric effect (%)	$10^4k'_{w(R\text{-}BI^-SO_3Na)}$	$\frac{k'_{w(R\text{-}BI^-SO_3Na)}}{k'_{w(BI^-SO_3Na)}}$
R=	1.00	18.1	1.48	16.6	1.00	—	0.12	1.00
$-CH_3$	0.45	5.62	1.48	4.14	0.25	44.4	0.12	1.00
$-C_3H_7$	0.42	5.02	1.48	3.54	0.21	50.0	0.13	1.08
$-C_5H_{11}$	0.40	4.41	1.48	2.93	0.18	50.0	0.14	1.17
$-C_7H_{15}$	0.39	3.74	1.48	2.26	0.14	64.1	0.14	1.17
$-C_9H_{19}$	0.39	4.63	1.48	3.15	0.19	51.3 (68.0)	1.68	14.0
$-C_{11}H_3$	0.38	5.24	1.48	3.76	0.22	42.1 (75.0)	3.91	32.0
$-C_{13}H_{27}$	0.38	6.24	1.48	4.76	0.29	23.7 (83.0)	4.34	36.2
$-C_{15}H_{31}$	0.37	6.82	1.48	5.34	0.32	13.5 (86.0)	5.21	43.2

$6.66\times10^{-6}M$ *p*-NPDPP, $10^{-4}M$ R-BISO$_3$Na, carbonate buffer (pH 10.7), 30 ± 0.2°C, the concentration ratios of R-BI$^-$SO$_3$Na and BI$^-$SO$_3$Na in the micellar pseudophase, the apparent first order rate constants of the reaction in micellar solutions (carbonate buffer, pH 10.7), the apparent first order rate constants of the reaction mediated by OH$^-$(carbonate buffer, pH 10.7) without including R-BISO$_3$Na in the micellar solutions, apparent first order rate constants of the reaction mediated by R-BI-SO$_3$Na in the micellar pseudophase, the first order rate constant ratio of the reaction mediated by R-BI$^-$SO$_3$Na and BI$^-$SO$_3$Na in the micellar pseudophase, steric effect(%) = A/B × 100, where A are theoretical ($k_{R\text{-}BI^-SO_3Na}/k_{BI^-SO_3Na}$) that are equal to [R-BI$^-$SO$_3$Na]/[Bi$^-$SO$_3$Na], B are experimental ($k_{R\text{-}BI^-SO_3Na}/k_{BI^-SO_3Na}$), values in ( ) are expected steric effect, the apparent first order rate constants of dephosphosphorylation in water (not including CTABr), [a]the first order rate constant ratios of dephosphorylation mediated by R-BI$^-$SO$_3$Na and BI$^-$SO$_3$Na in aquous solutions.

Table 3. Activation parameters[a,b] of dephosphorylation of *p*-NPDPP in carbonate buffer (pH 10.7), mediated by R-BI$^-$ or R-BI$^-$SO$_3$Na[c] in aqueous and CTABr micellar solution at 30 ± 2°C

	R-BI$^-$					R-BI$^-$SO$_3$Na					
	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^*	8.39 (20.4)	17.5 (20.8)	17.9 (21.0)	19.4 (21.5)	18.8 (22.1)	8.57 (19.7)	13.7 (20.6)	14.2 (20.9)	15.0 (20.9)	11.7 (17.5)	11.3 (16.8)
ΔG^*	19.8 (22.5)	20.7 (22.5)	20.8 (22.5)	20.8 (22.5)	20.8 (22.6)	19.9 (22.5)	20.7 (22.5)	20.7 (22.5)	20.8 (22.6)	20.7 (22.4)	20.6 (22.3)
ΔS^*	-37.8 (-6.83)	-10.5 (-5.68)	-9.84 (-5.28)	-7.91 (-5.16)	-6.73 (-5.07)	-37.5 (-9.10)	-23.1 (-6.19)	-21.5 (-5.40)	-19.2 (-5.51)	-29.8 (-8.23)	-30.7 (-9.56)

Temperature ranges of experiment are on 25-45°C, Units of ΔH^* and ΔG^* are Kcal/mole and ΔS^* is e.u., Data are of the reactions in $8\times10^{-4}M$ CTABr solution and data parentheses are of the reactions in aqueous solution, not including surfactant, $\Delta H^* = RT^2\times$ slope $\Delta G^* = -RT\ln K^* = -RT\ln(hk/k_BT)$, where h is plank constant and k_B is Boltzman constant, $\Delta S^* = (\Delta H^* - \Delta G^*)/T$.

Effect of R-BI⁻SO_3Na Concentration in Stern Layer on the Reaction Rates and "Steric" Effect. Dephosphorylations mediated by R-BI⁻SO_3Na with R varried from methyl to heptyl in CTABr solutions (carbonate buffer, pH 10.7) are slower than that mediated by BI⁻SO_3Na by factors of 0.14 to 0.25 fold. The larger binding constants (K_s) of substrate to micelle, generally lead to larger rate constants. However, rate constants mediated by R-BI⁻SO_3Na decreased with increasing K_s of the imidazoles as in the previous study of dephosphorylation of p-NPDPP mediated by R-BI⁻[3] and hydrolyses of carboxylic esters by R BISO_3Na[4]. We think that these decreases are due to one or two of the followings.

First, concentration of R-BI⁻SO_3Na in the micellar pseudophase may be only 0.14 to 0.25 fold of that of BI⁻SO_3Na. We tried to determine these values to know whether or not this assumption is correct.

Second, because of the bulky alkyl groups of R-BI⁻SO_3Na, there is a steric effect, and the steric hinderance could slow the reaction. And in addition alkyl groups of R-BI⁻SO_3Na may penetrate into the core of micelle due to their hydrophobicity and be relatively fixed at given position[9]. If this assumption is correct, the ability of R-BI⁻SO_3Na to attack p-NPDPP, as compared with that of BI⁻SO_3Na, may be decreased of mobility of molecules. We tend to believe the second explanation.

The relative rate constants($k'_{R\text{-}BI^-SO_3Na}/k'_{BI^-SO_3Na}$ in *Table* 2f) in the micellar pseudophase are decreased, as compared with the concentration ratios ([R-BI⁻SO_3Na]/[BI⁻SO_3Na] in the pseudophase. For example, for 10^{-4} *M*methyl-BISO_3Na the concentration ratio of the anions and the relative rate constant are 0.45 and 0.25 respectively (*Table* 2b and 2f). It is considered that the larger decrease of rate than that of concentration ratio is due to steric effect of the

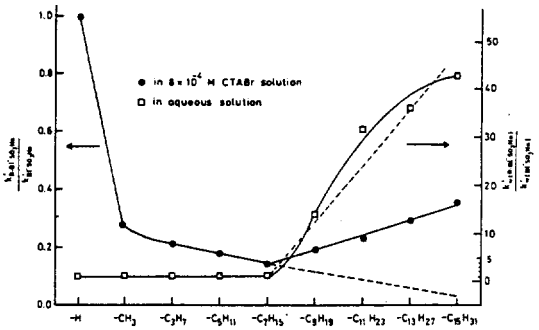


Fig. 2. Relationship between alkyl groups of R-BI⁻SO_3Na and the first order rate constantratios ($k_{R\text{-}BI^-SO_3Na}/k_{BI^-SO_3Na}$) on dephosphorylations in aqueous and 8×10^{-4} *M* CTABr solutions: carbonate buffer (pH 10.7). 6.66×10^{-6} *M* *p*-NPDPP, 10^{-3} *M* R-BISO_3 Na, 30 ± 0.2 °C.

methyl group in Stern layer of CTABr micelle. And, as shown in *Fig.* 2, same situation is occurred in all the reactions mediated by R-BI⁻SO_3Na with R varried from methyl to heptyl. However the rate-decrease followed by an increase in the reactions mediated by long alkyl-BI⁻SO_3Na.

We assume that the difference (0.20) of the two ratios mentioned above is due to second effect, that is, a steric effect of ca. 44%. We define this steric effect (%) of alkyl groups of nucleophiles as the equation 5, where A is theoretical first order constant-ratios ($k'_{R\text{-}BI^-SO_3Na}/k'_{BI^-SO_3Na}$) which is equal to concentration-ratios ([R-BI⁻SO_3Na]/[BI⁻SO_3Na]) in micellar pseudophase, and B is experimental rate constant-

$$\text{steric effect}(\%) = 100(A-B)/A \qquad (5)$$

ratios[3]. All the calculated steric effects are shown in *Table* 2g and *Fig.* 3. These steric effects are larger when the alkyl group-lengths of R- BISO_3Na are increased (from methyl to heptyl). This situation is similar to dephosphorylation[3] of p-NPDPP mediated by R-BI⁻. We proposed a model in the previous study[3] and refered it as an "anchor effect" of alkyl groups of the nucleophiles into micel-

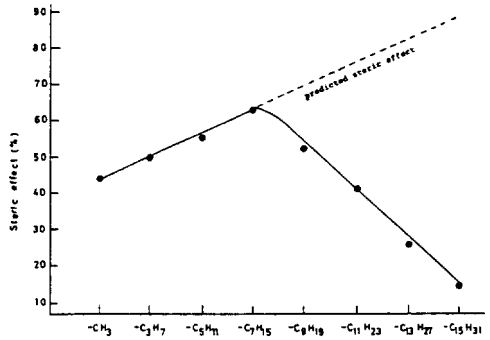


Fig. 3. Calculated percentage(%) of "Steric effect" in the whole decreasing of $k'_{R\text{-}BI^-SO_3Na}/k'_{BI^-SO_3Na}$) that are equal to [-$BI^-SO_3Na$]/[$BI^-SO_3Na$]. B are experimental ($k'_{R\text{-}BI^-SO_3Na}/k'_{BI^-SO_3Na}$).

lar core. This effect is characteristic of micellar reactions mediated by methyl to heptyl-BI^-SO_3Na, (*Table* 2i), which is not observed in aqueous solution, and it means not due to difference of inherent reactivities of BI^-SO_3Na and R-BI^-SO_3Na.

On the other hand, when we used nonyl to pentadecyl-$BISO_3Na$ as nucleophiles, the predicted steric effect was sharply decreased (*Fig.* 3). This interesting appearance can be explained by micellization of R-$BISO_3Na$ with long alkyl group [se first order rate constants of the reactions in aqueous solution, not including CTABr, (*Table* 2h and *Fig.* 2) and cmc values in *Table* 1].

Nucleophilic and Micellar Effect of R-BI^-SO_3Na. R-$BISO_3Na$ with long alkyl groups (nonyl to pentadecyl) are good micellar forming substances (*Table* 1). The steric effects of anions of these compounds on dephosphorylation are sharply decreased as compared with expected one (*Table* 2g and *Fig.* 3). We conclude that this appearance is due to micellization of the nucleophiles (R-BI^-SO_3Na), and the reaction rates are increased. As shown in *Table* 2h, the first order rate constants of dephosphorylation mediated by H- to heptyl-BI^-SO_3Na in aqueous solution without added CTABr micelle are very low and ca. 10^{-5} sec^{-1}.

However, the reactions mediated by nonyl- to pentadecyl-BI^-SO_3Na are increased by factors of 14 to 43 folds. It means that the expected large steric effect of long alkyl groups of R-BI^-SO_3Na is compensated by micellar effect of these nucleophiles. In other words, hydrophobic p-NPDPP comes into the Stern layer of micelles of R-BI^-SO_3Na and reacts with BI^- moity of these functional micelles followed by an increase of the reaction rate. That is, R-BI^-SO_3Na with long alkyl groups have dual effects to accelerate the reaction rates by nucleophilicity of their BI^- moities and by micellar catalytic effect of these compounds (R-BI^-SO_3Na with long alkyl groups act as imidazole-functional micelles in aqueous solution).

Activation Parameter of the Reactions. We measured activation parameters of reaction in aqueous and micellar solution to compare inherent reactivities of anions of R-BI (R-BI^-) and R-$BISO_3Na$ (R-BI^-SO_3Na) on dephosphorylation of *p*-NPDPP.

As shown in *Table* 3, activation enthalpies (ΔH^*), free energies (ΔG^*) of the reactions of p-NPDPP mediated by R-BI^- and R-BI^-SO_3Na in aqueous solutions, not including surfactant, are quite high. However, the values of the reactions in CTABr micellar solutions are relatively lower than values in aqueous solutions. It is consistent with increases of the reaction rates in micellar solutions as compared with the reactions in aqueous solutions.

When we compard the parameters (ΔH^* and ΔG^*) of the reactions mediated by R-BI^- and R-BI^-SO_3Na in aqueous solutions, there are not much differences between the values of the reactions by $BI^-$and methyl-BI^-, and BI^-SO_3Na and methyl-BI^-SO_3Na. However, in micellar solutions there are large difference between the values. It means that the inherent reactives of BI^- and R-

BI^- in water are almost equal, and the decrease of the reaction rates mediated by R-BI^- (or R-BI^-SO_3Na) as compared with those by BI^- (or BI^-SO_3Na) are due to an interaction of R group with micelle, a steric effect.

On the other hand, when we compared the ΔH^* values of the reactions mediated by R-BI^- and R-BI^-SO_3Na in micellar solutions, ones having longer group (methyl to butyl) 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 heptyl (*Fig.* 1 and *Table* 1 and 2). And ΔS^* values of the reactions by methyl-BI^- in the micellar solutions were sharply increased as compared with those of the reaction 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[10]. Thus, the mechanism of the enzymatic[10] and micellar[11] reactions would impose upon the reactants its own orientation and steric requirements, a different means of achiving spatical proximity of the reactants, and its own solvent and concentration effects.

However, in the reactions mediated R-BI^-SO_3Na with long alkyl groups, the ΔH^* values gradually decreased by changing the alkyl groups from nonyl to pentadecyl, and it is consistent with gradual increases of the reaction rates (*Table* 1 and 2) due to abilities of micellization of R-BI^-SO_3Na.

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