Nucleophilic Ion Pairs. 8. Facile Nucleophilic Cleavage of Dinitrophenyl Sulfate in the Presence of Micellar Zwitterionic Hydroxamates†

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The sulfate transfer reaction from dinitrophenyl sulfate to hydroxamate nucleophiles was studied in the presence of several types of aqueous micelles at 30 °C, pH 8—9. The zwitterionic hydroxamate was a nucleophile much better than the anionic hydroxamate in the CTAB micelle. The kinetic behavior of the zwitterionic hydroxamate nucleophile was not straightforward and the reactivity of the nucleophile increased with the increase in the relative concentration of the nucleophile and surfactant. These results in the CTAB micelle was analyzed in terms of the two phase model and the rate enhancement relative to the nonmicellar reaction was attributed to substrate binding in the micellar phase and the micellar activation of the hydroxamate nucleophile. The cleavage of dinitrophenyl sulfate by the micellar zwitterionic nucleophile was faster than that by the nonmicellar hydroxamate and the water cleavage by factors of *ca.* 10^4 and more than 10^7, respectively: the fastest cleavage ever observed at the ambient condition.

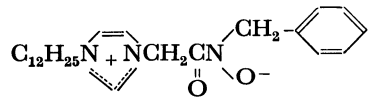
The hydrolysis of sulfate monoesters has been studied increasingly well in recent years, due to realization of the importance of sulfate group transfer *in vivo*.[1] In general, sulfate monoesters are difficult to be cleaved in the neutral pH region and detailed mechanistic studies have been rarely made, apart from acid and alkali hydrolyses.[2]

In relation to the enzymatic catalysis, the sulfate transfer reaction has been investigated in the presence of cyclodextrins,[3] macrocyclic compounds[4] and micelles.[5,6] The rate accelerations in these systems, however, are not large. In the hydrolysis of phenyl esters, the micellar hydroxamate and imidazole anions show extremely high nucleophilicities.[7] These reagents, however, are not effective for negatively-charged sulfate esters.

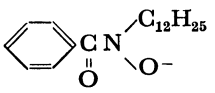
In order to circumvent this disadvantage, a zwitterionic nucleophile, *N*-benzyl-α-(1-dodecyl-3-imidazolio)acetohydroxamate (C_{12}-Im$^+$-HA, **1**), was used in the present study for the sulfate transfer reaction (Eq. 1) in the presence of aqueous micelles of representative surfactants.

The reaction with simpler nucleophiles, *N*-dodecylbenzohydroxamate(LBHA, **2**) and *N*-benzylbenzohydroxamate(BBHA, **3**) was also performed for the comparison purpose.

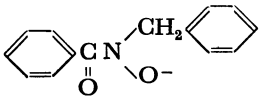
nucleophile:



1 C_{12}-Im$^+$-HA

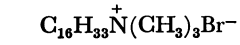


2 LBHA



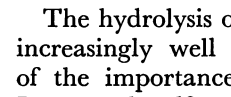
3 BBHA

surfactant:

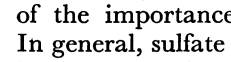


4 CTAB

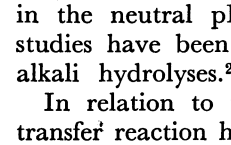
† Contribution No. 537 from Department of Organic Synthesis.



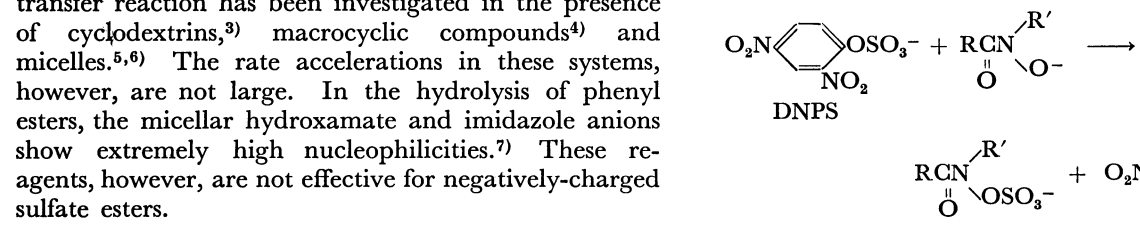
5 $C_{12}\overset{+}{N}2C_1CO_2^-$



6 POOA



7 $C_{18}\overset{+}{N}2C_1C_2OH$



DNPS

(1)

Experimental

Materials. The zwitterionic nucleophile, C_{12}-Im$^+$-HA, was prepared by the reaction of *N*-dodecylimidazole with benzyl *N*-benzylchloroacetohydroxamate accompanied by hydrogenolysis over Pd/$SrCO_3$,[8] mp 157—158 °C. It was identified by elemental analysis and by NMR and IR spectroscopies. Potassium 2,4-dinitrophenyl sulfate (DNPS) was prepared according to the procedure of Sunamoto *et al.*[4] Its purity was 95% as determined by UV spectroscopy: the impurity was 2,4-dinitrophenol. Hexadecyltrimethylammonium bromide (CTAB) was recrystallized two times from ethanol. Poly(oxyethylene)oleyl alcohol (n=10)(α-(9-octadecenyl)-ω-hydroxydeca(oxyethylene)), POOA was used without further purification. (Carboxymethyl)dodecyldimethylammonium chloride, $C_{12}N^+2C_1CO_2$ was obtained by reaction of *N*,*N*-dimethyldodecylamine and chloroacetic acid and recrystallized from ethyl acetate:[8] mp 158—160 °C. (2-Hydroxyethyl)dimethyloctadecylammonium bromide, $C_{18}N^+2C_1C_2OH$, was prepared by refluxing an ethanol solution of 10.0 g (0.03 mol) of octadecyl bromide and 3.5 g (0.04 mol) of 2-(dimethylamino)ethanol for 10 h. After solvent removal, the solid residue was recrystallized two times from acetone; colorless needles, mp 209—211 °C (dec), yield 9.3 g (73%). Found: C, 62.43; H, 11.42; N, 3.31%. Calcd for $C_{22}H_{48}NOBr$: C, 62.54; H, 11.45; N, 3.32%.

Rate Measurement. The hydroxamates and surfactants were dissolved in ethanol and water, respectively. DNPS was dissolved in a 3:7 mixture of water and acetonitrile and kept with ice cooling. These solutions were added to

buffer solutions in a UV cell which had been maintained at 30 °C. Water was added so that the fraction of organic solvents (acetonitrile and ethanol) became 3 v/v %. The reaction rate was determined by following the absorbance increase of 2,4-dinitrophenolate anion at 360 nm (ε_{360}= 12800 M^{-1} cm^{-1}), using a Hitachi UV-visible spectrophotometer (type 124 and 200).

Results

Sulfate Transfer to Anionic Hydroxamates. The time course of DNPS hydrolysis in the LBHA–CTAB system obeyed pseudo first-order kinetics: [DNPS]= 1.9×10^{-5} M, [CTAB]=4.50×10^{-3} M. However, the pseudo first-order rate constant $k_{1,obsd}$ did not vary with the concentration change ($(2—6)\times10^{-4}$ M) of LBHA. Furthermore, the logarithm of the apparent second-order rate constant, log $k_{2,obsd}$, increased linearly with pH at pH 8—10. This pH-rate profile is not consistent with the pK_a value(8.41) of LBHA in the CTAB micelle. Because of the complex kinetic behavior and a relatively small reactivity (*ca.* 10% of C_{12}-Im^+-HA under comparable conditions), LBHA was not used in the subsequent experiment.

The sulfate transfer reaction with a non-micellar hydroxamate, *N*-benzylbenzohydroxamic acid(BBHA),[9] was also studied under the following conditions: pH 9.23, 0.01 M borate buffer, μ=0.01(KCl), 30 v/v %EtOH–H_2O, [BBHA]=2.5×10^{-2} M and [DNPS] =2.0×10^{-5} M. $k_{1,obsd}$ obtained from the Guggenheim plot was only slightly larger than that obtained without the hydroxamate under otherwise the same conditions: 9.8×10^{-5} s^{-1} *vs.* 7.3×10^{-5} s^{-1}. Therefore, $k_{2,obsd}$ is estimated to be smaller than 1×10^{-3} M^{-1} s^{-1}.

Sulfate Transfer to Micellar Zwitterionic Hydroxamates. In the presence of excess DNPS, the nucleophilic attack of C_{12}-Im^+-HA obeyed the pseudo first-order kinetics for more than 80% consumption of the nucleophile: [DNPS]=$(0.52—4.6)\times10^{-4}$ M, [C_{12}-Im^+-HA]=0.13×10^{-4} M, [CTAB]=1.0×10^{-3} M, pH 9.2, 30 °C. The spontaneous hydrolysis was similarly carried out in the absence of the nucleophile and its rate constant, k_{spont}, was subtracted from the overall first-order rate constant, $k_{1,obsd}$. In reality, k_{spont} was approximately 1.0×10^{-4} s^{-1} without regard to the pH change, and much smaller than $k_{1,obsd}$ which was $(2—4)\times10^{-3}$ s^{-1}. Therefore, the correction was not necessary at pH 9.

The pseudo first-order rate constant was proportional to the substrate concentration: correlation coefficient= 0.993. Therefore, the reaction was first order with respect to nucleophile and substrate, and the second-order rate constant ($k_{2,obsd}$) was calculated to be 20.8 M^{-1} s^{-1}. Precipitates were formed when the substrate concentration was increased beyond 5×10^{-4} M.

The pseudo first-order kinetics were similarly observed when excess nucleophile was employed: [DNPS]= 1.7×10^{-5} M, [C_{12}-Im^+-HA]=$(0.51—2.6)\times10^{-4}$ M, [CTAB]=4.0×10^{-3} M, pH 9.0, 30 °C. However, the pseudo first-order rate constant was not a linear function of the nucleophile concentration beyond 1.5×10^{-4} M, as shown in Fig. 1. $k_{2,obsd}$ estimated from the linear portion of Fig. 1 is 2.45 M^{-1} s^{-1}.

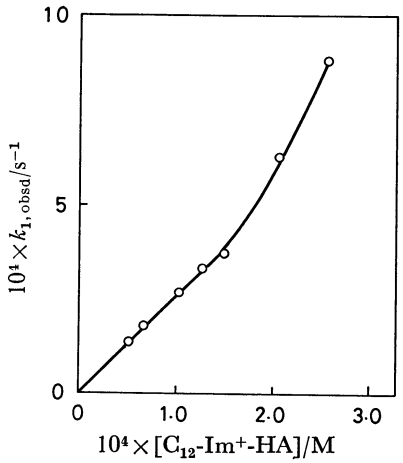


Fig. 1. Rate dependence on nucleophile concentration. pH 9.00±0.1, 30 °C, 3 v/v % EtOH–H_2O, 0.02 M borate buffer, μ=0.01(KCl), [DNPS]=1.72×10^{-5} M, [CTAB]=4.00×10^{-3} M.

This value is only 12% of the rate constant obtained by varying substrate concentrations. Since the pseudo first-order kinetics were always observed for a given run, the discrepancy must arise from the change in the relative concentration of nucleophile, substrate and/or surfactant.

Rate Dependence on Surfactant Concentration. The zwitterionic nucleophile C_{12}-Im^+-HA may form micelles by itself. The property of the mixed micelle of C_{12}-Im^+-HA and CTAB will be affected by their relative concentration, hence the reactivity change of C_{12}-Im^+-HA. Figure 2 shows the variation of the apparent second-order rate constant $k_{2,obsd}$ (pseudo first-order rate constant divided by the nucleophile concentration) with the surfactant concentration at fixed concentrations of DNPS and C_{12}-Im^+-HA. After abrupt increases $k_{2,obsd}$ decreases with increasing surfactant concentrations, irrespective of the type of the surfactant used. The same trend was observed for the hydrolysis of an anionic phenyl ester, 4-acetoxy-3-nitrobenzoic acid (NABA) catalyzed by C_{12}-Im^+-HA in the nonionic micelle.

On the other hand, $k_{1,obsd}$ exhibits a saturation tendency with the simultaneous increase in the concentrations of C_{12}-Im^+-HA and CTAB(the relative concentration of C_{12}-Im^+-HA and CTAB is fixed at 0.26): see Fig. 3. Therefore $k_{2,obsd}$ ($k_{1,obsd}$ divided by the hydroxamate concentration) decreases with the CTAB concentration as also shown in Fig. 3. This tendency corresponds to those in Fig. 2.

pH-*Rate Profile.* The pH-rate profile of the nucleophilic and spontaneous cleavages was studied in the presence of the CTAB and POOA micelles (Fig. 4). log $k_{2,obsd}$ in the presence of the CTAB micelle increases initially with pH but levels off at *ca.* pH 8. This profile appears to reflect the dissociation of the hydroxamic acid. In fact, a linear relation(r=0.997) was obtained when $k_{2,obsd}$ was plotted against α_{HA} (degree of dissociation) which was calculated from Eq. 2 assuming pK_{app}=7.70.

$$\alpha_{HA} = \frac{1}{1+10^{(pK_{app}-pH)}} \quad (2)$$

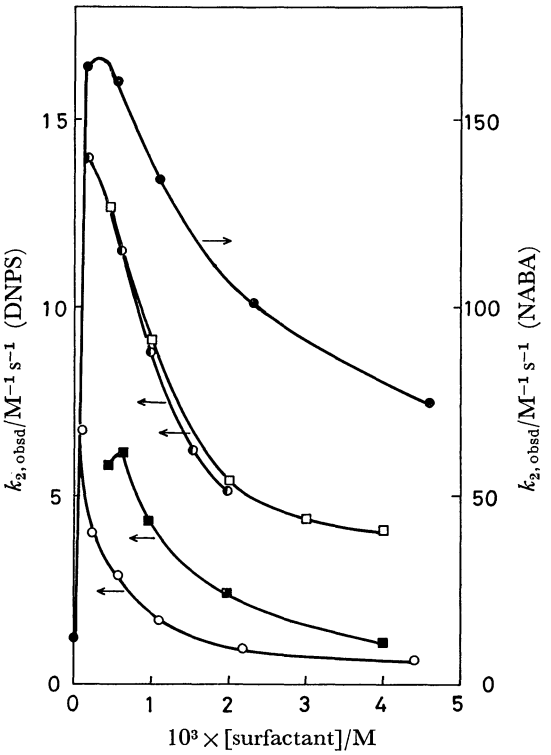


Fig. 2. Rate dependence on surfactant concentration. pH 8.5±0.1, 30 °C, 3 v/v % EtOH-H_2O, 0.02 M borate buffer, μ=0.01(KCl). a) [DNPS]=2.98×10^{-5} M, [C_{12}-Im^+-HA]=3.91×10^{-4} M. b) [NABA]=4.26×10^{-5} M, [C_{12}-Im^+-HA]=3.43×10^{-4} M. —●—, POOA(NABA); —□—, CTAB; —◐—, C_{18}-N^+-$2C_1C_2OH$; —■—, $C_{12}N^+2C_1CO_2^-$; —○—, POOA.

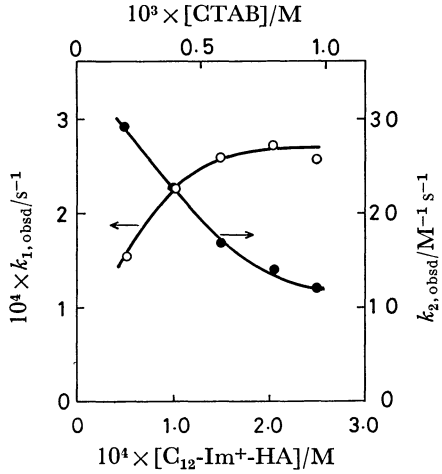


Fig. 3. Rate dependence on concentrations of nucleophile and surfactant at a fixed relative concentration. pH 9.0±0.1, 30 °C, 3 v/v % EtOH-H_2O, 0.02 M borate buffer, μ=0.01(KCl), [DNPS]=1.72×10^{-5} M, [C_{12}-Im^+-HA]/[CTAB]=0.26.

This pK_{app} value agrees with pK_{app} (7.78) obtained in the hydrolysis of *p*-nitrophenyl acetate in the CTAB micelle.[8]

In the POOA system, the pH-rate profile is bell-shaped with the maximum at pH 8.4. This behavior is quite different from what is observed with *p*-nitrophenyl acetate as substrate. In the latter case, a typical saturation profile was found with pK_{app}=8.18. The

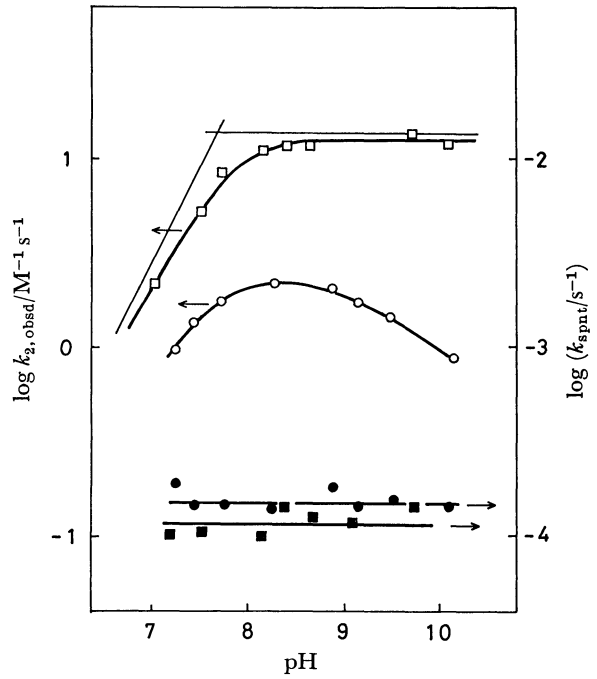


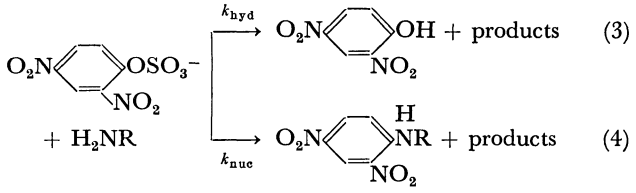
Fig. 4. pH-rate profile. 30 °C, 3 v/v % EtOH-H_2O, 0.01 or 0.02 M borate buffer, μ=0.01(KCl), [DNPS]=(3.2—3.5)$\times10^{-5}$ M, [C_{12}-Im^+-HA]=(2.7—3.0)$\times10^{-4}$ M, [CTAB]=5.13×10^{-4} M, [POOA]=1.00×10^{-3} M. —□—, —■—; CTAB. —○—, —●—; POOA.

interaction of anionic DNPS substrate with C_{12}-Im^+-HA in the nonionic micelle is not so straightforward as that in the cationic micelle.

Figure 4 also contains pH-rate profiles of the spontaneous hydrolysis in the presence of POOA and CTAB. The rate of the spontaneous hydrolysis($\approx10^{-4}$ s^{-1}) does not depend on pH, in consistence with the result of Fendler's.[2]

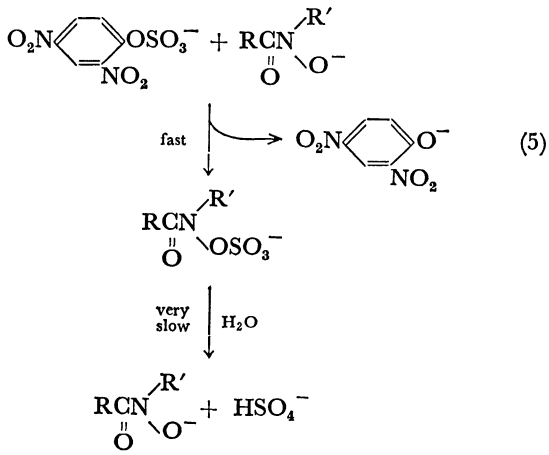
Discussion

Reaction Scheme. The nucleophilic reaction toward dinitrophenyl sulfate has been studied by several groups of the investigator. For instance, Fendler *et al.* noted that hydrolysis and aminolysis competed in the reaction with a variety of amines.[6]



Definite results on the reaction of DNPS with anionic nucleophiles have not been published, probably with the exception of the paper by Sunamoto *et al.*[4] They concluded that the reaction of DNPS with a paracyclophanone oxime involved sulfate transfer to the oximate anion. We do not have direct evidence for the formation of the sulfohydroxamate intermediate; however, the hydroxamate anion would be expected to behave in the same way as the oximate. In our system, the substrate, if decomposed, was completely

converted to dinitrophenol as confirmed spectrally. Therefore, the reaction would proceed by the following equation.



(5)

The stoichiometric reaction of DNPS and C_{12}-Im^+-HA was observed in the presence of excess DNPS; thus turnover of the hydroxamate nucleophile was excluded.

The undissociated hydroxamic acid is not involved in the reaction, because the sulfate transfer is observed only in the alkaline region.

Catalytic Efficiency. Some of the rate constants of the DNPS cleavage are collected in Table 1. The uncatalyzed hydrolysis of DNPS in the neutral to alkaline aqueous media is quite slow and barely detectable: $k_{1,obsd}=2.7\times10^{-5}$ s^{-1} at 25 °C, pH 8.0(or 4.9×10^{-7} M^{-1} s^{-1} when divided by 55.5 M). Some rate enhancements are observed in the presence of β-cyclodextrin and a paracyclophanone oxime; however these enhancements are mostly attributed to substrate binding and, in fact, the rate constant of the intracavity sulfate transfer is not necessarily large relative to that of simple alkaline hydrolysis under similar reaction conditions.[4] Micellar CTAB also shows rate acceleration of at most several fold. Larger rate enhancements are found for functional micelles such as CTAB–piperidine[6] and for a reversed micelle (dodecylammonium propionate in benzene).[10] The micellar hydroxamates possess much greater nucleophilicity. However, the coulombic repulsion of the nucleopile and the substrate renders the kinetic behavior rather complex, as observed for the LBHA–CTAB system. The use of the zwitterionic hydroxamate is advantageous in this respect and produces larger reaction rates. $k_{2,obsd}$ for C_{12}-Im^+-HA in the CTAB micelle is larger than that for CTAB–piperidine by at least 100 fold and is *ca.* 2×10^7 times larger than that of the water hydrolysis. The different behavior of the anionic and zwitterionic nucleophiles (LBHA and C_{12}-Im^+-HA) is observed only in the sulfate cleavage. They possessed similar reactivities in the cleavage of phenyl esters in the CTAB micelle.[8] The enhanced reactivity of a nucleophilic group bound to an ammonium group was also detected in the sulfate cleavage by a partly quaternized poly(ethylenimine).[11]

Kinetic Analysis of Micellar Catalysis. The kinetic behavior of the DNPS cleavage by the micellar hydroxamate is quite complex.

Several cases related to this behavior have been observed in the micellar catalysis. Gitler *et al.*[12] and Tonellato[13] proposed in the hydrolysis of hydrophobic phenyl esters that the saturation kinetics are explicable by assuming active and inactive binding sites in the micelle. However, this interpretation is difficult to accept, since the conventional micellar phase is quite mobile. In fact, the two phase model in which the micellar phase is assumed to be homogeneous has been successfully applied to micellar reactions by Berezin *et al.*[14] and more recently by other workers.[15,16]

This model may be applied to the present system. The kinetic derivation is given in the Appendix. Figure 5 gives plots of $1/k_{2,obsd}$ against the surfactant concentration for the data of Fig. 2. Linear relations are obtained for all cases. According to Eq. 17, the

Table 1. Nucleophilic reactivities in the DNPS cleavage

Catalyst or nucleophile	$k_{1,obsd}$/s^{-1}	$k_{2,obsd}$/M^{-1} s^{-1}	Conditions	Ref.
None	2.7×10^{-5}	4.9×10^{-7} a)	25 °C, pH 8.0	5
β-Cyclodextrin	1.75×10^{-3} b) ($K_S=2.4\times10^{-2}$ M)		37.3 °C, pH 9.98	3
Paracyclophanone oxime c)	4.4×10^{-4} b) ($K_S=1.5\times10^{-4}$ M)		40 °C, 0.1 M NaOH	4
CTAB	1.15×10^{-4} d) (at 1.0×10^{-3} M CTAB)		30 °C, pH 8—10	this study
DAP e)-benzene		0.0187	24.5 °C	9
Piperidine in CTAB		0.098	39 °C	6
BBHA f)		<0.001	30 °C, pH 9.23	this study
LBHA in CTAB	2×10^{-4} d) (at 2×10^{-4} M LBHA)		30 °C, pH 8.5—9.0	this study
C_{12}-Im^+-HA				
in DMOG		6.1	30 °C, pH 8.5—9.0	this study
in POOA		6.8		
in CTAB		11		

a) $k_{1,obsd}/55.5$ M. b) Michaelis-Menten kinetics are observed and the maximum values of $k_{1,obsd}$ is given. K_S is the substrate dissociation constant. c) 10-Hydroxy-11-hydroxyimino[20]paracyclophane. d) The kinetics are not straightforward and $k_{1,obsd}$ at the designated nucleophile concentration is given. e) Dodecylammonium propionate. f) *N*-benzylbenzohydroxamic acid; 30 vol/vol % EtOH-H_2O.

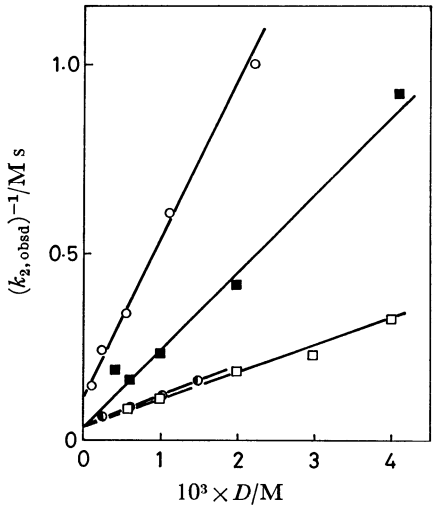


Fig. 5. Relation of $1/k_{2,obsd}$ and surfactant concentration. The data of Fig. 2 are used. —□—, CTAB; —◐—, $C_{18}N^+2C_1C_2OH$; —■—, $C_{12}N^+2C_1CO_2$; —○—, POOA.

TABLE 2. KINETIC CONSTANTS IN VARIOUS MICELLES[a)]

Micelle	$10^3 \times \bar{k}_M/s^{-1}$	K_b/M^{-1}
CTAB	14.6	1600
$C_{18}N^+2C_1C_2OH$	13.6	1600
POOA	2.38	1400
$C_{12}N^+2C_1CO_2^-$	7.06	3300

a) See Fig. 2 for the reaction condition.

reciprocal of the slope corresponds to the first-order rate constant in the micellar phase ($\bar{k}_M$): see Table 2. The "micellar" rate constant increases in the order: CTAB $\simeq$ $C_{18}N^+2C_1C_2OH$ > $C_{12}N^+2C_1CO_2^-$ > POOA. The same order of the micellar effectiveness was observed in the hydrolysis of *p*-nitrophenyl acetate by several zwitterionic hydroxamates.[8)]

The K_b value can be calculated from the intercept of Fig. 5 and is in the range of 1400—3300 M^{-1} as given in Table 2. These values are in reasonable agreement with those of Fendler *et al.*(1300—3100 M^{-1}) which were given as K/N in the hydrolysis of DNPS in the presence of the CTAB micelle.[2)]

These results suggest that the kinetic analysis based on the two phase model is essentially valid if the micellar phase is not greatly perturbed. Since dependencies of $k_{2,obsd}$ on the surfactant concentration are alike for an anionic phenyl ester(NABA) and for a sulfate ester(DNPS), the above-mentioned kinetic behavior is never specific to the sulfate ester. A very similar rate dependence was reported for the electron transfer between negatively-charged metal chelates in the presence of the CTAB micelle.[16)]

On the other hand, the simple two phase model fails when the micellar microenvironment is significantly altered by the varying nucleophile concentration. $k_{1,obsd}$ shows upward curvature in Fig. 1 beyond the nucleophile concentration of 1.5×10^{-4} M. $k_{2,obsd}$ obtained from the data of Fig. 2 does not agree with that estimated in Fig. 3. These anomalies appear to arise mainly from the change in the microenvironment of micelles which contain different amounts of the nucleophile molecule. The presence of a maximum in the pH-rate profile of the POOA system in Fig. 4 may be explained in the same context.

Appendix

The two phase model is used in the following kinetic analysis. Assuming that catalyst C forms comicelles with surfactants and that substrate S is distributed in the micellar and bulk phases,

$$[C]_{total} = [C]_M DV, \tag{6}$$

$$[S]_{total} = [S]_M DV + [S]_W(1-DV), \tag{7}$$

where D is the surfactant concentration and V is the molar volume of the surfactant. Suffix M and W indicate micellar and bulk (water) phases, respectively.

If the reaction proceeds only in the micellar phase, the overall reaction rate is given by

$$v = v_M DV = k_{2,obsd}[C]_{total}[S]_{total} \tag{8}$$

and

$$v_M = k_M[C]_M[S]_M, \tag{9}$$

where k_M is the second-order rate constant in the micellar phase. The partition coefficient of the substrate is given by

$$P_S = \frac{[S]_M}{[S]_W}. \tag{10}$$

The binding constant of the substrate K_b is expressed in terms of P_s as follows.

$$K_b = \frac{[S]_{total}-[S]_W}{[S]_W \cdot D} = \frac{1}{D} \cdot \frac{[S]_M DV - [S]_W DV}{[S]_W} = (P_S - 1)V. \tag{11}$$

When the substrate stays predominantly in the micellar phase ($P_S \gg 1$)

$$K_b = P_S V. \tag{12}$$

From Eqs. 6, 7, and 8,

$$k_M[C]_M \cdot [S]_M DV = k_{2,obsd}[C]_{total} \cdot [S]_{total}. \tag{13}$$

Therefore,

$$k_M P_S = k_{2,obsd}\{1+(P_S+1)DV\} \tag{14}$$

$$k_{2,obsd} = \frac{\bar{k}_M \cdot K_b}{1+K_b D}, \tag{15}$$

where $\bar{k}_M = k_M/V$. (16)

The reciprocal relation of Eq. 15 is

$$\frac{1}{k_{2,obsd}} = \frac{1}{\bar{k}_M \cdot K_b} + \frac{D}{\bar{k}_M}. \tag{17}$$

$\bar{k}_M$ and K_b are determined from the slope and intercept, respectively, of the relation of Eq. 17.

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