# Nucleophilic Ion Pairs. 6. Catalytic Hydrolysis of *p*-Nitrophenyl Acetate by Zwitterionic Hydroxamate Nucleophiles in Representative Micellar Systems[1]

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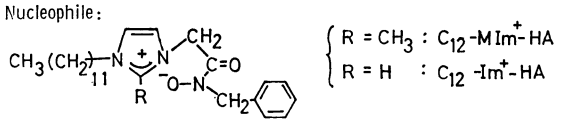
Several surfactant-like zwitterionic hydroxamates were synthesized and their reactions with *p*-nitrophenyl acetate were studied in water in comparison with those of simple, anionic hydroxamates. The zwitterionic hydroxamates showed enhanced reactivities in cationic, zwitterionic and nonionic micelles: 20—100 times relative to the nomicellar rate at pH 8.9, 30 °C. The rate enhancement was attributed to lowered $pK_a$ values and to activation of the hydroxamate anion in the hydrophobic domain. The rate was suppressed in an anionic micelle because of the enhanced $pK_a$ value. Deacylation of the acetyl hydroxamate intermediate was hydroxide-catalyzed. The enhanced reactivity of the zwitterionic hydroxamate in organic media was less sensitive to the water concentration than that of the hydroxamate ion pair. These results can be explained in terms of "*hydrophobic ion pair.*"

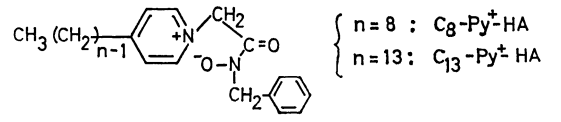
Anionic nucleophiles such as oximates, hydroxamates, thiolates and imidazole anions possess remarkably enhanced reactivities in the presence of cationic micelles and cationic polysoaps.[2] The increase in rate cannot be attributed to the peculiar microenvironment of these aqueous micelles, and we proposed that the formation of nucleophilic ion pairs in the hydrophobic microenvironment— "*hydrophobic ion pairs*" is essential for the rate enhancement. This is supported by the extremely high reactivity of tetraalkylammonium hydroxamate ion pairs in dry aprotic solvents[3,4] and by activation of hydrophobic anionic nucleophiles in the presence of the nonmicellar (in the conventional meaning) aggregate of trioctylmethylammonium chloride.[5]

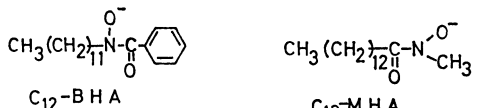
Zwitterionic nucleophiles may form hydrophobic ion pairs by themselves and could show high reactivities. Several papers describe their unexpectedly high nucleophilicities in the micellar[2,6] and polymeric[7–10] systems. However, no unified interpretation has so far been given.

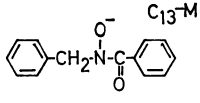
In the present study, we have systematically examined the reactivity of four zwitterionic nucleophiles in representative aqueous micelles (cationic, anionic, zwitterionic, and nonionic micelles) and in organic media. The structures of the nucleophiles and surfactants used are as follows.

Nucleophile:

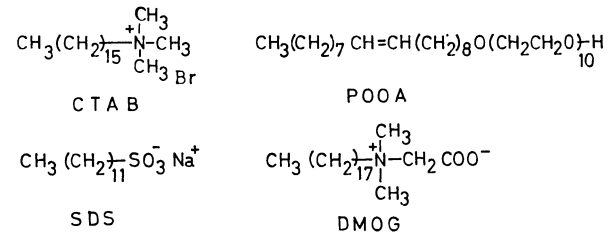



Surfactant:




## Experimental

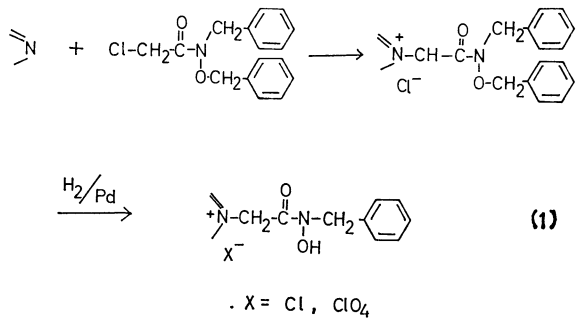
*Materials.* The preparation and purification of *N*-dodecylbenzohydroxamic acid($C_{12}$-BHA),[11] *N*-benzylbenzohydroxamic acid (BBHA),[12] *N*-methylmyristohydroxamic acid($C_{13}$-MHA),[13] and *p*-nitrophenyl acetate[11] has been described. Commercial CTAB was recrystallized from ethanol several times. *N,N*-Dimethyl-*N*-octadecylglycine (DMOG) was prepared by the reaction of *N,N*-dimethyloctadecylamine and chloroacetic acid and recrystallized twice from ethyl acetate, mp 140—142 °C. Its IR and NMR spectra were in line with the structure. Commercial SDS and POOA were used without further purification.

*N*-Dodecylimidazole was prepared as follows according to the procedure of Härig:[14] Imidazole (20 g, 0.3 mol) was dissolved in a mixture of ethanol (70 ml) and aqueous 20 M (1 M=1 mol dm$^{-3}$) NaOH (30 ml), and 99 g (0.4 mol) of dodecyl bromide was added at 80—85 °C with stirring over 2.5 h. Stirring was continued at room temperature for 5 h. The solvent was then removed *in vacuo* and the residue was extracted twice with chloroform. The extract was dried over $Na_2SO_4$, solvent removed and the residue distilled: yield 65%; bp 158—168 °C/35 mmHg (1 mmHg=133.322 Pa). IR and NMR spectra were in line with the expected structure.

A similar procedure was used for preparing *N*-dodecyl-2-methylimidazole from dodecyl bromide and 2-methylimidazole: bp 147—148 °C/3 mmHg (lit,[15] bp 174—176 °C/3 mmHg).

4-Octylpyridine was obtained from pyridine and octanoic anhydride according to the procedure of Arens and Wibaut[16] in 7% yield: bp 112—114 °C/4 mmHg (lit,[16] bp 265—268 °C). 4-Tridecylpyridine was prepared from 4-pyridylmethyllithium and dodecyl bromide by the procedure of Wibaut and Hey:[17] yield 26%, mp 129—131 °C (as hydrochloride). Found: C, 67.82; H, 10.09; N, 4.57%. Calcd for $C_{18}H_{31}N \cdot HCl \cdot H_2O$; C, 68.43; H, 10.84; N, 4.43%.

These alkylamines were quaternized by benzyl *N*-benzylchloroacetohydroxamate (bp 150—155 °C/0.03 mmHg)[9] in acetone at 50 °C for 2 h, the benzyl group being removed by hydrogenation in ethanol over 5% Pd/$SrCO_3$.



(1)

. X= Cl, $ClO_4$

$C_{12}$-$Im^+$-HA; mp 157—158 °C (from acetonitrile). Found: C, 66.03; H, 8.80; N, 9.66%. Calcd for $C_{24}H_{38}N_3O_2Cl$: C, 66.11; H, 8.78; N, 9.64%.

$C_{12}$-$MIm^+$-HA; mp 176—177 °C (from acetonitrile). Found: C, 66.75; H, 9.01; N, 9.29%. Calcd for $C_{25}H_{40}N_3O_2Cl$: C, 66.72; H, 8.96; N, 9.34%.

$C_8$-$Py^+$-HA; mp 88—89 °C (crystallized as perchlorate salt from ethanol and ether). Found: C, 57.69; H, 6.87; N, 6.12%. Calcd for $C_{22}H_{31}N_2O_6Cl$: C, 58.08; H, 6.87; N, 6.16%.

$C_{13}$-$Py^+$-HA; mp 176—177 °C (from acetonitrile). Found: C, 70.04; H, 8.90; N, 6.06%. Calcd for $C_{27}H_{41}N_2O_2Cl$: C, 70.33; H, 8.96; N, 6.08%.

*Kinetics.* The hydrolysis of PNPA in the aqueous system was conducted in 3 v/v% EtOH–$H_2O$ at 30 °C, $\mu$=0.01 (KCl) in the pH range 6—10. The reaction was followed by the appearance of *p*-nitrophenolate at 401 nm (Hitachi 200 UV-visible spectrophotometer with a thermostated cell compartment). In the presence of excess nucleophile the reaction followed the pseudo first-order rate law for more than 90% completion. The pseudo first-order rate constant was divided by the total nucleophile concentration to give the apparent second-order rate constant of acylation, $k_{a,obsd}$. In the case of the hydrolysis performed in organic media, the nucleophiles were neutralized by addition of 10 times excess of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

Burst-type kinetics were observed in the presence of excess substrate. The rate constants of acylation and deacylation were determined according to the procedure reported.[11]

Calculations were carried out with the aid of a programmable desk calculator, the least-squares procedure being applied wherever possible. The correlation coefficient was always better than 0.99. The pH measurement was carried out with a Toa Digital pH meter (Type HM-10A), pH variation of the aqueous reaction medium being confirmed to be smaller than ±0.05. The water content in the organic media was determined with a coulometric Karl-Fischer apparatus (Hiranuma Aquacounter, AQ-1).

## Results

*Acylation.* The reaction of PNPA with excess hydroxamate nucleophiles gives the apparent rate constant of acylation as

$$k_{a,obsd} = \frac{k_{obsd} - k_{spont}}{[HA]_{total}} \quad (2)$$

where $k_{obsd}$ and $k_{spont}$ are pseudo first-order rate constants of *p*-nitrophenol release in the presence and absence of the nucleophile, respectively, and $[HA]_{total}$ is the total hydroxamic acid concentration.

Table 1. Second-order rate constants of acylation in the micellar systems[a]

| Hydroxamate | $k_{a,obsd}$ ($M^{-1}s^{-1}$) | | | | |
|---|---|---|---|---|---|
| | Nonmicellar | SDS | CTAB | POOA | DMOG |
| $C_{12}$-$Im^+$-HA | 12 | 1.2 | 1000 | 270 | 1200 |
| $C_{12}MIm^+$-HA | 13 | 0.8 | 1300 | 250 | 1100 |
| $C_{13}$-$Py^+$-HA | 14 | 1.0 | 1100 | 310 | 1300 |
| $C_8$-$Py^+$-HA | 12 | — | 320 | 45 | 420 |
| $C_{12}$-BHA | — | 0.9 | 1500 | 25 | 75 |
| $C_{13}$-MHA | — | 1.3 | 1300 | 32 | 45 |
| BBHA | 12 | — | 1500 | 13 | 23 |

a) 30 °C, 3 v/v% EtOH–$H_2O$, $\mu$=0.01(KCl), pH 8.90 ±0.05 (0.01 M Borate). [PNPA]=$9.46\times10^{-6}$ M, [catalysts]=$(3.05—7.08)\times10^{-5}$ M. Surfactant concentrations are $1\times10^{-3}$ M except for ([SDS]=$1\times10^{-2}$ M).

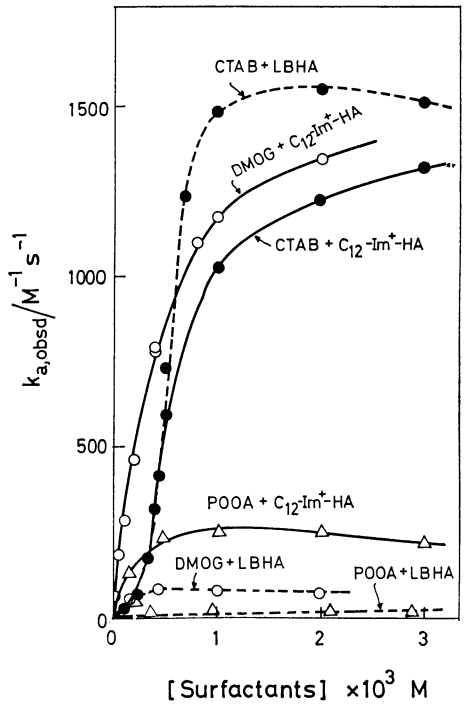



Fig. 1. Rate dependence on surfactant concentration. 30 °C, 3 v/v%EtOH–$H_2O$, $\mu$=0.01 (KCl), pH 8.90± 0.05 (0.01 M Borate). [$C_{12}$-$Im^+$-HA]=$7.08\times10^{-5}$ M [LBHA($C_{12}$-BHA)]=$7.49\times10^{-5}$ M

The $k_{a,obsd}$ values obtained in various micellar systems at pH 8.9 are summarized in Table 1. In the absence of micelles, the nucleophilic reactivity of the zwitterionic hydroxamates is similar to that of the simple hydroxamate (BBHA). $k_{a,obsd}$ of all hydroxamates was enhanced *ca.* 100 times by the cationic micelle (CTAB) and lowered to *ca.* 1/10 of the original value by the anionic micelle (SDS). As an exception, $C_8$-$Py^+$-HA was activated only *ca.* 30 times by the CTAB micelle because of its lower hydrophobicity. The non-zwitterionic hydroxamates ($C_{12}$-BHA, $C_{13}$-MHA, and BBHA) are not particularly activated in the nonionic and zwitterionic micelles, whereas the zwitterionic hydroxamates are activated to a greater extent. Since the nucleophiles cannot form micellar aggregates by

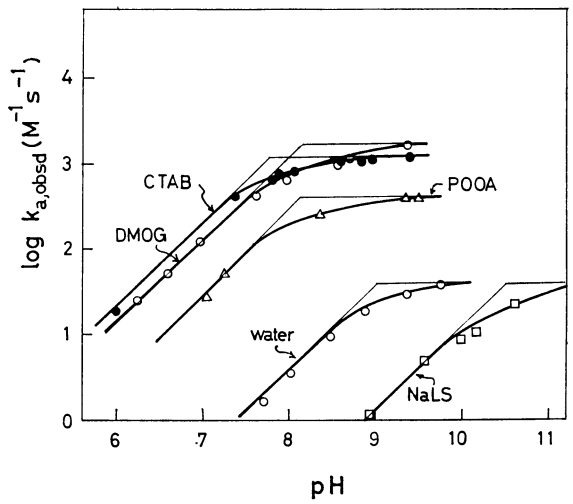



Fig. 2. pH-rate profile of the acylation of $C_{12}$-$Im^+$-HA. 30 °C, 3 v/v% EtOH-$H_2O$, $\mu$=0.01 (KCl), [$C_{12}$-$Im^+$-HA]=$7.08\times10^{-5}$ M, [PNPA]=$9.46\times10^{-6}$ M. Surfactant concentration: $1\times10^{-3}$ M for CTAB, DMOG and POOA. $1\times10^{-2}$ M for NaLS (SDS).

themselves under these conditions, the rate enhancement is closely related to the micelle formation of added surfactants. Figure 1 shows the dependence of $k_{a,obsd}$ on the surfactant concentration for $C_{12}$-BHA and $C_{12}$-$Im^+$-HA, $k_{a,obsd}$ increasing rapidly at the surfactant concentration near the critical micelle concentration: $8\times10^{-4}$ M for CTAB,[11] $3\times10^{-4}$ M for DMOG[18] and *ca.* $10^{-6}$ M for POOA.[19]

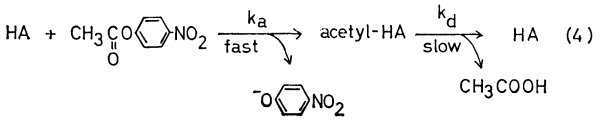
$C_{12}$-$Im^+$-HA was selected as a representative zwitterionic nucleophile and its pH rate prophiles were studied in the presence of various micelles (Fig. 2). The solid curves were obtained by means of

$$k_{a,obsd}=\frac{K_a}{K_a+a_H}\cdot k_a \qquad (3)$$

where $K_a$ and $k_a$ are the acid dissociation constant of the hydroxamic acid and the second-order rate constant of acylation for the effective hydroxamate species, respectively, and determined by the best-fit of the theoretical and experimental curves. The results are summarized in Table 2. As compared to the nonmicellar value, the p$K_a$ value in the anionic micelle is increased by *ca.* 1 p$K$ unit and decreased by the nonionic, cationic and zwitterionic micelles. The $k_a$ value in the anionic SDS micelle is similar to the nonmicellar value, but large increases are observed in other micelles: *ca.* 10 fold in POOA; 30—40 fold in CTAB and DMOG.

The influence of ionic strength on $k_{a,obsd}$ is shown in Fig. 3. $k_{a,obsd}$ decreases with increasing ionic strength in all the micellar systems studied. However, the decrease was smaller than that observed for the $C_{12}$-BHA–CTAB system.

*Deacylation.* In the reaction of $C_{12}$-$Im^+$-HA with excess PNPA, the *p*-nitrophenol release follows the burst kinetics: *i.e.*, rapid acylation and subsequent, slow deacylation.




(4)

Table 2. Rate constants of acylation and dissociation constant in the reaction of PNPA and $C_{12}$-$Im^+$-HA[a]

| Surfactant | $C_{12}$-$Im^+$-HA p$K_a$ | $C_{12}$-$Im^+$-HA $k_a$ ($M^{-1}s^{-1}$) | $\lambda_{max}$ of Methyl Orange in micelles (nm) |
|---|---|---|---|
| None | 9.03 | 38 | 465 |
| SDS ($1\times10^{-2}$ M) | 10.5 | 40 | — |
| POOA ($1\times10^{-3}$ M) | 8.18 | 420 | 440 |
| CTAB ($1\times10^{-3}$ M) | 7.78 | 1300 | 415 |
| DMOG ($1\times10^{-3}$ M) | 8.18 | 1580 | 420 |

a) 30 °C, 3 v/v% EtOH-$H_2O$, $\mu$=0.01 (KCl), [$C_{12}$-$Im^+$-HA]=$7.08\times10^{-5}$ M.

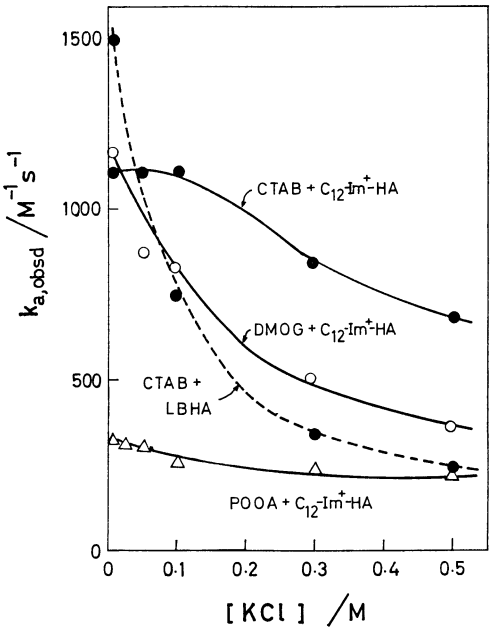



Fig. 3. Effect of ionic strength on the acylation rate. 30 °C, 3 v/v% EtOH-$H_2O$, pH 8.90±0.05 (0.01 M Borate). [$C_{12}$-$Im^+$-HA]=$7.08\times10^{-5}$ M, [LBHA($C_{12}$-BHA)]=$7.49\times10^{-5}$ M. Surfactant concentration; $1\times10^{-3}$ M.

The apparent rate constants of acylation and deacylation can be estimated by the following equations.

$$k_{a,obsd}=\frac{b\sqrt{B}}{[PNPA]_0\sqrt{[HA]_0}} \qquad (5)$$

$$k_{d,obsd}=b-k_a[PNPA]_0 \qquad (6)$$

where $B$ is the extrapolation at $t$=0 of the steady-state *p*-nitrophenol release, and $b$ is the pseudo first-order rate constant of the presteady state curve.[11,12]

Results obtained from analysis of the burst kinetics are given in Table 3. The $k_{a,obsd}$ values estimated by Eq. 5 agree fairly well with those obtained under the pseudo first-order conditions (Table 1).

The burst type experiment was carried out at pH 8—10. The resulting pH-rate profile of deacylation is shown in Fig. 4. In all the systems, log $k_{d,obsd}$ is a linear function of pH with the slope +1. This indicates that the deacylation process is hydroxide-catalyzed.

TABLE 3. RATE CONSTANTS OF ACYLATION AND DEACYLATION DETERMINED FROM THE BURST KINETICS[a)]

| Hydroxamate | Micelle | $k_{a,obsd}$ ($M^{-1}s^{-1}$) | $k_{d,obsd}$ ($\times 10^2 s^{-1}$) |
|---|---|---|---|
| $C_{12}$-Im$^+$-HA | CTAB | 1030 | 3.50 |
| $C_{12}$-Im$^+$-HA | DMOG | 1150 | 0.376 |
| $C_{12}$-Im$^+$-HA | POOA | 250 | 0.214 |

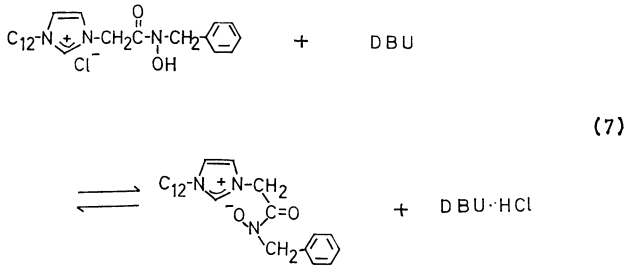
a) 30 °C, pH 8.9±0.1(0.01 B Borate), 3 v/v% EtOH-$H_2O$, $\mu$=0.01(KCl), [$C_{12}$-Im$^+$-HA]=$1.42\times10^{-5}$ M, [PNPA]=$1.89\times10^{-4}$ M. [Surfactant]=$1\times10^{-3}$ M.

TABLE 4. REACTION OF HYDROXAMATES WITH PNPA IN ORGANIC MEDIA[a)]

| Solvent | [$H_2O$] (mM) | $k_a$ ($M^{-1}s^{-1}$) | |
|---|---|---|---|
| | | $C_{12}$-Im$^+$-HA | $C_{12}$-BHA |
| Benzene | 1.0 | 1200 | 606 |
| | 10 | 900 | 105 |
| | 40 | 680 | 25 |
| Dimethylformamide | 15 | 3300 | 1000 |
| Acetonitrile | 10 | *ca.* 4000 | 1500 |
| Ethanol | 33 | 160 | 0.1 |

a) 30 °C, [Hydroxamic acid]=$1.42\times10^{-5}$ M, [PNPA]=$1.89\times10^{-4}$ M, [DBU]=$(1.42—13.2)\times10^{-4}$ M.

*Reaction in Organic Media.* The reaction of $C_{12}$-Im$^+$-HA with PNPA was studied in dry organic solvents. The hydroxamate anion was produced by addition of strongly basic DBU. Figure 5 shows the increase in the hydroxamate absorbance at 270 nm with increasing amounts of DBU added. We see that 10 times excess of DBU is sufficient to neutralize the hydroxamic acid completely.




(7)

The apparent rate constant of acylation shows the same trend as that of the absorbance change. The *p*-nitrophenol release is thus effected solely by the hydroxamate anion. It was confirmed in a separate experiment that DBU alone can cause no *p*-nitrophenol release.

Values of the second-order rate constant of acylation $k_a$ for $C_{12}$-Im$^+$-HA, determined in several organic media, are given in Table 4 together with those for $C_{12}$-BHA for the sake of comparison. The $k_a$ values of these two nucleophiles differ by factors of 2—3 in dry aprotic solvents, a large reactivity difference being observed in moist benzene and in ethanol. Thus, the reactivity of the $C_{12}$-BHA anion in benzene decreases drastically with increase in water concentrations. However, the reactivity of the $C_{12}$-Im$^+$-HA anion is much less sensitive to the water concentration. In the same vein, $k_a$ for $C_{12}$-Im$^+$-HA anion is 1600 times larger than that of $C_{12}$-BHA anion in ethanol.

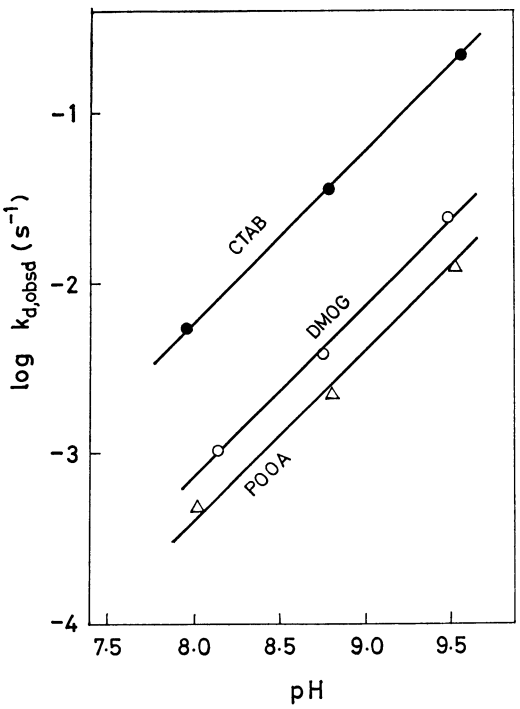



Fig. 4. pH-rate profile of the deacylation. 30 °C, 3 v/v% EtOH-$H_2O$, $\mu$=0.01 (KCl). Surfactant concentration, $1\times10^{-3}$ M.

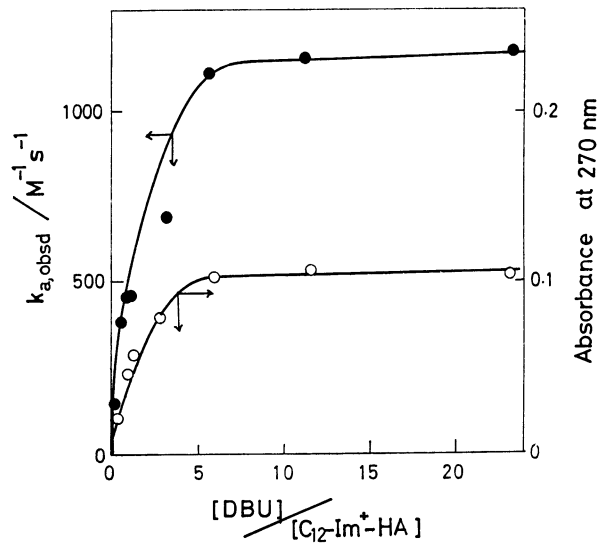



Fig. 5. Effect of DBU concentration in the reaction of $C_{12}$-Im$^+$-HA and PNPA in dry benzene. 30 °C, [$H_2O$]=1—3 mM, [$C_{12}$-Im$^+$-HA]=$4.75\times10^{-5}$ M, [PNPA]=$6.90\times10^{-6}$ M.

## Discussion

The results on the reactivity of zwitterionic nucleophiles are wholly consistent with the concept of "*hydrophobic ion pair.*" As shown in Table 1, simple hydroxamates such as $C_{12}$-BHA and $C_{13}$-MHA are highly activated in the cationic micelle due to the ion pair formation with the ammonium surfactant, but this activation mechanism cannot operate in other types of micelle. The zwitterionic hydroxamates are activat-

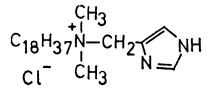
ed in the presence of the cationic, zwitterionic and nonionic micelles to various extents. In this case, the countercation is provided in the form of the intramolecular ammonium group. What is required is the hydrophobic microenvironment. The structure of the cationic moiety (imidazolium *vs.* pyridinium) does not affect the reactivity. The activation mechanism is better understood by examining the data in Table 2. The enhanced rate constant for $C_{12}$-Im$^+$-HA in the three micelles is produced by lower p$K_a$ values and increased $k_a$ values. The $k_a$ value is correlated with the hydrophobic microenvironment estimated by the absorption maximum of Methyl Orange. A smaller increase in $k_a$ in the nonionic micelle is in line with the limited hydrophobic nature of this micelle. The lowering of reactivity observed in the anionic micelle is caused by the increased p$K_a$ value. $k_a$ is not affected by the anionic micelle.

The reactivity of hydroxamate ammonium ion pairs in dry aprotic solvents is greatly reduced by minute amounts of water.[3,4] Similar data have been obtained in this study for $C_{12}$-BHA in benzene (Table 4). $k_a$ decreases by a factor of 24 with increasing water concentrations from 1 mM to 40 mM. However, the rate-depressing effect of water is much less pronounced for the zwitterionic nucleophile; it retained more than 50% of the original reactivity during the same increase in water.

The large $k_a$ difference (1600 fold) in ethanol between $C_{12}$-Im$^+$-HA and $C_{12}$-BHA should be related to the varied sensitivity of their reactivities to water. It is concluded that the zwitterionic hydroxamate forms a stable intramolecular ion pair which is deactivated less readily by protic solvents.

The deacylation reaction of the acetyl hydroxamate intermediate is mainly hydroxide-catalyzed. Figure 4 shows that the deacylation step is accelerated by the micellar microenvironment in the order: CTAB$\gg$ DMOG>POOA, reflecting the concentration effect of the hydroxide anion in the micellar phase.

The enhanced reactivity of the zwitterionic nucleophile has been utilized in several polymer catalysts.[7-8] In micellar catalysis, use of the well-defined zwitterionic nucleophile has been limited in number.[2,6] However, some of the reported functional micelles seem to show high reactivity because of their zwitterionic nature. The first example was reported by Tagaki *et al.* for an imidazole-containing ammonium surfactant micelle (**1**).[20] Since then several papers have appeared on the enhanced nucleophilicity of the hydroxyethyl and/or imidazole groups attached to the ammonium surfactant (**2**, **3**).[21-27]



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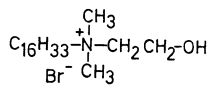

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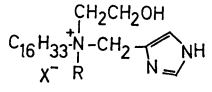

3 (R = $CH_3$, $C_2H_5$)

Rate enhancements in these examples should also arise from lowered p$K_a$ values and activation of the anionic nucleophiles formed.[22] However, zwitterionic hydroxamates are the particularly effective nucleophile since their p$K_a$ values are in the weakly alkaline region. The second-order rate constants of acyl transfer from PNPA to the other zwitterionic nucleophiles **1**, **2**, **3** are not quite as large, because the effective zwitterionic species are formed only in small amounts in the neutral pH region due to their high p$K_a$ values.

## References


1) Contribution No. 500 from Department of Organic Synthesis.
2) T. Kunitake, S. Shinkai, and Y. Okahata, *Bull. Chem. Soc. Jpn.*, **49**, 540 (1976) and papers cited therein.
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