Kinetic Studies of Alkaline Hydrolysis of N-Phenylbenzohydroxamic Acid in the Presence of Micelles

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The alkaline hydrolysis of N-phenylbenzohydroxamic acid has been studied under micellar (k_ψ) and nonmicellar (k_w) conditions using cationic (cetyltrimethylammonium bromide, cetylpyridinium chloride), anionic (sodium lauryl sulphate), and non-ionic (Triton X-100) micellar agents. The results are explained by the pseudophase ion-exchange model. Both the cationic and anionic micelles assist the hydrolysis, whereas nonionic micelle does not affect the rate. The micellar catalysis is inhibited by added salts. Temperature and substituent effects have been studied. The mechanism of the reaction has been proposed.

The micellar catalysis of organic reactions has been widely studied[1]. The study of both unimolecular and bimolecular reactions has received extensive coverage. Surprisingly much less is known about the micellar catalysis of hydroxamic acids[2]. The aim of the present investigation was to examine the effects of cationic, anionic and nonionic surfactants upon the alkaline hydrolysis of the model substrate, N-phenylbenzohydroxamic acid (PBHA). Micelles can incorporate hydrophobic solutes, and by virtue of their charge, ionic micelles attract counterions and repel co-ions. Micelles influence reaction rates and products in various ways. They provide a reaction medium apparently distinct from the bulk solvent, and rate constants may be different in aqueous and micellar pseudo-phases. In addition, micelles can accelerate bimolecular reactions by bringing reactants together, or inhibit reactions by keeping reactants apart. In the present work, we have used three different types of surfactants : (i) cationic (cetyltrimethylammonium bromide CTAB, $C_{16}H_{33}NMe_3Br$ and cetylpyridinium chloride CPC, $C_{21}H_{38}ClNH_2O$), (ii) anionic (sodium lauryl sulphate NaLS, $C_{12}H_{25}SO_4Na$, and (iii) nonionic (Triton X-100, $R_8C_6H_4(OCH_2CH_2)_{9.5}OH$). We have been interested in the micellar hydrolysis of hydroxamic acids, and micellar effects upon acidic hydrolysis of hydroxamic acids have been investigated[3]. The

purpose of this work is to describe the experimental data by means of the pseudo-phase ion exchange (PIE) model. The kinetics, effects of substitution and activation parameters have all been considered in formulating mechanistic pathways.

Results and Discussion

The experimental pseudo-first order rate constants (k_ψ) for the investigated reaction in micellar solutions of CTAB, CPC, NaLS and Triton X-100 are given in Table 1, and also illustrated graphically (Fig. 1). For all the surfactants (except Triton X-100), k_ψ increases with increasing concentration of the surfactant. Owing to the low solubility of PBHA
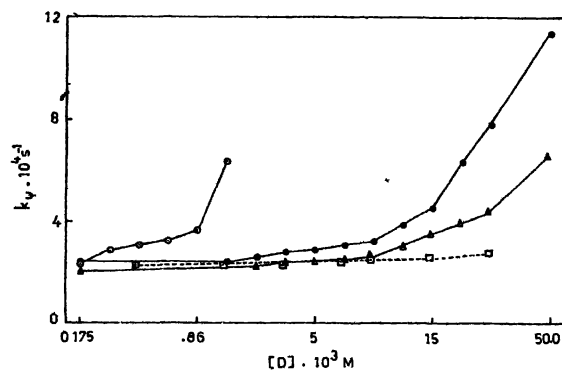

Fig. 1. Effect of surfactants upon hydrolysis of PBHA at 65°: (o) SLS, (•) CTAB, (Δ) CPC and (□) TX-100.

in water, 20% (v/v) dioxane has been used as the solvent. The cationic and anionic micelles enhanced the rate of hydrolysis, but a nonionic micelle has no significant effect. The micellar catalytic effect has been found to follow the order : CTABr > CPC > NaLS > Triton X-100. This rate acceleration in micellar solutions arises from different rates of reaction of the substrate in the micellar phase and in the bulk solution, and the distribution of the substrate between these two phases. Basically, these rate effects can be attributed to electrostatic and hydrophobic interactions between the substrate and the surfactant aggregate.

TABLE 1–EFFECT OF SURFACTANTS ON THE HYDROLYSIS OF
N-PHYENYLBENZOHYDROXAMIC ACID AT 65° IN 0.05 M NaOH
IN 20% (v/v) DIOXANE

| Sufactant | k_ψ ($\times$ 10^4 s^{-1}) | | | |
$\times$ $10^3 M$	CTAB	CPC	NaLS	TX-100
0.0	1 89	1.89	1.89	1.89
0.175	2 42	2.05	2.36	–
0.347	–	–	2.89	–
0.520	–	–	3 06	2 27
0.694	–	–	3.24	–
0.86	–	–	3 65	–
1.04	2.39	–	6 38	2.20
1.40	2.58	2.25	–	2.39
2.50	2.79	2.36	–	2.26
5.00	2.90	2.42	–	–
6.86	3.08	2.48	–	2.36
9.60	3.22	2.56	–	2.46
12.3	3.87	3 05	–	–
15.0	4.52	3.49	–	2.55
20.5	6.33	3.89	–	–
24.6	7.33	4.32	–	2.75
50.0	11.58	6.54	–	

Micellar effects upon reaction rates are generally analysed in terms of the pseudo-phase ion exchange model. Despite its shortcomings, it fits a great deal of data[4,5]. Micelles and bulk aqueous medium are treated as distinct reaction media with their own properties, that is, the micelles are regarded as a submicroscopic solvent. The variation of the rate constant with surfactant is generally treated on the assumption that substrate 'S' is distributed between the aqueous and micellar pseudo-phases, designated by subscripts 'W' and 'M' respectively (Scheme 1), and can react in each pseudo-phase, with the first order rate constants being k_W and k_M.

The concentration of micellised surfactant is
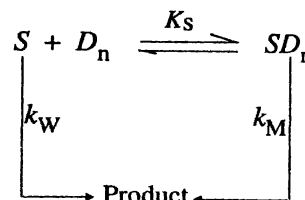
Scheme 1

designed D_n and its concentration is that of the total concentration (D) less that of monomeric surfactant, which will be approximately that of the critical micelle concentration under kinetic conditions (eq. 1),

$$D_n = [D] - cmc \qquad (1)$$

K_S is the equilibrium constant for substrate binding (eq. 2),

$$K_S = [SD_n] / (S) ([D] - cmc) \qquad (2)$$

This model leads to the relationship (eq. 3),

$$1/(k_W - k_\psi) = 1/(k_W - k_M) + N/K_S ([D] - cmc) (k_W - k_M) \qquad (3)$$

in which k_ψ is the observed pseudo-first order rate constant, and N the micellar aggregation number. Values of K_s/N and k_M were obtained (Table 2) from the slope and intercept of the linear relationship observed in a plot of $1/(k_w - k_\psi)$ vs $1/([D] - cmc)$. The data of Table 1 was analysed according to equation 3. Linear relationship resulted in values for the parameters in Table 2 (obtained by the least-squares treatment).
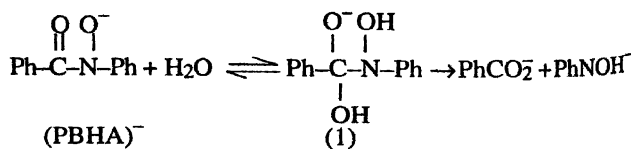
Scheme 2

Since the experimental conditions were identical for all the compounds, the value of N will be the same for these compounds. Therefore, the micellar binding constant (K_S) is proportional to the K_S/N values (Table 2). The cmc values are taken from the literature[6,7]. The qualitative explanation offered above, for the observed enhancement, would mean that the reaction occurs mostly in the micellar phase or that the reaction in bulk aqueous

phase is negligible. The rate is increased 10-fold in the presence of CTAB, 5-fold in presence of CPC, and by 5 to 6-fold in the presence of NaLS. The catalytic effects of nonionic surfactants (Triton X-100) on the reaction seems to be less significant.

The mechanism of alkaline hydrolysis of PBHA is shown in Scheme 2. The pK_{AH} of PBHA is 8.0, thus the substrate is ionised to PBHA⁻ in NaOH. The water molecule attacks the acid anion, resulting in the formation of a tetrahedral intermediate, which then decomposes to the product in a slow step. The acceleration or deceleration in the presence of micelles can be rationalised by considering the forces that would stabilise or destabilise the tetrahedral intermediate. Cationic micelles effectively accelerate attack by OH⁻ and other nucleophiles or bases[8]. The distribution of counteranions between water and ionic micelles indicates that the micellar Stern layer is similar to a concentrated ionic solution[4]. If this conclusion is correct, then the concentration of OH⁻ in the Stern layer of a cationic micelle could be such that a tetrahedral intermediate will always decompose to the products.

bound strongly to it at the micelle-water interface.

Activation parameters : The activation parameters were analysed by a least-squares method using computer program (Eyring equations) which gave values for $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ (Table 3). These were determined by studying the hydrolysis at different temperatures (55, 65, 75°). These values are in favour of a bimolecular mechanism. Although the micellar effects do not change markedly with temperature, the activation enthalpy and entropy are affected by ionic sufractants. Addition of micelles of both cationic and anionic surfactants leads to a decrease in entropy and enthalpy of activation because of favourable electrostatic interactions. However, the variation in $\Delta G^{\neq}$ is considerably small and can be taken as nearly constant.

Salt effects : Generally, added salts always reduce the micellar catalysis of bimolecular reactions[6,9], unless they introduce a new reaction path. Inhibition of catalysis by added salts could be caused by[10] (i) reduction of the micellar charge due to an increase in the number of counter ions in the Stern layer, (ii) exclusion of the substrate from the micelle by competition for the available sites, (iii) exclusion of hydroxide ion from the micelle. The retardation increases with decreasing charge density of the counterion to the micelle. The effect of added salts is shown in Table 4. In the present case, all the salts decrease the rate in the presence of CTAB. A cationic micelle could decrease the free energy of a bulky anionic transition state relative to that of the initial state, which is an uncharged molecule plus a small anion. The electrostatic interaction between the cationic micelle and the negatively charged transition state could be weakened by the binding of the inhibiting ions to the micellar surface.

TABLE 2—CORRELATION OF RATE DATA BY EQUATION (2) FOR PBHA

Surfactant	D_n range $\times 10^3 M$	K_s/N	Correlation coefficient
CTAB	1.40–12.5	121.5	0.910
CPC	5.00–20 5	26 3	0.946
SLS	0.35–0.86	75 7	0.996

Micellar enhancements of bimolecular reactions are due to the increased reactant concentration in the micellar phase. The present results indicate that the reaction takes place between the substrate solubilised into a micelle and the nucleophile residing at the Stern layer of the micelle, without being

TABLE 3—ACTIVATION PARAMETERS FOR N-PHENYLBENZOHYDROXAMIC ACID

Parameter	CTAB				CPC		NaLS	
	0.0	2.50×10^{-3}	15.0×10^{-3}	24.6×10^{-3}	$2 50 \times 10^{-3}$	15.0×10^{-3}	0.175×10^{-3}	0.520×10^{-3}
$\Delta H^{\neq}$ (kJ mol⁻¹)	96.1 ± 11.1	80 7 ± 1.31	78.6 ± 6.56	69.7±1 50	95 0±7.03	92.4 ± 3 19	69.5 ± 1.04	83.3 ± 1.01
$\Delta S^{\neq}$ (JK⁻¹ mol⁻¹)	−31 ± 4.4	−76 ± 3.89	−77 ± 19.4	−100 ± 4 45	−34 ± 3.2	−40 ± 9.47	−110 ± 3.09	−67 ± 2.99
$\Delta G^{\neq}$ (kJ mol⁻¹)	105.2 ± 8.74	103 2 ± 0.99	101.4 ± 4.94	99.3 ± 1.13	104.9 ± 5.29	104 1 ± 2.41	102.1 ± 0 79	103.1 ± 0.76
Corr. coeff.	0 984	0.999	0.993	0.999	0 994	0 999	0 999	0.999

TABLE 4–SALT EFFECTS UPON MICELLAR CATALYSIS OF PBHA

Temp = 65°, [CTAB] = 1 40 × 10^{-3} M, NaOH = 0 05 M

Salt*	k_ψ $\times 10^4$ s^{-1}
Nil	2 58
KCl	2 30
KBr	2.10
NaCl	1 92
NaBr	2 32
Na$_2$SO$_4$	2 14

*a = 0 04 M

Substituent effects : The rates of alkaline hydrolysis of a series of *para*-substituted *N*-phenyl-benzohydroxamic acids in nonmicellar phase and with CTAB, CPC and NaLS were also measured. The effects of substitution have been assessed by use of the Hammett equation. No definite trends have been observed (Table 5). The values of ρ were 0.15 (in water), 0.10 (in CTAB) and 0.14 (in CPC). This behaviour could be explained by the rate-limiting decomposition of the tetrahedral intermediate. The favourable influence of electron-withdrawing substituents on the formation of the tetrahedral intermediate would be counterbalanced by an opposite effect of the same substituents on its splitting. In the presence of NaLS, both the electron-withdrawing and electron-donating substituents retard the rate of hydrolysis.

TABLE 5–RATE OF HYDROLYSIS OF SOME *p*-SUBSTITUTED
PBHA IN MICELLAR AND NONMICELLAR PHASE

X	k_ψ ($\times 10^4$ s^{-1})			
	No surfactant	CTAB^a	CPC^a	NaLS^b
H	1 89	2 58	2.25	3.06
p-CH$_3$	2.22	2.70	2.03	1 77
p-OCH$_3$	2 37	3.06	2.13	1 75
p-NO$_2$	3 08	3.35	2 92	1 61
p-Cl	2.45	2 90	2 82	1 52

^{a}1.40 × 10^{-3} M. ^{b}0.520 × 10^{-3} M.

Experimental

The *N*-phenylbenzohydroxamic acid was prepared by a standard method[11]. NaOH (A.R.), dioxane (B.D.H.; L.R.), CTAB (E. Merk), CPC and NaLS (Loba) were used as such. The ferric chloride solution used in the colorimetric procedure was prepared

by dissolution of anhydrous ferric chloride (10 g; Reidel, A.R.), in distilled water (1 dm^3) containing concentrated HCl (100 ml). Kinetic measurements were made by the reported spectophotometric method[12] using an EC 5700 A digital spectrophotometer set at 520 nm. Least-squares analysis was carried out on a WIPRO 386 computer, under MS-DOS

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