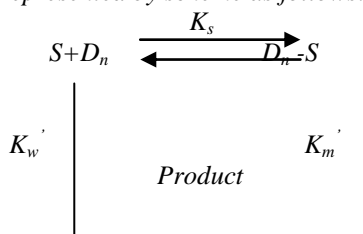


Quantitative Treatment of Micellar Catalysed Hydrolysis of Mono-2,5- Dimethoxy Phenyl Phosphoramidate

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Abstract

The micellar catalysed hydrolysis of mono-2,5-DMPP with $[OH^-]$ in presence of [CTABr] has been verified by ion exchange model. This quantitative treatment allows the rate constants related to the surfactant concentration in terms of distribution of reactants in aqueous and micellar pseudo phase may be represented by scheme as follows:



Where 'S' is ester-molecule, D_n is micellized surfactant, K_s is the Micellar substrate binding constant, $D_n \cdot S$ is the substrate complex, K_w' and K_m' are the rate constants in aqueous and micellar pseudophases for the formation of the products.

Keywords

Micellar, Hydrolysis, Phosphoramidate

I. INTRODUCTION

The equations used to determine ionexchange parameters may be given as:

$$K_{\psi} = \frac{K_w' + K_m' K_s [D_n]}{1 + K_s [D_n]} \quad \dots(1)$$

Where D_n is the concentration of micelles given as :

$$D_n = C_D - \text{cmc}$$

$$K_{Br}^{OH} = \frac{[OH_w^-][Br_m^-]}{[OH_m^-][Br_w^-]} \quad \dots (2)$$

$$K_m' = K_m \cdot m_{OH}^S = \frac{K_m [OH_m^-]}{D_n} \quad \dots (3)$$

$$[OH_T^-] = [OH_W^-] + m_{OH}^S [D_n] \quad \dots (4)$$

$$[Br_T^-] = [Br_W^-] + \beta m_{OH}^S [D_n] \quad \dots (5)$$

Where β is the fraction of head group neutralized by counterions have been calculated 0.75 and K_{Br}^{OH} is taken 10.0 from the literature. The value of m_{OH}^S found 0.460. The value of ion exchange parameters K_s , K_m , K_m^2 and $[OH_m^-]$ calculated at pH 9.0 by using above equations have been found 2.82×10^{-5} , 30.44×10^{-5} , 2.3×10^{-5} and 3.62×10^{-4} respectively.

The micellar catalysis have been found to be strongly dependent on the nature of the detergent, the initial counter ions present and the total ionic contents of the system due to local concentration of relative ions in the micellar pseudophase. The most commonly employed approach ion binding to micelles. Treat the system as a partition function of the type;

$$PI = PI_o \exp[-\Psi e/KT]$$

Where Ψ is the surface potential of the micelle and PI_o on account for the non electrostatic (hydrophobic) part of the interaction. It is assumed that degree of dissociation of the ionic micelle can be considered constant, which has been put forward by Romsted and modified by Berzin.¹

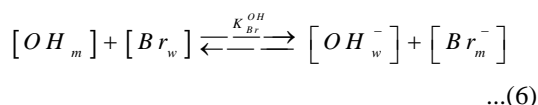
To analyze the interfacial effects of the reaction on the hydroxide ion with mono-2,5-DMPP treatment of ion exchange in micellar solution that explicitly considers the consequence of ion-ion exchange. This approach permits to analyze the effect that a given experimental conditions^{2,3} (buffered or unbuffered, added salt, present detergent concentrations, energy of activation, entropy of the reaction and solvent effect etc.) will have on the concentration and kinetic behavior or exchangeable ionic reactants in micellar pseudo phase because such effects have been found to be strongly dependent on the nature of the detergent head group, the total content of the system and the initial concentrations present.

The rate constants of micellar catalyzed hydrolysis of mono-2,5-dimethoxy phenyl phosphoramidate (2,5-DMPP) can be related to surfactant concentration in terms of the distribution of reactants in micellar and aqueous pseudo phase ion

exchange model which has been represented previously by scheme-(1). Where the second order rate constants in each pseudo phases have been determined by taking into consideration of first order rate constants for over all reactions give by eq. (1) where K_w and K_m are first order rate constants in aqueous and micellar pseudo phases respectively.

$$K_\psi = \frac{K'_w + K'_m K'_s [D_n]}{1 + K_s [D_n]} \quad \dots(5)$$

Where ' K_s ' is a binding constant and ' D_n ' is micellized surfactant, it is assumed that interaction of two or more counter ions with anionic micelles is governed by ion exchange equilibrium⁴ eq. (6).



Where 'm' and 'w' in paranthese denote micellar and aqueous pseudophases respectively. Equilibrium or ion exchange constant for OH^- and Br^- denoted by K_{Br}^{OH} can be given by eq. (7)

$$K_{Br}^{OH} = \frac{[OH_w^-][Br_m^-]}{[OH_m^-][Br_w^-]} \quad \dots(7)$$

By employing the following equations, the first order rate constants K_w and K_m are conveniently converted into second order rate constants K'_w and K'_m respectively.

$$K'_w = K_w [OH_w^-] \quad \dots(8)$$

$$K'_m = K_m m_{OH}^s = K_m \frac{[OH^-]}{[D_n]} \quad \dots(9)$$

Where m_{OH}^s is concentration of reactive ions in the micelle. Since m_{OH}^s is expressed in molar ratio, values of second order rate constant K_m cannot be compared directly with second order rate constant in water because of different dimensions. They can be converted into K_m^2 which is the second order rate constant expressed in terms of reactant per dm^{-3} (L) of the stern layer this quantity is estimated to be 140 ml. or 0.14 L for [CTABr] K_m^2 has been calculated from the following eq. (10)

$$K_m^2 = 0.14 K_m mol^{-1} dm^{-3} s^{-1} \quad \dots(10)$$

The first order rate equation (5) can be written in the following manner.

$$K_\psi = \frac{K'_w [OH_w^-] + K'_m K'_s m_{OH}^s [D_n]}{1 + K_s [D_n]} \quad \dots(11)$$

The fractions of head group K_{Br}^{OH} and β are assumed to be neutralized may be treated as independent of nature or concentration of counter ions⁵. For a mixture of OH^- and Br^- , β is identical with $m_{OH}^s + m_{Br}^s$, the concentration of $[OH_m^-]$ and $[OH_w^-]$ (in molarities) are expressed in terms of total concentration in solution volume, so that $[OH_T^-]$ and $[Br_T^-]$ can be given by following equation .

$$[OH_T^-] = [OH_w^-] - m_{OH}^s [D_n] \quad \dots(12)$$

$$[Br_T^-] = [Br_w^-] + (\beta - m_{OH}^s) [D_n] \quad \dots(13)$$

On substituting the values of $[OH_m^-]$, $[OH_w^-]$, $[Br_w^-]$ and $[Br_m^-]$ in eq.(6) leads to eq. (14)

$$(m_{OH}^s)^2 + m_{OH}^s \frac{[OH_T^-] + K_{Br}^{OH} [Br_T^-]}{(K_{Br}^{OH} - 1)[D_n]} - \frac{\beta [OH_T^-]}{(K_{Br}^{OH} - 1)[D_n]} = 0 \quad \dots(14)$$

Selecting the values of K_{Br}^{OH} and β as 10.0 and 0.75 respectively, m_{OH}^s has been calculated for the reaction at $20.8 \times 10^{-3} mol dm^{-3} [OH^-]$. For convenience eq. (11) may be rearranged as eq. (15).

$$\frac{(K_\psi - K'_w)}{m_{OH}^s [D_n]} = K'_m K'_s - K_s \frac{K_\psi}{m_{OH}^s} \quad \dots(15)$$

The plot of $\frac{(K_\psi - K'_w)}{m_{OH}^s [D_n]}$ Versus $\frac{-K_\psi}{m_{OH}^s}$ for runs of different [CTABr] with $[OH^-]$ are linear and yield values of K_s the bindings constant, m_{OH}^s , K'_m at $20.8 \times 10^{-3} mol dm^{-3} [OH^-]$. The estimated values of and has been summarized In Table (1) and Fig. (1) shows the relation between these terms.

TABLE-1: Relation between of $K_\psi - K'_w / m_{OH}^s [D_n]$ and $-K_\psi / m_{OH}^s$ MONO-2,5- Dimethoxy Phenyl Phosphoramidate in Borate Buffer At. Ph.-9.0 and Temp. $40 \pm 0.50^\circ C$

S.N.	$10^5 K_\psi S^{-1}$	$-K_\psi m_{OH}^s \times 10^5 S^{-1}$	$\frac{K_\psi - K'_w}{m_{OH}^s [D_n]} \times 10^2$
1	5.98	13.00	1.467
2	7.02	15.26	4.293
3	8.18	17.78	7.445

4	11.30	24.56	15.923
5	13.97	30.36	23.179
6	18.52	40.26	35.543
7	23.04	50.08	47.820
8	30.14	65.52	62.110

$$D_n = 0.8 \times 10^{-3} \text{ mol. dm}^{-3} \quad K'_w = 4.83 \times 10^{-5} \text{ S}^{-1}$$

at pH 9.0. The estimated values from the Fig.(1) have been summarized in Table (2).

TABLE-2: Ion Exchange Parameters and Second order rate constants for the reaction of Mono-2,5-Dimethoxy Phenyl Phosphoramidate with [OH⁻] in the micellar Pseudophase at Ph.-9.0 and Temp. 40±0.5°C.

K_{Br}^{OH}	$10^3 [OH^-]_T$ mol dm ⁻³	$10^4 [OH^-]_w$ mol dm ⁻³	$10^3 [OH^-]_m$ mol dm ⁻³	m^*_O H	$10^3 K_s$ mol dm ⁻³	$10^4 K_m$ s ⁻¹	$10^5 K_w$ mol dm ⁻³ s ⁻¹	$10^5 K^2$ mol ² dm ⁻³ s ⁻¹	β
10	20.8	3.6	20.4	0.46	2.8	30.4	5.4	2.3	0.7

These results suggest that pseudo phase ion exchange model can be applied as a first approximation to reactions of dianion of mono-2,5-DMPP with [OH⁻] in [CTABr] micelles. Bimolecular reactions of hydrophilic anionic nucleophiles [OH⁻] by hydroxylic solvents that strongly bind the hydrogen to dianion concentration of anions at the surface of cationic micelles in the stern layer have been calculated from the above equation as.

$$[OH^-]_m = 0.360 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[Br^-]_m = 0.282 \times 10^{-3} \text{ mol. dm}^{-3}$$

$$K_{Br}^{OH} = 10$$

Concentration of dianions of mono-2,5-DMPP ion micelles calculated from equation.

$$K_s = \frac{(2,5 - DMPP)_m}{(2,5 - DMPP)_w [D_n]}$$

Concentration of dianions of mono-2,5-DMPP in aqueous and micellar pseudo phases as under.

$$[2,5-DMPP]_m = 0.360 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[2,5-DMPP]_w = 0.282 \times 10^{-3} \text{ mol dm}^{-3}$$

The aryl part of mono-2,5-DMPP dianion is deeply buried in interior of micelles and the phosphate dianions are suitable exposed to nucleophilic attack by [OH⁻] ion which is present in lower concentration in the micelle. Besides of this, the dianions of mono-2,5-DMPP are relatively hydrophobic and polarisable anions bind to micelles by the specific interaction but

coulombic binding is much important in binding of hydrophilic anions, the dianions of mono-2,5-DMPP not very hydrophilic but are polarisable interact with oxygen atom of C—N—P linkage, present in zwitterionic forms of monoester. Forming hydrogen bonded cyclic intermediate by entrap of [OH⁻] ions reducing the coulombic interaction considerably. This interaction by [OH⁻] ions in cationic micelles was described to a higher surface charge density at cationic as compared with the anionic centers.

II. EFFECT OF TEMPERATURE

Presuming protonation of the neutral ester or the neutral species of the monoester the bend in the curve obtained by plotting rates constants against detergent concentration of the plot (1) was though due to the result of maximum protonation, which is common in amide system⁶, unless the heat of protonation, is small, the difference in activation energies should result at points before and after the bend. With this view kinetic runs were made at maximum where substrate is fully micellar bound at $D_n = 1.6 \times 10^{-3} \text{ mol.dm}^{-3}$ [CTABr] where maximum rates $K_\psi = 30.14 \times 10^{-5} \text{ s}^{-1}$ for the hydrolysis of Mono-2,5-DMPP with micelles Of [CTABr] in buffer solutions. The hydrolysis was studied in absence and presence of surfactant. Rate coefficient have been summarized in table-3 and the fig (2) a plot of log K_ψ against 1/T was found to be linear, the linearity of plot in fig (2) shows validity of arrhemous parameters.

Ester	ΔE K.Cal/mol	$-\Delta S^\ddagger$ (e.u.)
without [CTABr]	17.41	57.32
with [CTABr]	25.20	53.88

Table 3: Temperature Effect Upon Reaction of Mono-2,5-Dimethoxy Phenyl Phosphoramidate with [20.8X10⁻³] mol dm⁻³ NaOH IN [5x10⁻²] mol dm⁻³ Borate Buffer in Absence and Presence of [CTABr] AT pH 9.0

	t°C	T°K(abs)	[10 ⁵ /T]°K	10 ⁵ K _ψ s ⁻¹	5+log K _ψ
Absence of detergent	30	303	330.0	2.24	0.350
	40	313	319.5	5.44	0.735
	50	323	309.6	11.32	1.053
Presence of detergent	30	303	330.0	15.12	1.176
	40	313	319.5	30.14	1.479
	50	323	309.6	62.33	1.794

Table 4: Arrhenious Parameters for the hydrolysis of Mono-2,5-Dimethoxy Phenyl Phosphoramidate

III. EFFECT OF ELECTROLYTES

Salts inhibit the reaction of mono-2,5-DMPP dianions with hydroxide ion in presence of [CTABr] detergent. We speculated that the anions of salts intended to exclude the hydroxide ion from the neighborhood of the micelles. In view of this, investigations have been carried out at $40 \pm 0.5^\circ\text{C}$ of the above reaction and the effect of added salts NaCl, KCl, NaBr and $\text{C}_6\text{H}_5\text{COONa}$ on the rate of reaction has been summarized in table-5. Fig. (3) Shows the dependence of rate constants on inhibition by added salts.

TABLE-5: Effect of Inhibiting Salts upon Hydrolysis of Mono-2,5-Dimethoxy Phenyl Phosphoramidate with $[20.8 \times 10^{-3}] \text{ mol.dm}^{-3}$ $[\text{OH}^-]$ IN $[5 \times 10^{-2}] \text{ mol. dm}^{-3}$ Borate Buffer in Presence of $1.6 \times 10^2 \text{ mol.dm}^{-3}$ [CTABr] AT pH 9.0 and $40 \pm 0.5^\circ\text{C}$

Salt mol.dm ⁻³	Rate Constant 10^{-5} s^{-1}			$\text{K}_\Psi \times \text{X}$ $\text{C}_6\text{H}_5\text{COONa}$
	KCl	NaCl	NaBr	
0.1	16.98	15.28	12.92	18.84
0.2	15.91	13.79	10.94	12.08
0.3	14.73	11.83	09.65	5.82
0.4	13.02	10.64	08.90	-
0.5	12.79	09.98	08.01	-
0.6	11.36	08.87	07.32	-
0.7	10.06	07.74	05.16	-
0.8	08.10	06.12	04.02	-

The pattern for the effect of inorganic salt mainly depends upon the anions chloride, bromide and acetate of K^+ , Na^+ have a little effect on the rates i.e. depress it slightly. Some anions of high charge density have been found to enhance the rates due to organizing water molecules about them such as sulphate, NaOH and phosphate^{7,8} etc.

In these solutions of high ionic strength ions will be closed to micellar surface in the solutions of high ionic strength and may compete with counterion of micellised surfactant for water molecules and therefore, change the micellar structure Any effect which decreases the ability of water molecules at the micellar surface to hydrogen—dianions of mono-2,5-DMPP should assist reaction, first by decreasing the ability of the water molecules to hydrate, the substrate which bound to the micelle and secondly by reducing screening of phosphate dianions whose aryl part buried deeply in the interior of micells of the surfactant. It has been noted that ions can change the dynamic basicity of water. Analogous results have been obtained by C.A. Bunton and Moffatt by the salt effect studies of sodium benzoate in presence of [CTABr] detergent⁹.

IV. EFFECT OF SUBSTRATE CONCENTRATION

Kinetic runs were carried out at $1.6 \times 10^{-3} \text{ mol dm}^{-3}$ [CTABr] detergent on the reaction of mono-2,5-DMPP dianion with $[\text{OH}^-]$ ion $[20.8 \times 10^{-3}] \text{ mol dm}^{-3}$ at $40 \pm 0.5^\circ\text{C}$ with varying concentration of 2,5-DMPP. The kinetic order with respect of the mono-2,5-DMPP was determined. Table (6) summarizes the rate constants which were obtained by the use of first order rate equation. The results show that the rate constants are fairly similar and independent of initial concentration, hydrolysis of the reaction may be taken to be kinetically first order.

Table-6: Concentration Effects upon the Reaction of Mono-2, 5-Dimethoxy Phosphoramidate with $[20.8 \times 10^{-3}] \text{ mol.dm}^{-3}$ NaOH IN $[5 \times 10^{-2}] \text{ mol. dm}^{-3}$ Borate Buffer in Presence of $1.6 \times 10^2 \text{ mol. dm}^{-3}$ [CTABr] AT Ph 9.0 AND $40 \pm 0.5^\circ\text{C}$.

S.N.	$10^4[\text{Substrate}]$ mol.dm^{-3}	Rate Constant $\text{K}_\Psi \times 10^{-5} \text{ s}^{-1}$
1	2.5	28.79
2	5.0	30.14
3	7.5	30.92

V. BOND FISSION AND MOLECULARITY

The mono-2,5-DMPP under the investigation it has been found that mono-2,5-DMPP may undergo hydrolysis uni-or bimolecularly with either 'C—N' or 'P—N' bond fission in the reaction at pH 8 to 10. It has been found that the only reactive species of the phosphate monoester is dinegative species. At these pH values, the nucleophilic attack of $[\text{OH}^-]$ at the phosphorous atom of phosphate group. Facilitate 'P—N' rather than 'C—N' bond fission and undergoes bimolecular hydrolysis. The examination of Arrhenius parameters such as energy of activation, values of entropy of reaction being highly negative support bimolecular nature of the hydrolysis.

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