



## ORIGINAL ARTICLE

### Effect of Micellar Catalysed Hydrolysis of Mono-2-Methoxy Phenyl Phosphoramides

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#### ABSTRACT

*Micellar effect upon nucleophilic substitution reactions between hydroxide ions [OH<sup>-</sup>] and mono-2-methoxy phenyl phosphoramides (2-MPPA) in presence cetyl trimethyl ammonium bromide (CTABr) has been examined in buffer medium (at pH 8.0-10). The First Order rate constant (K) are increased with the constration of the surfactant can be analysed in terms of Br-ions in micellar pseudophases, which occur readily by aqueous CTABr and calculated second order rate constants.*

**Key words:** micellar, CTABr, 2-MPPA, nucleophilic attack

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#### INTRODUCTION

The rate enhancement of the rate constant (K) of the reaction catalysed by the micelles is largely due to the increased concentration of the reactant in the micellar pseudophase<sup>1</sup>. It is difficult to examine the partitioning of hydrophilic reactants between aqueous and micellar pseudophases instead of hydrophobic ions. The widely used approach is to assume that counterions complete for ionic sites on the micellar surface and that the fraction  $\beta$  of these sites which are neutralized by approaches counterions is approximately constant<sup>2-3</sup>. This approach has been applied to the rate and equilibrium constant of many reactions<sup>4-8</sup>.

A reactive ion surfactant in which ionic reagent is the micellar counter ions<sup>9-12</sup> can be used to eliminate the problem of inter ionic competition. Therefore, its constration in the micellar pseudophase should be constant provided that  $\beta$  is constant. The first order rate constant (K) increases with increasing surfactant constration to the maximum value  $33.45 \times 10^5 \text{ s}^{-1}$  at  $1.6 \times 10^{-3} \text{ mol dm}^{-3}$ , CTABr for 4-CMPP. This behavior has been observed for reactions involving hydroxide ions for nucleophilic addition<sup>13</sup> by Br<sup>-</sup>.

#### MATERIAL AND METHODS

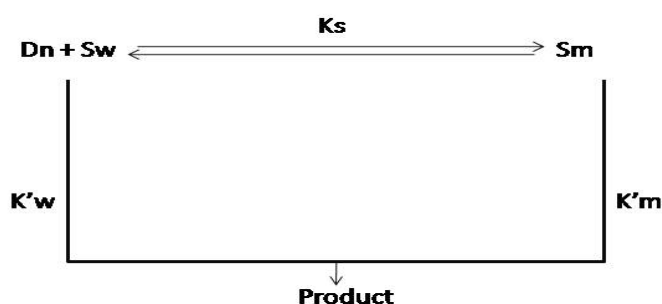
The amidol solution was filtered in to a solution containing 100 ml solution of sodium metabisulphate (20%). 12.4 gm of 2-methoxy aniline dissolved in benzene (100ml) and 9.0ml of phosphorus oxy-trichloride was added slowly during in about an hour. After addition of POCl<sub>3</sub>, mixture was refluxed for 18 hours on soxhlet at constant temperature 65°C in order to ensure complete reaction and then distilled under reduced pressure. The first fraction of benzene and unreacted phosphorus oxy-trichloride was removed by distillation at  $b_{67} 160^\circ\text{C}$ . The second fraction of a pungent smelling liquid which was supposed to be 2-methoxy phenyl phosphoramidate dichloridate was distilled at  $b_{67} 160-180^\circ\text{C}$ . It was dissolved in 100 ml of icephenyl phosphoramidate dichloridate converted into

2-methoxy phenyl phosphoramidate dihydrogen phosphate, was extracted with solvent ether. After removing the solvent ether a light brown coloured crystalline solid was obtained which on recrystallisation with absolute ethyl alcohol gave a white crystalline solid and it was identified to be mono-2-methoxy phenyl phosphoramidate.

Amidol (1.4gm) was taken in conical flask covered with carbon paper, activated charcoal (2gm) and water (10ml) were added in to the conical flask and then it was shaken. Substrate in solution has the specific property of absorbing light of wave length characteristic of the particular substance. The basic principle of absorption is utilized in the measurement of various concentrations. The Beckmann's spectrophotometer instrument utilizes a source of radiation energy, a means to isolate a band of radiant energy which is focused on the solution and then measured with a detector. Kinetic study for the hydrolysis was followed spectrophotometrically. This method involved the quantitative estimation of inorganic phosphates formed from the hydrolysis of phosphate esters. The inorganic phosphate react with the ammonium molybdate and forms a phosphate molybdate complex  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ , which is reduced to molybdenum blue, a soluble complex by addition of mixture of 2,4 diamino phenyl hydrochloride (amidol). CTABr used A.R. grade.

### RESULT AND DISCUSSION

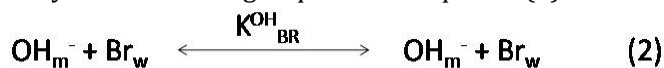
The reactions of mono phosphate were strongly catalysed at different concentration of CTABr at which the pseudophase first order rates constant were obtained. In Table.1, summarization the effect of cationic micelles of CTABr on the rate constants of  $\text{OH}^-$  with MPPA, which is shown in fig 1. The reaction between the observed pseudo first order rate constant (K) and surfactant concentration (Dn) for a spontaneous phosphorylation of MPPA may be shown in following scheme-1.



Where  $S_w$  and  $S_m$  are substrate in aqueous and micellar pseudophases respectively,  $K'_w$  and  $K'_m$  are the related first order rate constant and  $K_s$  is binding constant<sup>14</sup>. The concentration of micellised surfactant,  $D_n$  is that of total surfactant concentration less than that of monomeric surfactant which is assumed to be given by Critical Micelle Concentration  $\text{CMC}$ <sup>15</sup> provided that equilibrium is maintained between micelle and aqueous phases.

$$K_\psi = \frac{K'_w + K'_m + K_s (D_n - \text{CMC})}{1 + K_s (D_n - \text{CMC})} \quad (1)$$

It is assumed that interaction of two or more counterions with anionic micelles are governed by the ion exchange equilibrium equation (2)



Where  $m$  and  $w$  in parentheses denotes micellar and aqueous pseudophases respectively. Equilibrium or ion exchange constant for  $\text{OH}^-$  and denoted by  $K_{\text{OH}_{\text{BR}}^{\text{OH}}}$  can be given by the equation (3)

$$K_{Br}^{OH} = \frac{[OH^-]_w [Br^-]_m}{[OH^-]_m [Br^-]_w} \quad (3)$$

By employing the following equation (4) and (5), the first order rate constant  $K'_w$  and  $K'_m$  are conveniently converted in to second order rate constant  $K_w$  and  $K_m$  respectively.

$$K'_w = K_w [OH^-]_w \quad (4)$$

$$K'_m = K_m m_{OH}^s = \frac{[OH^-]}{[Dn]} \quad (5)$$

Where  $m_{OH}^s$  is the concentration of reactive ions in micelles. Since  $m_{OH}^s$  is expressed in the molar ratio values of the second order rate constant  $K_m$  can not be compared directly with second order rate constants intricate because of different dimensions. They can be converted in to  $K_2m$ , which is second order rate constant expressed in terms mole of reactant per  $dm^3$  (L) of stern layer. This quantity is estimated to be 140 ml or 0.14L for [CTABr]  $K_2m$  has been calculated from following eq.(6)

$$K_2m = 0.14 K_m \cdot 2.3 \times 10^5 \text{ mol}^{-1} \text{ dm}^{-3} \text{ sec}^{-1} \quad (6)$$

The order reaction (1) can be written in the following manner as in eq.(7)

$$K_\psi = \frac{K_w [OH^-]_w + K'_m K_s m_{OH}^s [Dn]}{1 + K_s [Dn]} \quad (7)$$

It is assumed that  $K_{OH}^{Br}$  and  $\beta$  is the fraction of micellar head groups neutralized by counter ions may be treated as independents nature of concentration of counter ions (8) for a mixture of  $OH^-$  and  $Br^-$  is identical with  $m_{OH}^s + m_{Br}^s$  the concentration of  $OH^-_w$  and  $OH^-_m$  (in molarities) are expressed in terms of total concentration in solution volume so that  $[OH^-]_T$  and  $[Br^-]_T$  can be equation (8) and (9)

$$[OH^-]_T = [OH^-] + m_{OH}^s [Dn] \quad (8)$$

$$[Br^-]_T = [Br^-] + [\beta - m_{OH}^s] [Dn] \quad (9)$$

Substitution for  $[OH^-]_T$   $[OH^-]_w$   $[Br^-]_T$  with  $[OH^-]_T$  and  $[Br^-]_T$  in equation (3) leads to equation (10)

$dm^3 [OH^-]$  ion in table (2). For convenience equation (7) may be arrange as (11).

$$[m_{OH}^s] + (m_{OH}^s) \left\{ \frac{[OH^-]_T + K_{OH}^{Br} [Br^-]_T}{[K_{OH}^{Br} - 1] [Dn]} - \beta \right\} - \frac{\beta [OH^-]_T}{(K_{OH}^{Br} - 1) [Dn]} = 0 \quad (10)$$

The selecting values of  $[K_{OH}^{Br}]$  and  $\beta$  as 10 and 0.75 respectively,  $m_{OH}^s$  has been calculated for reaction at  $0.451 \times 10^{-2}$  mol.

$$\frac{K_\psi - K'_w}{m_{OH}^s [Dn]} = K'_m K_s - K_s \left[ \frac{K_\psi}{m_{OH}^s} \right] \quad (11)$$

A graph plotted between  $K_\psi - K'_w / m_{OH}^s [Dn]$  and  $-K_\psi / m_{OH}^s$  is shown in fig.2 which are linear at different [CTABr] and yield values of  $K_s, K_m, [OH^-]$  summarized in table(3). From the results present in table (3), it is evident that maximum rate enhancement occur in the region of [CTABr] at which bulk of the substrate incorporated in to the micelles. The aryl part of the substrate dianion is deeply buried in interior of micelles and the phosphate dianions are suitably exposed to nucleophilic attack by  $[OH^-]$  ions which is present lower concentration in the micelles. Besides of this dianion of mono phosphate ester are relatively hydrophobic and polarisable anions bind to micelles the specific interaction but coulombic binding is much important in binding of hydrophilic anions. The di anions of mono phosphate ester is polarisable and not very hydrophilic interact with phosphate atom of C-O-P linkage present in zwitter ions of mono phosphate ester forming hydrogen bonded cyclic intermediate by entrap of reducing this interaction considerably the

coulombic interactions  $[\text{OH}^-]$  ions in cationic micelles was ascribed to a higher surface charge density at cationic as compared with anionic centres.

**Table 1:** Pseudo first order rate constant for reaction  $[2.2 \times 10^{-2}]$  NaOH mol.dm<sup>-3</sup> with  $[5.0 \times 10^{-4}]$  mono 2-MPPA in presence of  $10^{-3}$ [CTABr] at pH 9.0 of borate buffer and temp.  $40 \pm 0.5^\circ\text{C}$

S.N.	CTABr $\times 10^{-3}$ mol.dm <sup>-3</sup>	$K_{\psi} \cdot 10^{-5}$ sec <sup>-1</sup>
1	0.2	4.61
2	0.4	5.69
3	0.6	6.93
4	0.8	7.89
5	1.0	8.62
6	1.2	9.37
7	1.4	10.40
8	1.6	10.98
9	1.8	9.86
10	2.0	8.75

**Table 2:** Relation between  $K_{\psi} - K'w/m^{s_{\text{OH}}}$ [Dn] and  $-K_{\psi}/m^{s_{\text{OH}}}$  for reaction of mono-2-MPPA with  $[\text{OH}^-]$  at different CTABr at pH 9.0 and temp.  $40 \pm 0.5^\circ\text{C}$

S.N.	$K_{\psi} \cdot 10^5$ s <sup>-1</sup>	$-K_{\psi} \cdot 10^5 \text{s}^{-1} / m^{s_{\text{OH}}}$	$K_{\psi} - K'w \cdot 10^{-5} / m^{s_{\text{OH}}}$
1	5.69	49.48	7.93
2	6.93	60.28	14.67
3	7.89	68.61	19.89
4	8.62	74.95	23.86
5	9.37	81.48	27.93
6	10.40	90.43	33.53
7	10.98	95.48	36.68

**Table 3:** Ion exchange parameter and second order rate constant for reaction of mono-2-MPPA with OH<sup>-</sup> in presence of CTABr at pH 9.0 and  $40 \pm 0.5^\circ\text{C}$ .

$K^{\text{OH}_{\text{Br}}}$	$10^2$ [OH] <sub>T</sub> mol dm <sup>-3</sup>	[OH] <sub>m</sub> mol dm <sup>-3</sup>	[OH] <sub>w</sub> mol dm <sup>-3</sup>	$m^{s_{\text{OH}}}$ mol <sup>-1</sup>	Ks mol dm <sup>-3</sup>	$10^5$ Km mol dm <sup>-3</sup> s <sup>-1</sup>	$10^5$ K'w s <sup>-1</sup>	$10^5$ K <sub>2m</sub> Mol <sup>-1</sup> s <sup>-1</sup>	$\beta$
14.7	2.2	0.80	0.0218	0.115	198	9.55	4.23	1.4	0.91

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