



## Effect of the Micellar Catalysed Hydrolysis of BIS -4-Chloro-3-Methyl Phenyl Phosphate Ester

Singh A.P.<sup>1</sup>, Verma R.C.<sup>1</sup> and Kushwaha R.S.<sup>3</sup>

<sup>1</sup>Department of Chemistry, Janta College, Bakewar, Etawah, INDIA

<sup>3</sup>Department of Chemistry, Agra College, Agra, UP, INDIA

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### Abstract

The micellar catalysed reactions between hydroxide anions and bis-4-chloro-3-methyl phenyl phosphate ester (bis-4-CMPP) has been examined in buffered medium at pH 8 to 10. The first order rate constant ( $K_p$ ) for the reaction of OH with 4-CMPP go through maxima with increasing the concentration of cetyltrimethyl ammonium bromide (CTABr). Concentration of the surfactant can be analyzed in terms of Br<sup>-</sup> ions in micellar pseudophases, which occur readily by aqueous CTABr and calculated second order rate constants.

**Keywords:** Bis-4CMPP

### Introduction

The rate enhancement of first order rate constant ( $K_p$ ) of the reaction catalysed by the micelles is largely due to the increased concentration of the reactant in the micellar pseudo phase<sup>1-3</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 'β' of these sites which are neutralized by approaches counter ions is approximately constant<sup>4,5</sup>. This approach has been applied to the rate and equilibrium constant of many reactions<sup>6-10</sup>.

A reactive ion surfactant in which ionic reagent is the micellar counter ions<sup>11-14</sup> can be used to eliminate the problem of interionic competition. Therefore, its concentration in the micellar pseudophase should be constant provided that 'β' is constant. The first order rate constants ( $K_p$ ) increases with increasing surfactant concentration to the maximum value at  $1.6 \times 10^{-3}$  mol dm<sup>-3</sup> CTABr for 4-CMPP. This behavior has been observed for reactions involving hydroxide ions for nucleophilic addition by Br<sup>-</sup><sup>15</sup>.

### Material and Methods

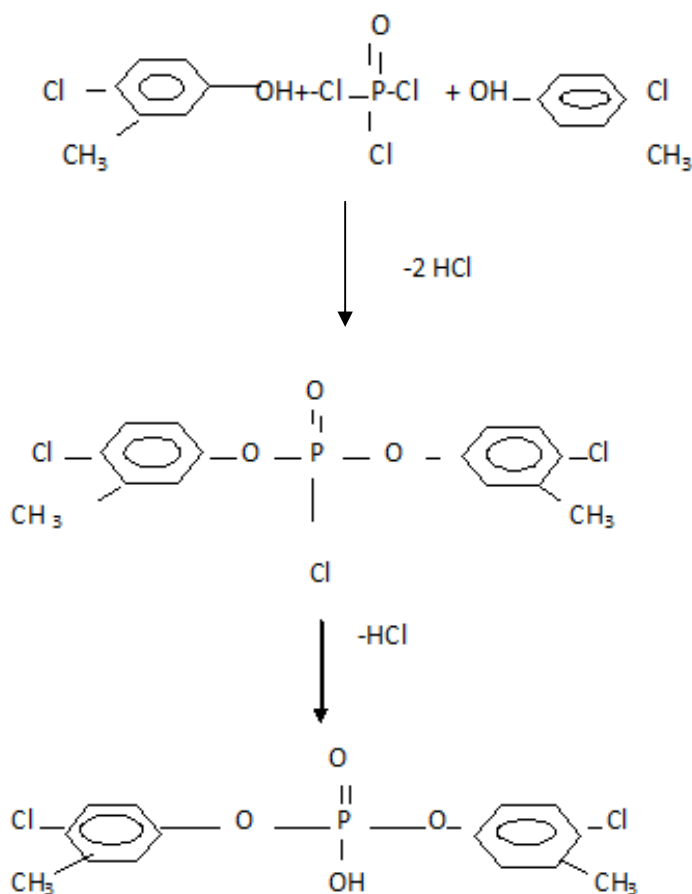
Preparation Bis ester of 4-chloro-3-methylphenyl phosphate the residue left after removing mono- 4-chloro -3- methyl phenyl phosphate at b<sub>p</sub> 120-140°C was washed several times with boiling distilled water and 0.2 NaOH solution to remove 4-chloro- 3-methyl phenyl phosphate monoester, unreacted phosphorus oxy tri-chloride and the phenol and finally digested in hot water 0.5 NaOH solution. It was filtered and the filtrate acidified with dilute HCl using phenolphthalein as an indicator. A white precipitate obtained was separated by filtration and made free from hydroxyl ions with repeated washings with

boiling water. It was then dried at room temperature and recrystallised with absolute ethyl alcohol gave a white crystalline solid and it was identified to be Bis- 4-chloro -3-methyl phenyl phosphate as shown under:

Cetyltrimethyl ammonium bromide was purified by given method 4-chloro -3-methyl phenyl phosphate were washed with anhydrous ether acetone until no amine is detected in the eluent recrystallised from methanol and then at least 4 times from methanol with addition of anhydrous ether.

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 thoroughly for 15-20 min. The colourless amidol solution so obtained was filtered in to a solution containing 100ml solution of sodium meta bisulphate (20%). The reagent obtained was kept in a dark at low temperature (0°C). This solution gradually decomposed and turned yellow after 6-8 days, than it was of no use and hence, discarded. Each time amidol was purified before use.

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 spectrophotometer instrument utilize a source of radiant energy, a means to isolate a band of radiant energy which is focused to on the solution and then measured with a detector. Kinetic study for the hydrolysis of all the mono-, di- and tri-ester 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 (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.12MoO<sub>3</sub>, which is reduced to molybdenum blue, a soluble complex by addition of mixture of 2, 4-diamino phenyl hydrochloride (amidol, diamol or nerol).

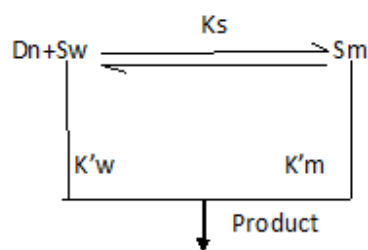


Phosphate mono esters were prepared by standard methods<sup>16</sup> purified by re crystallisation from absolute ethyl alcohol and examined by IR, CTABr used analytical grade, strength of borate buffer were prepared and purified by standard methods<sup>17</sup>.

All kinetic runs were performed using doubly or triply distilled water. All reactions were carried out at  $40 \pm 0.5^\circ\text{C}$  and pH 9.0. Reactions were followed by spectrophotometer at the absorbance 662 nm. To obtain first order rate ( $K_v$ )

### Result and Discussion

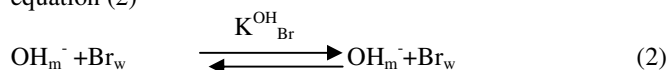
The reactions of both Mono phosphate were strongly catalyzed at different concentration of CTABr at which the pseudophases first order rates constant were obtained. In table 1, summarization the effect of cationic micelles of CTABr on the rate constants of OH with 4-CMPP which is shown in figure 1. The reaction between the observed pseudo first order rate constant ( $K_v$ ) and surfactant concentration  $[D_n]$  for a spontaneous phosphorylation of 4- CMPP may be shown in following scheme



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>18</sup>. The concentration of micellised surfactant,  $D_n$  is that of total surfactant concentration less that of monomeric surfactant which is assumed to be given by Critical Micelle Concentration  $CMC$ <sup>19</sup> provided that equilibrium is maintained between micelle and aqueous

$$K_v = \frac{K'w + K'm + K_s (D_n - CMC)}{1 + K_s (D_n - CMC)} \quad (1)$$

It is assumed that interaction of two or more counter ions 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 constants for OH<sup>-</sup> and denoted by K<sub>Br</sub><sup>OH</sup> can be given by the equation (3)

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

By employing the following equation (4) and (5), the first order rate constants K'<sub>w</sub> and K'<sub>m</sub> are conveniently converted in to second order rate constants K<sub>w</sub> and K<sub>m</sub> respectively,

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

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

Where m<sub>OH</sub><sup>s</sup> is the concentration of reactive ions in micelle. Since m<sub>OH</sub><sup>s</sup> is expressed in the molar ratio values of the second order rate constant K<sub>m</sub> cannot be compared directly with second order rate constants intricate because of different dimensions. They can be converted in to K<sub>2m</sub>, which is the second order rate constant expressed in terms mole of reactant per dm<sup>3</sup> (L) of stern layer. This quantity is estimated to be 140 ml or 0.14 L for [CTABr] K<sub>2m</sub> has been calculated from following equation (6).

$$K_{2m} = 0.14 K_m 2.3 \times 10^5 \text{ mol}^{-1} \text{ dm}^{-3} \text{ sec}^{-1} \quad (6)$$

The order equation (1) can be written in the following manner as in equation (7)

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

It is assumed that K<sub>Br</sub><sup>OH</sup> and β is the fraction of micellar head groups neutralized by counter ions may be treated as independent nature of concentration of counter ions (8) for a mixture of OH<sup>-</sup> and Br<sup>-</sup> is identical with m<sub>OH</sub><sup>s</sup> + m<sub>Br</sub><sup>s</sup> the concentration of OH<sub>w</sub><sup>-</sup> and OH<sub>m</sub><sup>-</sup> (in molarities) are expressed in terms of total concentration in solution volume so that [OH]<sub>T</sub> and [OH]<sub>T</sub> can be equation (8) and (9).

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

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

Substitution for [OH]<sub>T</sub> [OH<sub>w</sub><sup>-</sup>] [Br<sub>w</sub><sup>-</sup>]<sub>T</sub> with [OH]<sub>T</sub> and [Br]<sub>T</sub> in equation (3) leads to equation (10)

$$[m_{\text{OH}}^s]^2 + m_{\text{OH}}^s \left\{ \frac{[\text{OH}]_T + K_{\text{Br}}^{\text{OH}} [\text{Br}]_T}{[K_{\text{Br}}^{\text{OH}} - 1] [\text{Dn}]} - \beta \right\} - \frac{\beta [\text{OH}]_T}{[K_{\text{Br}}^{\text{OH}} - 1] [\text{Dn}]} \quad (10)$$

The Selecting values of [K<sub>Br</sub><sup>OH</sup>] and β as 10 and 0.75 respectively, m<sub>OH</sub><sup>s</sup> has been calculated for reaction at 0.451x10<sup>-2</sup> mol dm<sup>3</sup> [OH<sup>-</sup>] ion in table (2). For convenience equation (7) may be arrange as (11).

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

A graph plotted between  $\frac{K_\psi - K'_w}{m_{\text{OH}}^s [\text{Dn}]}$  and  $-\frac{K_\psi}{m_{\text{OH}}^s}$

in figure (2) which are linear at different [CTABr] and yield values of K<sub>s</sub>, K<sub>m</sub>, [OH<sup>-</sup>] 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<sup>-</sup>] ions which are present lower concentration in the micelles. Besides of this Di<sup>-</sup> anion of mono phosphate ester are relatively hydrophobic and polarisable anions bind to micelles the specific interaction but coulombic binding in much important in binding of hydrophilic anions. The dianions of mono phosphate ester is polarisable and not very hydrophilic interact with phosphate atom of C-O-P linkage present in zwitterionic forms of mono phosphate ester forming hydrogen bonded cyclic intermediate by entrap of reducing this interaction considerably the coulombic interactions [OH<sup>-</sup>] ions in cationic micelles was ascribed to a higher surface charge density at cationic as compared with the anionic centre.

**Table-1**  
**Pseudo first order rate constants for the reaction of NaOH with BIS 4-CMPP in presence of CTABr at pH-9.0 and 40 ± 0.5°C**

S.N.	CTABr x10 <sup>-3</sup> mol dm <sup>-3</sup>	Pseudo first order constant of bis-4- CMPPX10 <sup>5</sup> sec <sup>-1</sup>
1.	0.2	4.05
2.	0.4	5.61
3.	0.6	7.21
4.	0.8	8.97
5.	1.0	13.41
6.	1.2	16.12
7.	1.4	19.05
8.	1.6	26.61
9.	1.8	18.06
10.	2.0	0.09

## Conclusion

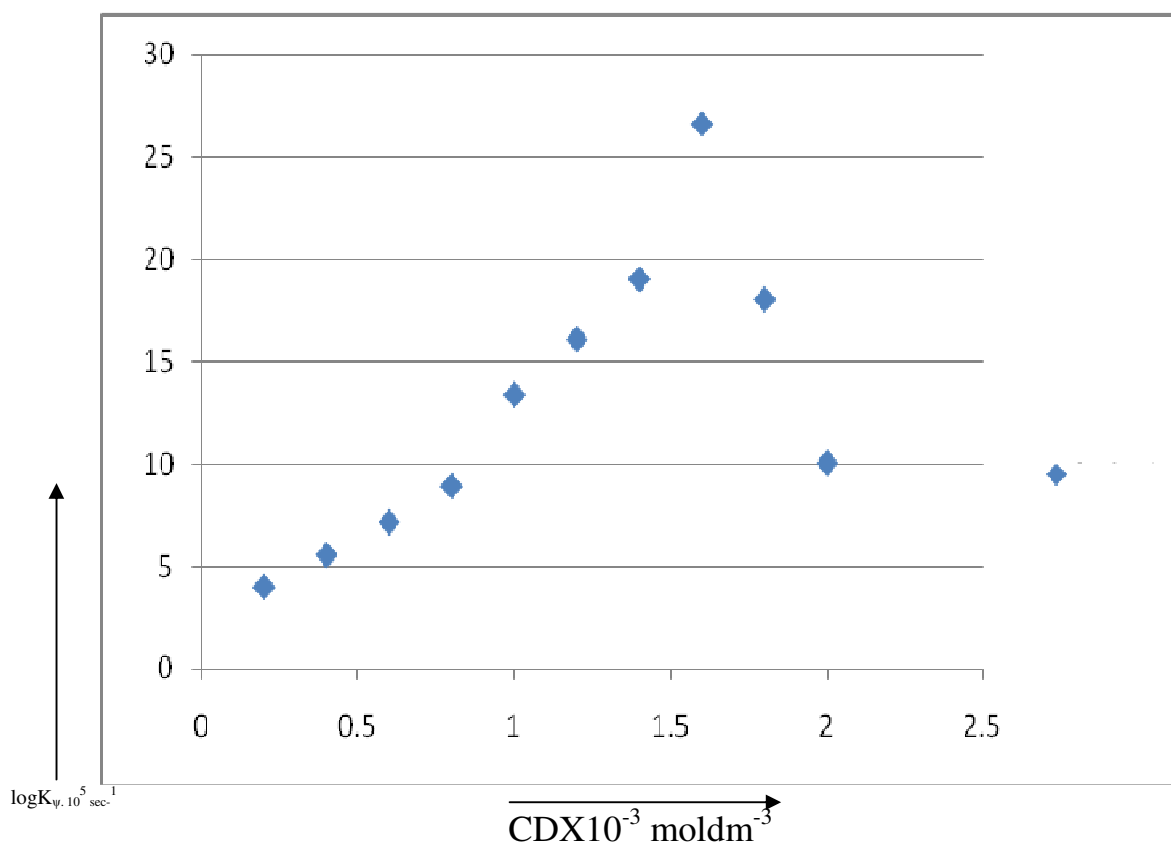
The order rate constant (K<sub>ψ</sub>) increases with increasing surfactant concentration to the maximum value at 1.6x10<sup>-3</sup> mol dm<sup>3</sup> for bis 4-CMPP. It is evident that maximum rate enhancement occurs in the region of CTABr at which bulk of the substrate incorporate in to the micelles.

**Table-2**  
 Relation between  $K_{\psi} - K'w/m_s^{OH}$  and  $-K_{\psi}/m_s^{OH}$  of bis-4-CMPP pH- 9.0 and  $40 \pm 0.5^{\circ}C$

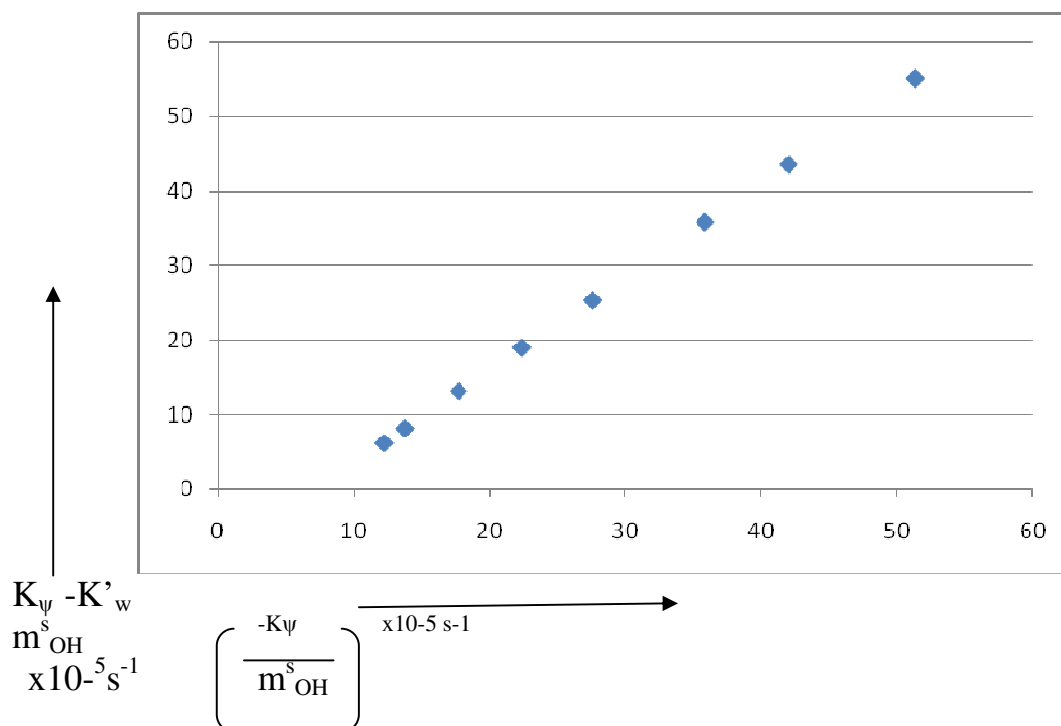
S.N.	$10^5 K_{\psi} \text{sec}^{-1}$	$-K_{\psi} m_s^{OH}$	$(K_{\psi} - K'w) \cdot 10^5$	$10^2 (K_{\psi} - K'w) m_s^{OH} [Dn]$
1.	5.55	12.30	2.26	6.14
2.	6.22	13.79	2.93	8.12
3.	8.01	17.76	4.73	13.10
4.	10.12	22.43	6.83	18.93
5.	12.41	27.59	9.11	25.27
6.	16.19	35.89	12.90	35.75
7.	18.96	42.03	15.69	43.48
8.	23.15	51.33	19.86	55.00

**Table-3**  
 Ion exchange parameter and second order rate constant for reaction of 4-CMPP with  $OH^-$  in presence of CTABr at pH-9.0 and  $40 \pm 0.5^{\circ}C$

$K_{Br}^{OH}$	$10^3$	$10^4$	$10^3$	$m_s^{OH}$	$10^3$	$10^4$	$10^5$	$10^5$	$\beta$
	$[OH^-]_T$	$[OH^-]_m$	$[OH^-]_w$		$K_s$	$K'_m$	$K'_w$	$K_m^2$	
	mol	mol	mol		$\text{mol}^{-1}$	$\text{s}^{-1}$	$\text{mol}^{-1}$	$\text{mol}^{-1}$	
	$\text{dm}^{-3}$	$\text{dm}^{-3}$	$\text{dm}^{-3}$		$\text{dm}^{-3}$		$\text{dm}^{-3}$	$\text{dm}^{-3}$	
10	20.8	3.61	20.439	0.451	38.61	29.6	3.29	1.792	0.75



**Figure-1**  
 Reaction of bis-ester(4-CMPP)with Hydroxyl ions in micellized CTABr at pH-9.0 and  $40 \pm 0.5^{\circ}C$



**Figure-2**  
Quantitative treatment of micellar effect on the nucleophilicity of bis-4-CMPP

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