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Effect of the micellar catalysed hydrolysis of mono-4-chlorl-3-methyl phenyl phosphate ester

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Abstract

Micellar effect upon nucleophilic substitution reactions between hydroxide anions [OH^-] and mono-4-chloro-3-methyl phenyl phosphate ester (mono-4-CMPP) in presence cetyltrimethyl ammonium bromide(CTABr) has been examined in buffered medium (at pH 8.0 to 10). The first order rate consant (K_{ψ}) are increased with the concentration of the surfactant can be analyzed in terms of Br^- ions in micellar pseudophases, which occur readily by aqueous CTABr and calculated second order rate constants.

Key words: Micelles, Micellar Catalyses, 4-CMPP, CTABr

Introduction

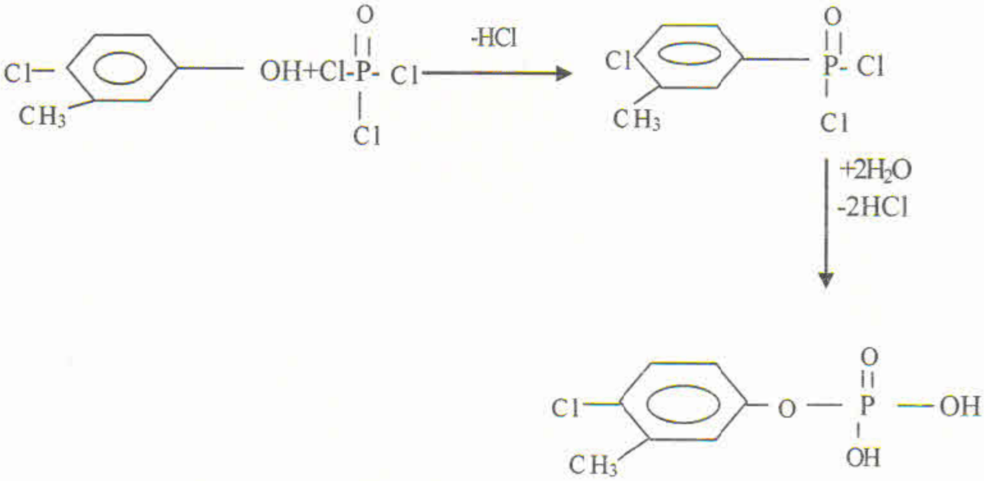
The rate enhancement of first order rate costant (K_{ψ}) of the reaction catalysed by the micelles is largely due to the increased concentration of the reactant in the micellar pseudo phase[1]. It is difficult to examine the partitioning of hydrophillic reactants between aqueous and micellar pseudophases 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 counterions is approximately constant[2,3]. This approach has been applied to the rate and equilibrium constant of many reactions[4-8].

A reactive ion surfactant in which ionic reagent is the micellar counterions[9-12] can be used to eliminate the problem of inter ionic competition. Therefore, its concentration in the micellar pseudophase should be constant provided that 'β' is constant. The first order rate constants (K_{ψ}) increases with increasing surfactant concentration to the maximum value $33.45 \times 10^5 \, s^{-1}$ at 1.6×10^{-3} mol dm^{-3}. CTABr for 4-CMPP. This behavior has been observed for reactions involving hydroxide ions[9] for nucleophillic addition[13] by Br^-

Experimental

Mono ester of 4-chloro-3-methyl phenyl has been prepared by treating excess of phosphorylating agent (phosphorus oxy tri chloride $POCl_3$) with 4-chloro-3-methyl phenol in dry benzene. Pure 4-chloro-3-methyl phenol (14.25 gm) was dissolved in dry benzene (100ml) in a round bottom flask. Phosphorus oxy tri chloride (9.03 ml) was added drop by drop with constant stirring to the ice cooled phenol in about half an hour with the help of separating funnel. After addition of $POCl_3$, mixture was refluxed for about 18 hours on the sexhelt heater at constant temperature 65^{0}C. In order to ensure complete reaction and then distilled at reduced pressure. The first reaction of benzene and unreacted $POCl_3$, was removed by distillation at b_p 120 ^{0}C.

The second reaction of a pungent smelling liquid which was supposed to be 4-chloro -3- methyl phenyl phosphate dichloride was distilled at b_p 120-140 ^{0} C. It was dissolved in ice cooled water (100ml) and kept at low temperature over night .The 4-chloro-3-methyl phenyl phosphate dichloridate converted in to 4-chloro-3-methyl phenyl phosphate dihydrogen 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 awhite crystalline solid and it was identified to be mono 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 than 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 than 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 metabisulphate (20%). The reagent obtained was kept in a dark at low temperature (0^0C). 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.

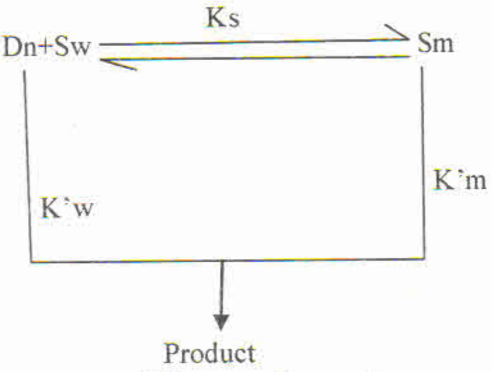
Method: substrate in solution have the specific property of absorbing light of wave length characteristic of the particular substance. The basic principle of absorption is utilized in the measurement of various concentrations. The spectrophotometer instrument utilize a source of radiant energy, a means to isolate a band of radiant energy which is focused on the solution and than measured with a detector. Kinetic study for the hydrolysis of all the mono-, di-, and triester 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 $(NH_4)_3PO_4.12MoO_3$ which is reduced to molybdnum blue, a soluble complex by addition of mixture of 2,4-diamino phenyl hydrochloride (amidol,diamol or nerol).

Material: Phosphate mono esters were prepared by standard methods[14a] purified by recrystalisation from absolute ethyl alcohol and examined by IR. CTABr used analytical grade, strength of borate buffer were prepared and purified by standard methods[14].

Kinetics : All kinetic runs were performed using doubly or triply distilled water. All reactions were carried out at 40 ± 0.5^0C and pH 9.0. Reactions were followed by spectrophotometer at the absorbance 662 nm. To obtain first order rate (K_ψ)

Result and Discussion

The reactions of both Mono phosphate were strongly catalyzed 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 OH-with 4-CMPP and 4-CDMPP, which is shown in fig. 1. The reaction between the observed pseudo first order rate constant (K_ψ) and surfactant concentration [Dn] for a spontaneous phosphorylation of 4-CMPP and 4-CDMPP may be shown in following **scheme** I



Where Sw and Sm are substrate in aqueous and micellar pseudophases respectively, K'w and K'm are the related first order rate constant and Ks is binding constant[15]. The concentration of micellised surfactant, Dn is that of total surfactant concentration less than that of monomeric surfactant which is assumed to be given by Critical Micelle Concentration CMC[16] provided that equilibrium is maintained between micelle and aqueous phases.

$$K_\upsilon = \frac{K'w + K'm + Ks\,(Dn - CMC)}{1 + Ks\,(Dn - CMC)}$$

It is assumed that interaction of two or more counterions with anionic micelles are governed by the ion exchange equilibrium[9] equation (2)

$$OH_m^- + Br_w \underset{OH_m^- + Br_w}{\overset{K^{OH}_{Br}}{\rightleftharpoons}} \qquad (2)$$

Where m and w in parenthises denotes micellar and aqueous pseudophases respectively. Equilibrium or ion exchange constants for OH^- and denoted by K^{OH}_{Br} can be given by the equation (3)

$$K^{OH}_{Br} = \frac{[OH^-_W]\,[Br^-_m]}{[OH^-_m]\,[Br^-_w]} \qquad (3)$$

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

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

$$K'_m = K_m\, m^s_{OH} = \frac{[OH^-]}{[Dn]} \qquad (5)$$

Where m^s_{OH} is the concentration of reactive ions in micelle. Since m^s_{OH} is expressed in the molar ratio values of the second order rate constant Km cannot be compared directly with second order rate constants intricate because of different dimensions. They can be converted in to K_2m, which is the 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 0.14 L for [CTABr] K_2m has been calculated from following eq.(6).

$$K_2m = 0.14\,Km\,2.3x10^5\,mol^{-1}\,dm^{-3}\,sec^{-1} \qquad (6)$$

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

$$K_\upsilon = \frac{K_w[OH^-_w] + K'_m\,K_s\,m^s_{OH}\,[Dn]}{1 + K_s\,[Dn]} \qquad (7)$$

It is assumed that K^{OH}_{Br} and β 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 $m^s_{OH} + m^s_{Br}$ 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 $[OH^-]_T$ can be equation (8) and (9)

$$[OH^-]_T = [OH^-] + m^s_{OH}\,[Dn] \qquad (8)$$

$$[Br^-]_T = [Br^-] + [\beta - m^s_{OH}]\,[Dn] \qquad (9)$$

Substitution for $[OH^-]_T$ $[OH^-_w]$ $[Br^-_w]_T$ with $[OH^-]_T$ and $[Br^-]_T$ in equation (3) leads to equation (1o)

$$[m^s_{OH}]^2 + m^s_{OH}\{-\beta\} - \frac{[OH^-]_T + K^{OH}_{Br}\,[Br^-]_T}{[K^{OH}_{Br} - 1]\,[Dn]} \qquad \frac{\beta[OH^-]_T}{[K^{OH}_{Br} - 1][Dn]} \qquad (10)$$

The selecting values of $[K^{OH}_{Br}]$ and β as 10 and 0.75 respectively, m^s_{OH} has been calculated for reaction at 0.451×10^{-2} mol dm^3 $[OH^-]$ ion in table (2). For convenience equation (7) may be arrange as (11).

$$\frac{K_\upsilon - K'_w}{m^s_{OH}[Dn]} = K_m K_s - K_s \frac{K_\upsilon}{m^s_{OH}} \qquad (11)$$

A graph plotted between $\frac{K_\psi - K'_w}{m^s_{OH}[Dn]}$ and $-\frac{K_\psi}{m^s_{OH}}$ is shown in figure (2) which are linear at different [CTABr] and yield values of Ks, Km, [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 in 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 zwitterions of mono phosphate ester forming hydrogen bonded cyclic intermediate by entrap of reducing this interaction considerably the coulombic interactions [OH-] ions in cationic micelles was ascribed to a higher surface charge density at cationic as comparaed with the anionic centres.

Table 1. Pseudo first order rate constants for the reaction of NaOH with 4-CMPP and 4-CDMPP presence of CTABr at pH 9.0 and 40 ± 0.5^{0}C

S.N.	CTABr x 10^{-3} mol dm^{-3}	$K_\upsilon.10^5 s^{-1}$ 4- CMPP (obsd.)	$K_\upsilon 10^5 s^{-1}$ 4-DMPP(obsd.)
1.	0.2	6.54	8.53
2.	0.4	7.61	10.38
3.	0.6	9.38	12.49
4.	0.8	11.45	15.97
5.	1.0	15.12	21.03
6.	1.2	20.59	28.00
7.	1.4	23.95	33.47
8.	1.6	33.45	44.53
9.	1.8	29.75	35.60
10.	2.0	25.57	20.95

Table 2. Relation between $\frac{K_\psi - K'_W}{m^S_{OH}[Dn]}$ $\frac{-K_\psi}{m^S_{OH}}$ of mono-4-CMPP at pH -9.0 and 40±0.5°C

S.N.	$K_\psi\ 10^5 s^{-1}$	$\frac{-K_\psi}{m^s_{OH}}\ X10^5 s^{-1}$	$\frac{K_\psi - K'_w}{m^s_{OH}} x10^2$
1.	6.54	14.50	2.411
2.	7.61	16.87	5.376
3.	9.38	20.80	10.282
4.	11.45	25.38	16.019
5.	15.12	33.70	26.191
6.	20.59	45.65	41.352
7.	23.95	53.10	50.665
8.	33.45	74.16	76.995

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±0.5°C

K^{OH}_{Br}	10^3 $[OH^-_T]$ mol dm^{-3}	10^4 $[OH^-_m]$ mol dm^{-3}	10^3 $[OH^-_w]$ mol dm^{-3}	m^s_{OH}	10^3 K_s mol^{-1} dm^{-3}	10^4 K_m s^{-1}	10^5 K'_w mol^{-1} dm^{-3}	10^5 K^2_m mol^{-1} dm^{-3}	10^5 Kw mol^{-1} dm^{-3}	β
10	20.8	3.61	20.439	0.451	1.25	1.6	5.67	2.24	277.41	0.75

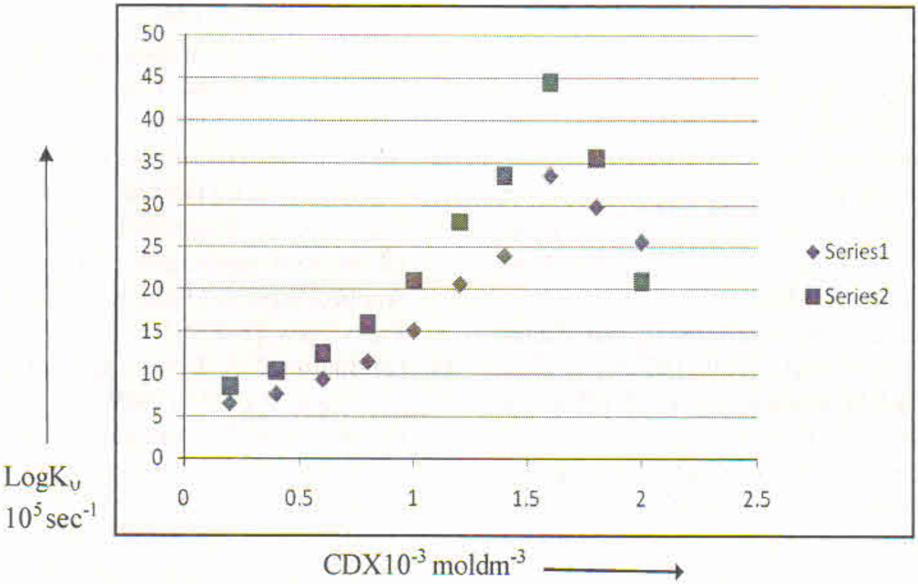


Fig.1. Reaction of mono ester(4-CMPP&4-CDMPP)with Hydroxyl ions in micellized CTABr at p^H -9.0 and 40±0.5^{0}C.

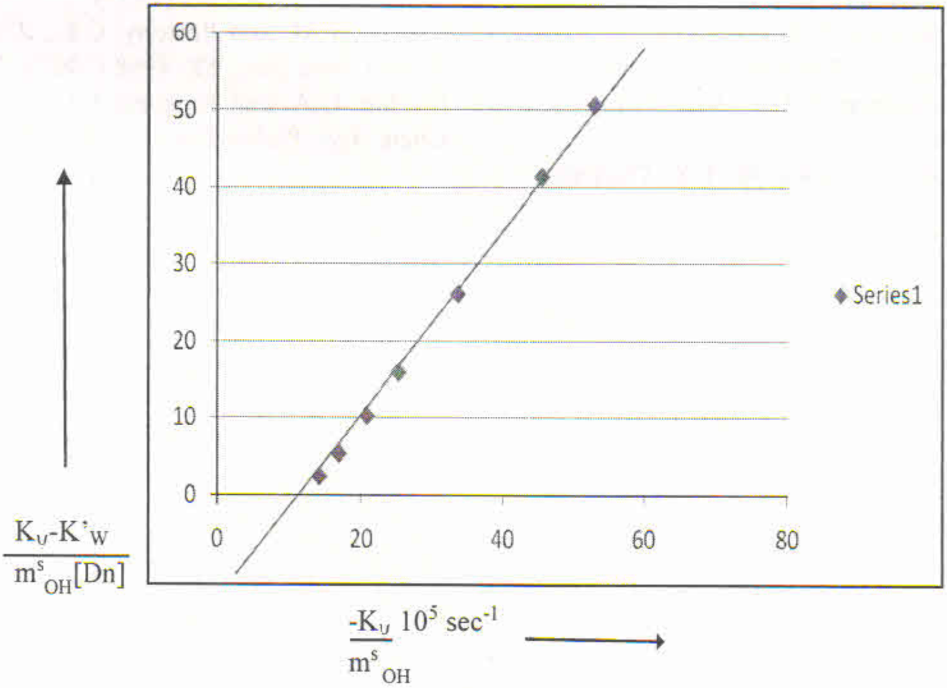


Fig.2. Quantitative treatment of micellar effect on the nucleophiliocity of 4-CMPP

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