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Effect of cationic micelles of CTA Br on the reaction of hydroxide ions with tri-2-methoxy phenyl phosphoramide ester

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Abstract

Micellar effect upon nucleophilic substitution reactions between hydroxide ions and tri-2-methoxy phenyl phosphoramide (2-MPPA) in presence of cetyl trimethyl ammonium bromide (CTABr) has been examined in buffered medium at pH 8-10. The first order rate constant (Kψ) are increased with the concentration of the surfactant can be analysed in terms of Bromide ions in micellar pseudophase, which occur readily by aqueous CTABr and calculated second order rate constants.

Keywords: micelles, micellar catalysis, tri-2-mppa, ctabr

Introduction

The enhancement rate of first order rate constant (Kψ) of the reaction catalysed by the micelles is largely due to the increased concentration of reactant in the micellar pseudophase [1-4]. It is difficult to examine the partitioning of hydrophilic reactants between aqueous and micellar pseudophase instead of hydrophobic ions. The widely used approach is to assume that counter ions complete for ionic sites on the micellar surface and fraction 'β' of these sites which are neutralized by approaches counter ions is constant[5]. This approach has been applied on the rate and equilibrium constant of many reactions.

The surfactant reactive ions in which ionic reagent is the micellar counter ions [6-10] can be used to eliminate the problem of inter ionic competition. Its concentration in the micellar pseudophase should be constant, provided that 'β' is constant. The first order rate constants (Kψ) increases with increasing surfactant concentration to the maximum value at 1.6×10^{-3} mol dm^{-3}, CTABr for 2-MPPA. This behaviour has been observed for reaction involving hydroxide ions [11] for nucleophilic addition by Bromide ions [12].

Interfacial region at a micellar surface can act as a reaction medium which can be regarded as a pseudophase distinct from bulk solvent with water [13-14]. The quantitative analysis of bimolecular reactions in pseudophase model require estimation of local concentration of both reactants in micellar and aqueous pseudophases and second order rate constants in each region [15-20]. Micellar effects on many bimolecular rate constants have been treated quantitatively in this model, which shows that micellar accelerated against counting ionic reactions are to a large extent due to the concentration of reactants in the small volume of the interfacial regions. The cationic micelles effectively promote bimolecular attack by anion or non-ionic bases or nucleophiles in water and these reactions widely studied [21-24].

Materials and Methods

The preparation of tri-2-methoxy phenyl phosphoramide (2-MPPA) and the residue was left after removing mono-2-MPPA at b.p. 160-180^{0}C. The residue was washed several times with boiling water and sodium hydroxide solution (0.2N) to remove 2-methoxy phenyl phosphoramide mono ester. The unreacted phosphorus oxy tri- chloride and aniline then finally digested in hot water and sodium hydroxide solution (0.5N). It was filtered and filtrate acidified with dil HCl using phenolphthalene as an indicator, obtained while precipitate was separated by filtration and made free from hydroxyl ions with boiling water. It was dried at room temperature and recrystallized with absolute alcohol, yielded white crystalline solid mass was identified as: tri-2- methoxy phenyl phosphoramide (2-MPPA) as shown in the following reaction (Figure-1).

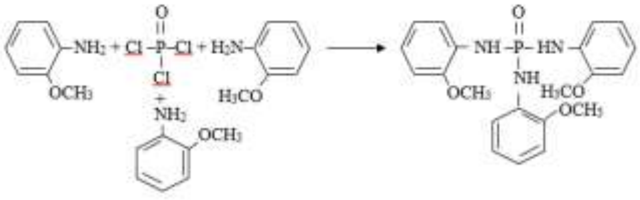


Fig 1: Tri-2-methoxy phenyl phosphoramide (2-MPPA) ester.

Characterization of tri-2-methoxy phenyl phosphoramide ester

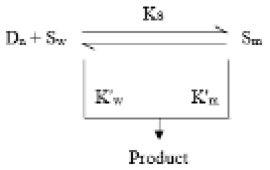
The cetyl trimethyl ammonium bromide (CTABr) was purified by given method formed 2-methoxy phenyl phosphoramide (2-MPPA) were washed with anhydrous ether and acetone until no amine is detected in the eluant recrystallized from methanol and four times with methanol with addition of anhydrous ether. Amidol (1.4 gm) was taken in a conical flask covered with a carbon paper, added activated charcoal (2 gm) and water (10 ml) then shaken thoroughly for 15-20 minutes. The colourless amidol solution so obtained was filtered into a solution containing sodium metabisulphate solution (20%,100 ml). Reagent so obtained was kept in a dark at low temperature (0^{0}C). This solution gradually decomposed and turned yellow after 6-8 days, than it was no used and discarded before use.

Substrates was in the solution and the specific property of absorbing light of wavelength characteristic of the particular substances. Basic principle of absorption is utilised in the measurement of various concentrations. The spectro photometer utilised a source of radiant energy, to isolate a band of radiant energy which is focused on to the solution than measured with a detector. Kinetic study for the hydrolysis of all the mono, di and tri ester was followed by spectrophotometrically. This method was involves the quantitative estimation of inorganic phosphates formed from the hydrolysis of phosphate esters. The inorganic phosphate react with ammonium molybdate and forms a phosphomolybdate complex, $(NH_4)_3 PO_4.12 MoO_3$, which is reduced to molybdenum blue, a soluble complex by addition of a mixture of 2, 4-diamino phenyl hydrochloride and sodium metabisulphite solutions. The blue colour so produced took seven min. to reach its maximum intensity then it remained stable for next 30 min. The intensity of blue colour is directly proportional to the amount of free phosphoric acid. It is independent to temperature over the range of $8\text{-}26^0C$. The optical density of blue colour so generated was measured by spectrophotometer, filtered with red filter of "Kodak" 360 mm and purified by standard method [11].

Kinetic runs were performed using double distilled water. All reactions were carried out at 40 ± 0.5^OC and pH 9.0. The reactions were followed by spectrophotometer at the absorbance 662 nm to obtain the first order rate constant (K_ψ).

Results and Discution

Reactions of tri methyl phosphate were prepared at different concentration of CTABr at which the pseudophase first order rates are constant. The effect of cationic micelles of CTABr on the rate constants of hydroxyl ion with tri-2-MPPA are given in Table-1. The reaction between the observed pseudo first order rate constant (K_ψ) and surfactant concentration [Dn] for a spontaneous phosphorylation of tri-2-MPPA may be shown in the following scheme:



Where, S_w and S_m are substrate in aqueous and micellar pseudophase respectively, which K' and K'm are the related first order rate constant and K_s is binding constant [12]. The concentration of micellized surfactant, D_n is that of total surfactant. Concentration less than of monomeric surfactant, which is assumed to be given by Critical Micelle Concentration (CMC) [13] provide that equilibrium is maintained between substrate in micelle and aqueous solution shown in equation (1).

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

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

$$OH^-_m + Br_w \xrightleftharpoons{K_{Br}^{OH}} OH^-_m + Br_w \qquad \text{- - - - - (2)}$$

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

$$K^{OH}_{Br} = [OH^-_w][Br^-_m] \Big/ [OH^-_m][Br^-_w] \qquad \text{- - - - - (3)}$$

By employing the following equation (4) and (5), the first order rate constants K'w and K'm are conveniently converted into second order rate constants Kw and Km respectively.

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

$$K'_m = [K_m m^s OH] - [OH] \Big/ [D_n] \qquad \text{- - - - - (5)}$$

Where, m^S_{OH} is the concentration of reactive ions in micelle, since m^s_{OH} is expressed in the molar ratio values of second order rate constant Km cannot be compared directly with second order rate constants indicate because of different dimensions. They can be converted into K_2m, which is the second order rate constant expressed in moles 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 the following equation (6).

$$K_2m = 0.14\,K_m\,2.3 \times 10^2\ mol^{-1}\ dm^3\ sec^{-1} \qquad \text{- - - - - (6)}$$

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

$$K_\psi = K_w[OH^-_w] + K'_m K_s m^s_{OH} [D_n] \Big/ 1 + K_s [D_n] \qquad \text{- - - - - (7)}$$

It is assumed that K^{OH}_{Br} and β is the fraction of micellar head groups neutralised by counter ions may be treated as independent nature of a concentration of counter ions (8) for mixture of OH^- and Br^- is identical with $m^s_{OH} + m^s_{Br}$. The concentration of OH^-_w and OH^-_m are expressed in terms of total concentration in solution, so that $[OH^-]_T$ and $[Br\text{-}]_T$ can be shown in the equation (8) and (9).

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

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

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

$$[m^s_{OH}]^2 + m^s_{OH} \left[\frac{[OH^-]_T + K^{OH}_{Br} [Br^-]_T}{[K^{OH}_{Br} - 1][D_n]} - \beta - \frac{\beta[OH^-]_T}{[K^{OH}_{Br} - 1][D_n]} \right. \qquad \text{- - - - -(10)}$$

The selecting value of $[K_{Br}^{OH}]$ 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 as given in Table-2. For convenience equation (7) may be arrange as shown in equation (11).

$$K_\psi - K'_w \Big/ m^s_{OH} = K_m K_s - K_s, K_\psi \Big/ m^s_{OH} \qquad \text{- - - - -(11)}$$

The reaction between K_ψ -K'w/m^s_{OH} and K_ψ/m^s_{OH} are linear at different [CTABr] and yield value of Ks, Km [OH-]

summarised 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 in corporated into the micelles. The aryl part of substrate, dianion is deeply buried in interior of micelles and the phosphates di-anion are suitably exposed to nucleophilic attack by [OH^-] ion which is present lower concentration in the micelles. Besides of this di-anion 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-N-P linkages present in Zwitter ionic forms 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 described 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 tri-2- MPPA in presence of different CTABr concentration at pH 9.0 and Tem. 40±0.5^{O}C

S. No.	CTABr × 10^{-3} mol dm^{-3}	Pseudo first order rate constant of tri-2-MPPA, K_ψ 10^5 sec^{-1}
1.	0.4	2.99
2.	0.6	3.52
3.	0.8	4.07
4.	1.0	5.18
5.	1.2	5.80
6.	1.4	6.64
7.	1.6	6.97
8.	1.8	5.76
9.	2.0	4.80

Table 2: Relation between K_ψ -K'_w/m^s_{OH} and -K_ψ/m^s_{OH} of tri-2-MPPA at pH 9.0 and Tem. 40±0.5^{0}C.

S. No.	K_ψ $10^5 sec^{-1}$	K_ψ -K'_w × 10^2 m^s_{OH} [D_n]	-K_ψ^2 × 10^5 sec^{-1} m^s_{OH}
1.	2.99	8.26	26.00
2.	3.52	11.14	30.61
3.	4.67	17.39	40.61
4.	5.18	20.16	45.04
5.	5.80	2353	50.43
6.	6.64	28.10	57.74
7.	6.97	29.89	60.61

Table 3: Ion exchange parameter and second order rate constant for reaction of tri-2- mppa with oh^- in micellar pseudophase at ph 9.0 and tem. 40±0.5^{0}c.

S. No.	KOH Br	10^2×[OH^-]$_T$ mol dm^{-3}	m^s_{OH} mol^{-1}	K_s mol dm^{-3}	10^5 K'_w sec^{-1}	10^5 KW mol dm^{-1} sec^{-1}	K_m 10^5 mol dm^{-3} sec^{-1}	$K^m{}_2$×10^5 mol^{-1} sec^{-1}	$[OH]_m$ mol dm^{-3}	$[OH^{-1}]_w$ mol dm^{-3}	β
1.	14.7	2.2	0.115	26.3	1.47	67.43	6.06	0.85	0.77	0.0218	0.87

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