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RESEARCH ARTICLE

MECHANISTICALLY CATIONIC MICELLE ON THE HYDROLYSIS OF TRI-p-METHOXYPHENYL PHOSPHATE ESTER

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ABSTRACT

Hydrolysis of tri-p-methoxyphenyl phosphate ester (tri-p-MPPE) was studied in micelle medium of cetyl tri methyl ammonium bromide $n\text{-C}_{16}\text{H}_{33}\text{N}^+(\text{CH}_3)_3\text{Br}$ (CTABr) at pH-9.0. The hydrolysis followed first order kinetics with respect to tri-p-MPPE concentration. At the critical micelle concentration (CMC) the rate of hydrolysis increased with increasing CTABr concentration. Micelle with cationic or polar head group form micelle in water with hydrocarbon like interior or polar groups at the surface and bind cationic solute. The binding constant of micelle for tri-p-MPPE and the rate constant in micelle pseudo phase were determined from kinetics data using the pseudo phase model.

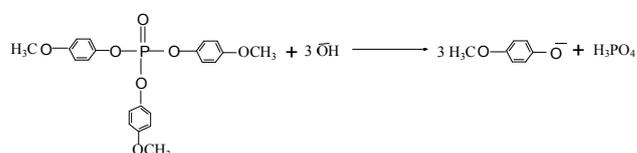
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INTRODUCTION

Several of the vital chemicals in living processes are phosphate esters. These including the hereditary substances DNA and RNA as well as cyclic AMP, in accumulation, the transportation of phosphate groups among ATP and ADP is of essential substance of in the life systems. Every part of the heritable reactions involving configuration and hydrolysis of these phosphate esters and polyphosphates are exaggerated by enzyme catalysis. Appropriate to importance such substance the hydrolysis of phosphate esters has established greatly original study. Phosphate esters are extremely imperative biologically and most occurring phosphorous compounds containing a terminal unsubstituted- $\text{PO}(\text{OH})_2$ groups. Foreword of these groups into molecule is known as phosphorylation. Stipulation the protected group is not used. Then polymers containing the P-O-P linkage are obtained. In no small determine because of the importance of such substances and process as these just mentioned, the hydrolysis of phosphate esters has acknowledged much essential study. Tri esters are attacked by OH^- at phosphorus atom and H_2O at carbon atom.

The largest part work has implicated macrobiotic reactions, commonly in water, mediated by organic micelles which attract reactants, on condition that a reaction region dissimilar from the bulk solvent. Hydrolysis of tri ester depends upon the experimental conditions. (Kumar, 2015) In the most kinetic studies of micelle catalyzed reactions, in the case of substrate in to the micelle segment brings pull to the micelle by the electrostatic energy, (Ghosh, *et al.*, 2008, Domingos, *et al.*, 2003) or it gets chemically bonded in it. (Brinchi *et al.*, 2000) Interface between ester in finding the conditions in which micelles would enhance the hydrolysis of tri substituted phenyl phosphate esters. Tri-p-MPPE was the preferred substrates because with tri-p-MPPE the neutral species is the most reactive species. (Behme *et al.*, 1965) At pH-9.0 tri-p-MPPE reacts also with hydroxide ion (Bruice *et al.* 1968) and therefore by appropriate choice of a substrate. It is possible to examine the micelle effects upon the mechanism of tri-p-methoxyphenyl phosphate ester hydrolysis (Scheme-1)



Scheme 1 Hydrolysis of tri-p-methoxyphenyl phosphate ester.

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MATERIALS AND METHODS

The details of preparation of the phosphate esters of p-methoxy phenol involves with direct reaction of phosphorus oxytrichloride (POCl_3) mono-, bis- and tri- phosphate esters of the above mentioned phenol have been prepared by the standard method (Cox and Ramasay, 1964) (Bunton *et al.* 1968) described as under, 12.4 gm of p-methoxy phenol dissolved in benzene (100 ml) and 9.05 ml of phosphorus oxytrichloride was added slowly during 20 minutes with constant stirring. The reaction mixture was refluxed for 18 hours and distilled at reduced pressure. The first fraction of benzene and unreacted phosphorus oxytrichloride was removed by distillation at b_{72} 60-80 $^{\circ}\text{C}$. It was dissolved in 100 ml of ice cold distilled water and kept at low temperature overnight. The mono-p-methoxy phenyl phosphorodichloridate was converted into mono-p-methoxy phenyl dihydrogen phosphate, was extracted with solvent ether.

The residue left after removing mono-p-methoxy phosphate at b_{72} 60-80 $^{\circ}\text{C}$ was washed several times with boiling distilled water and 0.2N NaOH solution to remove mono-p-methoxy phosphate ester, unreacted phosphorus oxytrichloride and the phenol and finally digested in hot 0.5N 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 recrystallized with absolute ethyl alcohol to give a white crystalline solid which was identified bis-p-methoxy phenyl phosphate. The residue left behind after removal of bis-p-methoxy phenyl phosphate with 0.5N NaOH solution was washed several times with boiling distilled water to render it free from hydroxyl ions. It was dried and recrystallized in absolute ethyl alcohol to give a white crystalline solid, was identified to be tri-p-methoxyphenyl phosphate by the following physical characteristics.

Kinetics and Mechanism

Investigation of micellar catalysis in mechanism of tri-p-MPPE with hydroxide ion has been carried out at temp. [40 \pm 0.2 $^{\circ}\text{C}$]. Kinetics runs were performed by using double distilled water. Reactions were followed by spectrophotometrically at using the wavelength (λ) 660 nm by the rate of development of inorganic phosphate.

RESULTS AND DISCUSSION

The I.R. spectrum showed the appearance of absorption bands characteristics bands of tri-p-methoxyphenyl phosphate ester is γ -C-H [Aromatic ring] = 3399.6 cm^{-1} , γ -P=O = 1733.8 cm^{-1} , γ -C=C-C=C- = 1523.7 cm^{-1} , γ -P-O = 1453.3 cm^{-1} , γ -C-O = 1012.8 cm^{-1} , γ -C-H [out of plane bending] = 1040-936 cm^{-1} , characterised the structure of tri-p-methoxyphenyl phosphate. In previous work on chemical reaction base equilibrium was examined by using visual indicators and apparent base dissociation continuous was sensitive to cationic micelles. (Bunton *et al.*, 1967) The reactions of phosphate tri-ester were strappingly catalyzed at different concentration of (CTABr) at which pseudo first order rate constants were obtained.

Investigation of micelles catalyzed hydrolysis (Silva, *et al.*, 2009, Bunton, 2011, Reale *et al.*, 2010) of tri-p-MPPE with hydroxide ion has been carried out at temperature [40 \pm 0.2 $^{\circ}\text{C}$] in presence or absence of detergent [10 $^{-3}$ to 10 $^{-4}$ mol.dm. $^{-3}$] at pH-8.0 to 10.0 using borate buffers. Effect of cationic [CTABr] micelle on rate of hydrolysis of tri-p-MPPE in presence of hydroxide ion has been measured spectrophotometrically by the rate of appearance of inorganic phosphate (Kumar and Singh, 2011) and rate increases sharply at CTABr concentration increases than the critical micelle concentration (CMC) for CTABr at pH-9.0 in 2.5 \times 10 $^{-3}$ mol.dm. $^{-3}$ borate buffer CMC = 80 \times 10 $^{-3}$ M determined by dye method. (Jaks, *et al.* 2010, Duynstee, and Grunward, 1959) The pseudo first order rate constant for tri-p-MPPE has been carried out in presence of detergent. It has been observed that whether the increasing detergent concentration the rate increases to a maximum value of $K_{\psi} = 59.01 \times 10^{-5} \text{sec}^{-1}$ at 1.6 \times 10 $^{-3}$ mol.dm. $^{-3}$ CTABr respectively. This maximum rate has been shown in rate constant against detergent concentration [Table-1]. Investigation of the relation between the observed pseudo rate constant K_{ψ} and the surfactant concentration for a spontaneous dephosphorylation of tri-p-MPPE may be shown in [Fig.-1]

Table 1. Reaction of [5X10 $^{-4}$] mol.dm. $^{-3}$ tri-p-methoxyphenyl phosphate with constant [OH $^{-}$] in presence of different 10 3 [CTABr] at pH-9.0 and temperature [40 \pm 0.2 $^{\circ}\text{C}$]

S.N.	10 3 [CTABr] mol.dm. $^{-3}$	10 5 K $_{\psi}$ s $^{-1}$
1	0.2	10.15
2	0.4	17.15
3	0.6	18.96
4	0.8	30.06
5	1.0	34.99
6	1.2	45.38
7	1.4	52.25
8	1.6	59.01
9	1.8	54.90
10	2.0	50.27

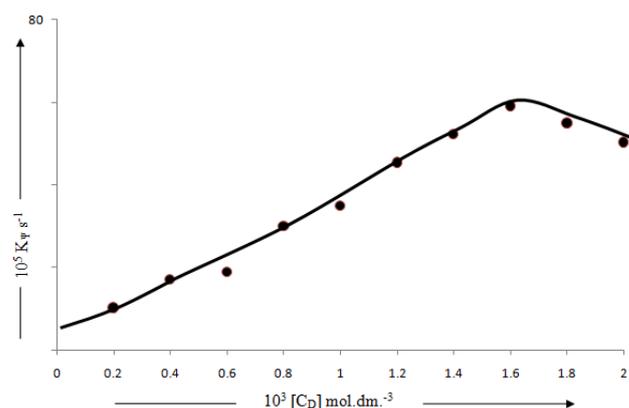
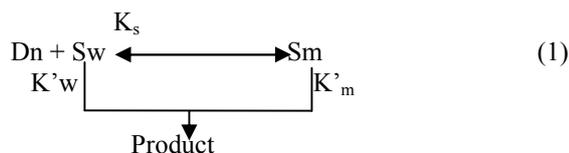


Fig. 1. A plot of rate constants against detergent concentrations [CTABr] to 20.8 \times 10 $^{-3}$ mol. dm. $^{-3}$ [OH $^{-}$] with [5 \times 10 $^{-4}$] mol.dm. $^{-3}$ tri-p-methoxyphenyl phosphate at pH- 9.0 and [40 \pm 0.2 $^{\circ}\text{C}$]

Presuming protonation of the neutral ester or neutral species of the tri-p-MPPE the bend in the obtained by rates constants against detergent concentration was through due to the result of the maximum protonation which is common in amide system, (Bunton and Moffatt, 1986) unless the energy of protonation is small, the difference in activation energies

should result at point before and after the bend with this view kinetic runs were made at maximum where substrate is completely micellar bound at $1.6 \times 10^{-3} \text{ mol.}^{-1} \text{ dm.}^{-3}$ CTABr where maximum rates $K_{\Psi} = 59.01 \times 10^{-5} \text{ s}^{-1}$ for the hydrolysis of tri-p-MPPE with micelles of CTABr in buffer solutions. The hydrolysis was studied in absence and in presence of surfactant. Investigations of Arrhenius parameters for the hydrolysis of tri-p-MPPE are shown [Table 2]. The rate of enhance arise approximately complete from a lowering of activation energy in absence of CTABr $-\Delta E = 20.2 \text{ K. Cals. / Mole}$ and entropy of $-\Delta S \neq 56.79 \text{ (e.u.)}$ and in presence of CTABr $-\Delta E = 19.01 \text{ K. Cals. / Mole}$ and entropy of $-\Delta S \neq 52.71 \text{ (e.u.)}$.



Scheme -2

Where,

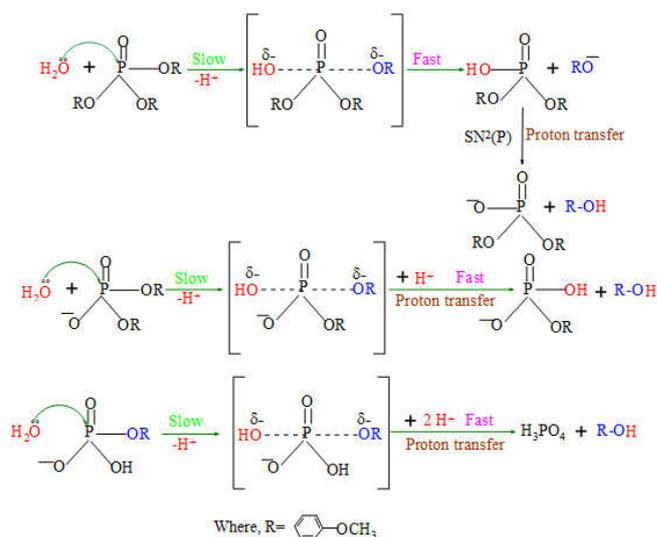
Sw and Sm are substrates in aqueous and micellar pseudo phase respectable. K'_w and K'_m are the related first order rate constants and K_s are the binding constant (Chaimovich *et al.*, 1983). Reactions in the water make minor contribution to the observed rate constant. The first order rate constant for K_{Ψ} OH ion is given by the following equation (Profio *et al.*, 2010).

$$K_{\Psi} = \frac{K'_w + K'_m K_s [\text{Dn}]}{1 + K_s [\text{Dn}]} \quad (2)$$

- The value of K'_m can be obtained by analysis of the variations of K_s with Dn or by choosing conditions such that substrate is essentially fully micellar bound. (Bunton *et al.*, 1979). The main feature of the mechanism of micelle catalyzed hydrolysis of tri-p-MPPE in presence of $[\text{OH}^-]$ ions from the above discussion may be summed up point wise to get the final conclusion as under. The study of substrate concentration and solvent composition shows insignificant increase in rates hence reaction is taken kinetically of first order. Where $[\text{OH}^-]$ ion, attack bimolecularly, forming a transition state hence reaction is considered kinetically bimolecular.
- The neutral species of tri-p-MPPE is the only reactive species at higher pH region (8.0 to 10.0) appears to favor nucleophilic attack by $[\text{OH}^-]$ ion on the phosphorus atom of phosphate group which is present at the micelle surface of CTABr while anionic micelles and nonionic micelles both inhibit the reaction, the neutral ion of ester is deeply buried in the interior of the micelles which hinder the approach of nucleophile, therefore autocatalysis is shown by the micelles of both anionic and nonionic detergents the rate coefficients in CTABr micelles do not increase linearly with the increase of detergent concentration suggesting that the monoanion of phosphate intramolecularly involved in proton transfer to the leaving group in the transition states, forming a

meta-phosphate ion in bimolecular hydrolysis which is supported by high negative value of entropy and energy of activation.

- The comparative values of $K'_m = 11.17 \times 10^{-5} \text{ mol.dm.}^{-3} \text{ s}^{-1}$ at pH -9.0, $K'_w = 5.18 \times 10^{-5} \text{ s}^{-1}$, and $K'_m = 79.8 \times 10^{-5} \text{ s}^{-1}$ along with the value of $\beta = 0.75$ for tri-p-MPPE resembles that of literature value, are exchange application, from which we draw conclusion that the local concentration of $[\text{OH}^-]$ bound to micelle is $3.60 \times 10^{-5} \text{ mol.dm.}^{-3}$ in borate buffer at pH-9.0 and that in water $[\text{OH}^-] = 20.42 \times 10^{-5} \text{ mol.dm.}^{-3}$ shows smaller volume of $[\text{OH}^-]$ ion and neutral ion of tri-p-MPPE is present in aqueous micelle pseudophase. This reasonably accounts for intramolecularly proton transfer by concerted mechanism. The values and ranges of ion exchange parameters show that the nucleophile $[\text{OH}^-]$ anion bind strongly to the micelles in which neutral ion of tri-p-MPPE buried in the interior of the micelles such that the phosphate group of neutral ion is situated at the stern layer of the micelle is suitably exposed to the nucleophilic attack of $[\text{OH}^-]$ ions. The isokinetic data and ranges of Arrhenius parameters i.e. energy of activation and entropy of the reaction support bimolecular nucleophilic attack of $[\text{OH}^-]$ ion on the phosphorus atom of tri-p-MPPE transitory through a transition state involving 'P-O' bond fission. Thus the indispensable hydrolysis of tri-p-MPPE involve attack of hydroxide ion on the phosphorus atom of phosphate group of neutral species forming monoanion of diester by intramolecular proton transfer to the p-methoxy phenoxide ion which then undergoes base catalyzed hydrolysis more slowly by intramolecular proton transfer finally to give phosphate anion. Scheme-3 illustrates the mechanism of the reaction. The mechanism of the reaction may be suggested as shown in Scheme-3.



Scheme 3. Bimolecular nucleophilic substitution of hydroxide ion with 'P-O' bond fission

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