

Kinetic Study of the Micellar Catalysis and Effect upon Dephosphorylation of Diphosphate Ester by Peroxy Anions

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Abstract

The Micellar catalysed reactions between hydroxide or hydroperoxide anions and diphosphate ester of 4-CDMPP has been examined in buffered medium (at pH 8 to 10) with borate ions. First order rate constant (K_{ψ}) for the reaction of OH^- with 4-CDMPP go through maxima with increasing the concentration of cetyltrimethyl ammonium-bromide (CTABr). Micelles of CTABr are very effective catalysts to the reactions of phosphate diester. Rate enhancement depends upon the hydrophobicity of the nucleophile for the reactions of phosphate diester. Rate constants measured with ions are approximately twice and thrice than that of OH^- ions in presence of CTABr. It has been known much early about the importance of organic phosphate esters as phospholipids, complex lipids (i.e. fatty acid esters containing phosphours, nitrogen bases or sugars) which have been ascribed to spherical, helical and folded laminar type micelles.¹² Many phospholipids exist in both α and β forms as well as different stereo chemical configurations which can be isolated in phospholipids¹³, diolipids¹⁴, sphingolipids¹⁵. An extensive amount of research carried out in recent years on chemical model system for specific enzymatic interactions¹⁶, similarities between nonionic micelles and globular proteins¹⁷ render micelles potentially useful as model for investigation of hydrophobic interaction. The micellar catalysis in all biochemical reactions may provide a basic model for interpretation for some aspects of metabolic process undergoing biochemical change in the body pass-through biogenesis of different types of natural surfactants. Since it is the easiest organism to handle in development of DNA to produce new organism in plants and flowers by fusing a particular gene to produce new DNA molecules. The most popular types of paste, cream, shampoo are currently employing sodiumlaurylsulphate as the detergent and sodiumstearate as the opacifying cream foaming agent and the thickening agents. Low molecular weight, cationic agents and detergent of the type have been used. Detergent to be use in tooth past must be specially purified and certified and inherently non-toxic. The cationic surface active agents for such diverse designificating purpose of designification in military and naval establishments, sterilization of instruments and skin surgery etc.

Keywords: Micelles, Miceller Catalyses, 4-CDMPP, CTABr, H_2O_2 , Buffer Solution, Systemic Spectrophotometer, IR-Spectra, NMR

1. Introduction

Orthophosphoric acid being a tribasic acid will form a series of esters with phenols, alcohol, aryl amine and their derivatives. Orthophosphoric acid intracts with 2,4-dichlorophenol to form mono-, di- and tri-esters. Hydrolysis of these esters depends upon the experimental conditions.

Although it has been known a long ago about the importance of organic phosphate esters which play a great role and are essential for biological and physiological activity in living organism but almost negligible kinetic work has been done till 1942. A systematic approach to the kinetic study of esters of orthophosphoric acid was strated by Sir Alexander Todd²² et al. in the university college, London after 1950. Phosphate esters having C-O-P and C-N-P linkage may be reviewed under separate headings.

During recent years a log of work has been performed on the chemical kinetics of (mono-, di- and tri-) substituted esters of orthophosphoric acid. Orthophosphate esters comprised of a group of mono-, di- and tri-esters depending upon the presence of two, one and none hydroxy groups in the phosphate moiety of the ester respectively.

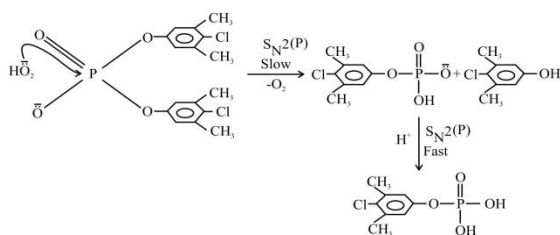
The micellar effect on the hydrolysis of phosphate monoester is also consistant with the results of inhibition studies²³⁻²⁴ (Bunton et al). The CTAB catalysed hydrolysis of dinitrophenylphosphate dianion was found to inhibited by low concentrations of number of salts. Simple electrolytes such as sodiumchloride, sodiumsulphate and sodiumtetraborate had a little effect on the micellar catalysis, however, salts with bulky organic anions such as sodium-p-toluenesulphonate, sodiumaryloxylate etc. dramatically inhibited micellar catalysis. It has been

assumed that inhibition is mainly due to incorporation of an inhibitor to micelle, prevents incorporation of the substrate. The comparison of micellar catalysis by cationic, anionic and nonionic surfactants has shown that inhibition of p-nitrophenylphosphate is smaller than those of 2,4-dinitrophenylphosphate.

These observations, therefore, demonstrate the importance of both electrostatic and hydrophobic interactions as well as the nature of micellar surface in micelle-substrate binding and illustrate the utility of micelles as the model for specific interactions in enzyme-substrate binding.

Micellar catalysis in the hydrolysis of phosphate triesters particularly tri-4-nitrophenylphosphate has been studied extensively in presence or absence of hydroxide, fluoride and organic anions in suitable buffer solution. Micellar catalysis of phosphate diesters has been reported by Bunton et. al., and Bengunov et. al.,¹⁻³, but little attention has been devoted to the micellar catalysis of hydroperoxy anion (HO_2^-) assisted hydrolysis. Bunton and Mhala⁴ recently reported that micelles of CTAB catalyse the reaction of hydrolysis by adding ions which interested us to investigate the micellar catalysed hydrolysis of 4-CDMPP diester with OH^- and HO_2^- ions.

The effect of ionic strength⁵ was studied by carrying out kinetic runs at different ionic strengths. In most of the micellar catalysed reactions, the substrate is incorporated into the micellar pseudophase and is attacked by an external reagent or decomposes spontaneously⁶. On taking into the consideration, the above mentioned observations, following scheme has been suggested for the mechanism of the hydrolysis of 4-CDMPP and OH^- ions.



A closely related use is, for the treatment of fungal infections in dermatology. Carionic surface active agents appear to have same general order of toxicity towards fungi as toward fungi as towards bacteria. The anionic detergents have been found to be effective against gram positive bacteria. Germicidal and fungicidal composition have been prepared by incorporating compounds of mercury, gold, silver or copper into soaps and variety of anionic detergents.

A 2% ointment of sodium lauryl sulphate has been used to promote healing of wounds and underlying tissues following festulas of stomach intestine²¹.

Material and Method

Ammonium-phosphomolybdate $(NH_4)_3PO_4 \cdot 12MoO_3$ with the mixture of ammonium molybdate, and 2,4-

diaminophenolhydrochloride (i.e. amidol, diamol, or nerol) in sodium metabisulphate solution.

1. 8.3% ammoniummolybdate solution.

2. Amidol reagent.

8.3gms of ammoniummolybdate was dissolved in water by shaking to make it up to 100 mL. The reagent used was of analytical B.D.H. grade.

1.4 gms of impure amidol, a brownish black in colour is taken in a conical flask covered with a carbon paper, 2.0 gms of activated charcol and 5.0 mL of distilled water were added into the flask and then it was shaken for 15 minutes and filtered.

Cetyltriamethylammoniumbromide (CTAB) and sodiumlauryl sulphate (SLS) of analytical grade (B.D.H. Ranbaxy) was purified by given methods were washed with anhydrous ether acetone until no amine is detected in the eluant, recrystallised from methanol and then recrystallised at least 4 times from ethanol with the addition of anhydrous ether.

0-26 ml. of H_2O_2 (density-M gm./L and strength-30%) was dissolved in distilled water and make it upto 250-0 mL. The solution used was of analytical grade.

The borate buffer solution and other solution were prepared in double distilled water and boric acid and sodium hydroxide used were of B.D.H. analytical grade.

Diester of 4-Chloro-3, 5-dimethylphenylphosphate (4-CDMPP) is synthesized by the method of Auger and Dupius⁷ and recrystallised by absolute EtOH and was fully characterized by IR spectrum at different strengths of OH^- ions were used to study the rate enhancement at different pH (as for pH 8 - 3.9×10^{-3} mol dm^{-3} , for pH 9 - 20.8×10^{-3} mol dm^{-3} , for pH 10 - 43.8×10^{-3} mole dm^{-3}) with different concentrations of CTABr (Cetyltrimethyl ammonium bromide). The CTABr used was of analytical grade. Other reagents and surfactants used were prepared and purified by standard methods.⁸⁻¹⁰

Reactions were followed by 'sistrionics' spectrophotometer at absorbance 662nm to obtain pseudo first order rate constants. The pH of the reaction mixtures were adjusted to the above given values. All the reactions were carried out at $40 \pm 0.5^\circ C$.

Result and Discussion

Pseudo first order rate constant were determined in the aqueous medium, where a small amount of sodium hydroxide is ionized to give hydroxide ions which gave small values of rate constants without surfactant at different pH, are given in table-1. The reactions of OH^- and HO_2^- ions are very strongly catalysed by cationic micelles of CTABr. The rate constants have been calculated and shown in terms of concentration of CTABr at different pH.

Conclusion

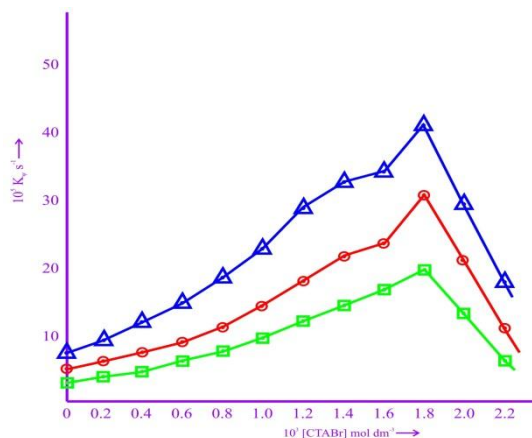
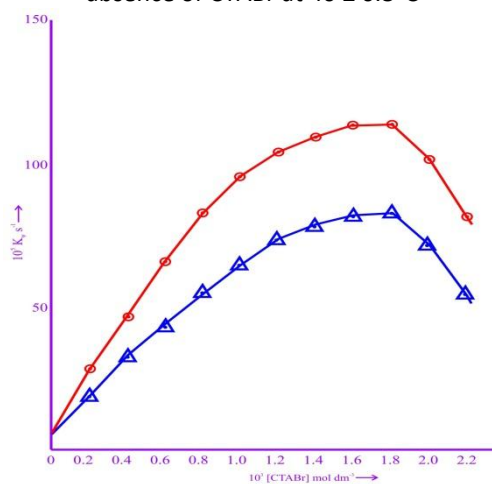
Pseudo first order constants for the hydrolysis of Bis-4-CDMPP (5×10^{-4} moldm⁻³) at pH9 and $40 \pm 0.5^\circ C$. The study

Table-1: Pseudo first order constants for the hydrolysis of bis-4-CDMPP ($5 \times 10^{-4} \text{ mol dm}^{-3}$) at pH 9 and $40 \pm 0.5^\circ\text{C}$

pH	$10^3 [\text{OH}^-] \text{ mol dm}^{-3}$	$10^5 k'_w \text{ s}^{-1}$	$10^5 k_\psi \text{ s}^{-1} \text{ in } 10^3 [\text{CTABr}] \text{ mol dm}^{-3}$										
			0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2
8	3.9	3.42	3.75	4.23	6.08	7.16	9.41	12.11	13.62	16.65	19.17	11.87	5.36
9	20.8	5.23	6.15	7.13	8.76	11.15	14.31	17.83	21.36	22.77	29.86	20.14	9.42
10	43.8	7.25	8.92	11.31	14.19	18.32	22.75	28.52	31.64	33.57	40.74	29.11	17.26

Table 2: Rate constants for reaction with H_2O_2 in presence of CTABr at pH 9 and $40 \pm 0.5^\circ\text{C}$

S.No.	$10^3 [\text{CTABr}] \text{ mol dm}^{-3}$	$10^5 k_\psi \text{ s}^{-1} \text{ in presence of } [\text{CTABr}]$	
		$\text{H}_2\text{O}_2 0.8 \times 10^{-3} \text{ mol dm}^{-3}$	$\text{H}_2\text{O}_2 1.2 \times 10^{-3} \text{ mol dm}^{-3}$
1.	0.2	19.24	29.11
2.	0.4	32.83	47.25
3.	0.6	43.16	66.85
4.	0.8	55.12	82.73
5.	1.0	64.79	96.15
6.	1.2	73.68	104.21
7.	1.4	78.17	108.77
8.	1.6	81.84	113.76
9.	1.8	83.37	114.26
10.	2.0	72.31	101.81
11.	2.2	55.42	82.27

**Fig. 1** Reaction of 4-CDMPP with OH^- ions in presence and absence of CTABr at $40 \pm 0.5^\circ\text{C}$ **Fig. 2** Reaction of bis-4-CDMPP with H_2O_2 in presence of CTABr

structure was determined by systronics spectrophotometer, IR-Spectra NMR techniques. rate constant, for reaction with H_2O_2 in presence of CTAB at PH 9 rate constant have been calculated and shown in terms of concentration of CTAB at different PH.

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