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Miceller catatysis and its effect upon dephosphorylation of 2-Methoxy phenyl phosphoramides by peroxy anions in buffer medium

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Abstract

Micellar catalysed reactions between hydroxide or hydroperoxide anions and diphosphate ester of 2-MPPA has been examined in buffered medium at pH 8 to 10 with borate ions. First order rate constant (K) for the reaction of OH- ion with 2-MPPA go through maxima with increasing the concentration of cetyltrimethyl ammonium-bromide (CTABr). Micelles of CTABr are very effective catalysts to the reactions of 2- methoxy phenyl phosphoramide. Rate enhancement depends upon the hydrophobicity of the nucleophile for the reactions of 2- methoxy phenyl phosphoramide. 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 as fatty acid esters containing phosphorus, nitrogen bases or sugars which have been described to spherical, helical and folded laminar type micelles. Many phospholipids exist in both α and β forms as well as different stereo chemical configurations which can be isolated in phospholipids, diollipids and sphingolipids. An extensive amount of research carried out in recent years on chemical model system for specific enzymatic interactions, similarities between nonionic micelles and globular proteins 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 sodiumstreate 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.

Keywords: micelles, miceller catalyses, 2-MPPA, CTABR, H_2o_2, buffer solution, systronics spectrophotometer, Ir- spectra, NMR)

Introduction

Orthophosporic acid being a tribasic acid will form a series of esters with phenols, alcohol, aryl amine and their derivatives. Orthophosphoric acid in tracts 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. A systematic approach to the kinetic study of esters of orthophosphoric acid was strated by Sir Alexander tood [1] 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 moity of the ester respectively.

The micellar effect on the hydrolysis of phosphate monoester is also consistant with the results of inhibition studies [2, 3]. The CTAB^r catalysed hydrolysis of dinitrophenyl phosphate dianion was found to in hibited by low concentrations of number of salts. Simple electrolytes such as sodium chloride, sodium sulphate and sodium tetraborate had a little effect on the micellar catalysis, However, salts with bulky organic anions such as sodium-p-toluenesulphonate, sodium aryloxylate etc. dramatically in hibited micellar catalysis. It has been assumed that inhibition is mainly due to incorporation of an inhibitor to micelle, prevents in corporation of the substrate. The comparision of micellar catalysis by cationic, anionic and nonionic surfactants has shown that inhibition of p-nitrophenylphosphate is smallar than those of 2, 4-dinitrophenyl phosphate. 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 abssence of hydroxide, fluoride and organic anions in suitable buffer solution. Micellar catalysis of phosphate diesters has been reported [4-6], but little attention has been devoted to the micellar catalysis of hydroperoxy anion (OH_2^-) assisted hydrolysis. Bunton and Mhala [7] recently reported that micelles of CTABr catalyse the reaction of hydrolysis by adding ions which interested us to investigate the micellar catalysed hydrolysis of 2-MPAA with OH^- ions. The effect of ionic strength [8] 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 spontaneously [9]. On taking into the consideration, the above mentioned observations, following scheme has been suggested for the mechanism of the hydrolysis of 2-MPPA and OH^- ions. A closely related use is for the treatment of fungal infections in dermatology. Cationic 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. Ointment of sodium lauryl sulphate (2%) has been used to promote healing of wounds and underlying tissues following festulas of stomach intestine.

Materials and Methods

Ammonium-phosphomolybdate $(NH_4)_3$ PO_4. $12MoO_3$ with the mixture of ammonium molybdate, and 2, 4-diaminophenolhydrochloride (i.e. amidol, diamol, or nerol) in sodium metabisulphate solution.

1. 8.3% ammonium molybdate solution.
2. Amidol reagent.

Ammonium molybdae (8.3gms) 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. Cetyltrimethylammonium bromide (CTABr) and sodiumlauryl sulphate (SLS) of analytical grade (B.D.H.) was purified by given methods were washed with anhydrous ether acetone untill no amine is detected in the eluant, recrystallised from methanol and then addition of anhydrous etherof H_2O_2 (0.26 ml, density-M gm./L and strength-30%) was dissolved in distilled water and make it upto 250-0 mL. 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 2-methoxy phenyl phosphoramide (2-MPPA) is synthesized and recrystalysed by absolute ethyl alcohal 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 [10, 11, 12].

Reactions were followed by 'Sistronics' 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 ± 0.5^{0}C. The many phospholipide exist both in $\alpha -$and $\beta - type\ and$ linkages at different stress chemical configuration were isolated in Phospholipide[13]. diolipids[14] and sphingolipids[15]

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- 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 and result are shown in Table-2. Pseudo first order constants for the hydrolysis of bis- 2 -MPAA (5×10^{-4} mol dm^{-3}) at pH 9 and 40 ± 0.5^{0}C.

Table 1: Pseudo first order rate constants for the hydrolysis of bis-2-MPPA (5×10-4 mol dm-3) at pH 9 and 40 ± 0.50^0 C

pH	**10^3 [OH^-] mol dm-3**	**10^5K'w s-1**	**10^5 K s^{-1} in 10^3 [CTABr] mol $dm^{-3}\psi$**										
			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	3.44	3.75	4.26	6.08	7.16	9.41	12.12	13.62	16.65	19.17	11.88	5.38
9	20.8	5.22	6.15	7.13	8.78	11.15	14.36	17.83	21.36	22.77	29.86	20.16	9.44
10	43.8	7.26	8.92	11.31	14.19	18.34	22.75	28.54	31.64	33.57	40.74	29.12	17.26

Table 2: Rate constants for reaction with H_2 O_2 in presence of CTABr at pH 9 and 40 ± 0.50^0 C

S. no.	**10^3 [CTABr]mol dm^{-3}**	**10^5 K s^{-1} in presence of [CTABr] ψ**	
		H_2O_2 0.8×10^{-3} mol dm^{-3}	**H_2O_2 1.2×10^{-3} mol dm^{-3}**
1.	0.2	19.26	29.12
2.	0.4	32.84	47.26
3.	0.6	43.18	66.85
4.	0.8	55.14	82.74
5.	1.0	64.79	96.15
6.	1.2	73.68	104.24
7.	1.4	78.17	108.77
8.	1.6	81.84	113.78
9.	1.8	83.38	114.26
10.	2.0	72.32	101.81
11.	2.2	55.44	82.28

The study structure was determined by systronics spectrophotometer, IR-Spectra NMR techniques. The rate constant, for reaction with H_2O_2 in presence of CTABr at pH 9. The reaction of phosphate di ester were strongly catalyzes of different concentration of (CTABr) at which the Pseudo first order rate constants were obtained. The investigation of micellar catalysed hydrolysis of bis-2-MPPA with hydroxide ion have been carried out at 40 ± 0.5^0C. In presence of detergent at pH 9 using borate buffers. Effect of cationic CTABr detergent on rate of hydrolysis of 2-MPPA in presence of hydroxide ion has been measured by speetrophtometrically by the ratio of appearance of inorganic phosphate and rate of increases sharply at CTABr concentration. The investigation of the relation between observe pseudo first order rate constant K^{ψ} and the surfactant concentration for a spontaneous depnospnodylation [16, 17, 18] at 2-MPPA (2-methoxy phenyl phoshporamide).

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