

Effect of Cationic Micelles and Reaction Rates of Bis-2, 4-Dichlorophenyl Phosphate with Hydroxide Ions

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Abstract: The reaction of hydroxide ion with bis-2, 4-dichlorophenylphosphate in presence of micelles of cationic, (cetyltrimethyl ammoniumbromide). Since, the concentration of reactants at micellar surface is a major source of enhancement of rates of bimolecular reactions involving counterions. Therefore effect of added peroxyanions on the above reaction which is strongly catalysed by the micelles of cationic detergent has been extensively studied. For the convenience the micellar rate effects and added peroxyanions have been described under varied experimental conditions of cationic. Kinetic study of micellar catalysed hydrolysis of bis-2, 4-DCPP with different concentrations of $[OH^-]$ ion has been carried out at $40 \pm 0.5^\circ C$ in aqueous-dioxan mixture (20 : 8 v/v) in presence and absence of $\{[CTAB] [SLS] \text{ and } [POEDE]\} \times 10^{-3} \text{ mol dm}^{-3}$ in solutions of borate buffer pH 8.0, 9.0 and 10.0. It has been known much early about the importance of organic phosphate esters as phospholipids, complex lipids (i.e. fatty acid esters containing phosphorus, nitrogen bases or sugars) which have been ascribed to spherical, helical and folded laminar type micelles.¹ The most popular types of paste, cream, shampoo are currently employing sodiumlaurylsulphate as the detergent and sodiumstearate as the opacifying cream foaming agent⁴ and the thickening agents. Low molecular weight, cationic agents and detergent of the type have been used. 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 towards bacteria. The anionic detergents have been found to be effective against gram positive bacteria. A 2% ointment of sodium lauryl sulphate has been used to promote healing of wounds and underlying tissues following fistulas of stomach intestine⁵ etc. The surface active agents are used in agriculture for two major purpose, the more important of the use in as an ingredient in wide variety of spraying compositions for combating insects fungi and other enemies of plant life. The second use is in washing fruits and vegetables before marketing in order to remove hazardous spray residues. The residue left after removing mono-2,4-dichlorophenylphosphate at $60-120-140^\circ C$ was washed several times with boiling distilled water and 0.2N NaOH solution to remove 2,4-dichlorophenylphosphate monoester, unreacted phosphorousoxy-trichloride and the phenol are 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 recrystallised with absolute ethyl alcohol to give a white crystalline solid which was identified to be bis-2,4-chlorophenylphosphate by the following physical characteristics.

(i) Melting Point (Observed)	=	148
(ii) Theoretical percentage of 'P'	=	8.17
(iii) Observed percentage of 'P'	=	8.23
(iv) Aromatic ring	=	3060 cm^{-1}

Keywords: Micellar Catalyses, 4-CDMPP, CTABr, H_2O_2 , Buffer Solution, Systronics Spectrophotometer, IR-Spectra, NMR

1. Introduction

Micellar catalysis is currently a rapidly expanding area of research. Systematic and careful collection of data is necessary in the effects of micelles on organic reaction. In quantitative investigations of micellar catalysis and interactions, it is desirable to determine the binding and association constant for the formation of the substrate micelle complex and it feasible to elucidate the nature of environment of the substrate in the molecular aggregate.

Orthophosphoric acid being a tribasic acid will form a series of esters with phenols, alcohol, aryl amine and their derivatives. Orthophosphoric acid in reacts 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 started by Sir Alexander Todd⁷ et al. in the university college, London after 1950.

During recent years a lot of work has been performed on the chemical kinetics of (mono-, di-and tri-) substituted and unsubstituted esters of orthophosphoric acid. In general cases, the rate constant of organic phosphate ester was not possible to determine but only percentage of reaction products in fixed time was determined. According to the data in Ingold's⁸ book about studies on the influence of the pH of the medium on the rate of hydrolysis of monoalkyl phosphate is described by the experimental data which shown that the rate of reaction depends only on the concentration of monoanions over a wide range of pH.

The literature does not provide much information regarding hydrolysis of phosphate triesters as the triesters of phosphoric acid been studied negligibly.

The hydrolysis of tri-methylphosphate, tri-phenylphosphate have been studied in detail by Vernon, Buton⁹ et al. and found that the later is much faster than that of the former in

75% dioxan and attributed the bimolecular nucleophilic attack of hydroxide anion on phosphorous atom of the tri-esters with 'P-O' bond fission.

D.F. Health and P. Kaspari¹⁰ (1950) investigated the hydrolysis of mono-, di- and tri-esters of dimethylaminephosphate at 25°C, 40°C & 76°C in acid, alkaline, neutral solution and observed 'P - N' bond fission. The hydrolysis of phosphate esters having C-N-P linkage have been studied recently under the name of phosphoramides, phosphoramidates or aminophosphates and phosphoramidic acid. In (1956) Tara and Thomas Rosenberg¹¹ have studied the hydrolysis of phosphoramidate derivatives in water and heterocyclic base containing pyridine or imidazole ring.

Halman and Lapidote¹² studied mono-benzylaminephosphate in the region pH 1.0 to 8.0 and observed rate maxima at pH 4.0 at which slowly mono-negative species govern rate of hydrolysis. The increase in rates in D₂O has been attributed to the formation of more reactive cyclic intermediate with water similar to alkyl phosphates. It is clear from the above survey that very limited kinetic study of the hydrolysis of the phosphate esters having C-N-P linkage has been performed and there is much scope for systematic study in this field.

Bunton et al.¹³⁻¹⁴ have been reported systematically kinetic and thermodynamic data of cationic, anionic, zwitterionic and nonionic surfactants on the hydrolysis of mono aryl phosphates. The use of 2,4- and 2,6-dinitrophenyl phosphate, glucose-6-phosphate and p-nitrophenylphosphate as the substrate permitted the examination and comparison of the effects of micellar systems on the several types of phosphate esters hydrolysis such as monoanion and dianion hydrolysis in presence and absence of hydroxide ions or pyridine catalysed hydrolysis of dianion have been studied extensively in all four types of detergents.

The micellar effect on the hydrolysis of phosphate monoester is also consistent with the results of inhibition studies¹³⁻¹⁴ (Bunton et al.). The CTAB catalysed hydrolysis of dinitrophenylphosphate dianion was found to be inhibited 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 xyloxyolate etc. Kinetic study of micellar catalysis of bis-p-nitrophenyl and bis-2, 4-dinitrophenylphosphate have been studied in detail. Since the hydrolysis of 2,4-dinitrophenylphosphate occurs in two steps, selection of suitable condition allowed the investigation of the effect of micelles on both K_1 & K_2 ¹³ (Bunton et al. 1970) at pH < 10, $K_2 > K_1$.

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 solutions. Thus shielding the phosphoryl group from nucleophilic attack in addition the inhibition of micelle catalysed reactions by added electrolyte have been observed (Bunton & Robinson 1969a, 1970a).

The influence of the potentially nucleophilic surfactant and their intramolecular participation by micelles on the rates of reaction of hydroxide and fluoride ions with tri-4-nitrophenyldiphenylphosphate has been investigated¹⁵ (H. Morawetz-1970). The stereospecificity of these optically active surfactants due to the presence of hydroxyl group than that of CTAB or its methoxy analogue, the reaction mechanism therefore involves intramolecular attack of the ionized hydroxyl group of the stereospecific surfactant on phosphoryl phosphorus. Similarly phosphate esters with long chain alkyl substituent's form micelles at the concentration above their cmc which provide a simplified system in which micelle formation and structure are not affected by " β " the presence of foreign solubilizer in the micellar catalysed reaction of these esters.

The phosphate esters (mono-, di- and tri) formed by the reaction of orthophosphoric acid with primary and secondary amines which contains C-N-P linkage present in complex bio-organic molecules such as enzymes, lipids and proteins. An extensive research study needed as a chemical model system for specific enzymatic interactions. The kinetics of micellar catalysis resembles, in many respect that of enzyme catalysis is of deliberate necessity to study catalytic activity of micelles, denaturing process by added salt, their magnitude of binding capability and to understand their specific nature towards pH of the medium, concentration and temperature.

An extensive amount of research carried out in recent years on chemical model system for specific enzymatic interactions², similarities between nonionic micelles and globular proteins³ render micelles potentially useful as model for investigation of hydrophobic interactions.

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. The unparalleled biological diversity of this country is goldmine for the development of bacterial technology theme of 21st century. The richest microbial flora is available in humid tropics of Kerala containing thousands of bacteria for which no inventory exist while the west have only three bacteria, started revolution in bacterial technology. 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.

These technologies of bio-organic molecules are entirely dependent on the study of micellar catalysis. Therefore, in recent years investigation of micellar catalysis has provided great interest in the mechanism of micellar catalysis of phosphate esters due to presence of phosphate residue in bio-organic molecules. The phosphate esters (mono-, di- and tri-) are formed by reaction of orthophosphoric acid, a tribasic acid with alcohols, phenols, amines and thioalcohols.

2. Result and Discussion

Micellar Catalysed Hydrolysis of Bis-2, 4-Dichloro-Phenyl Phosphate:

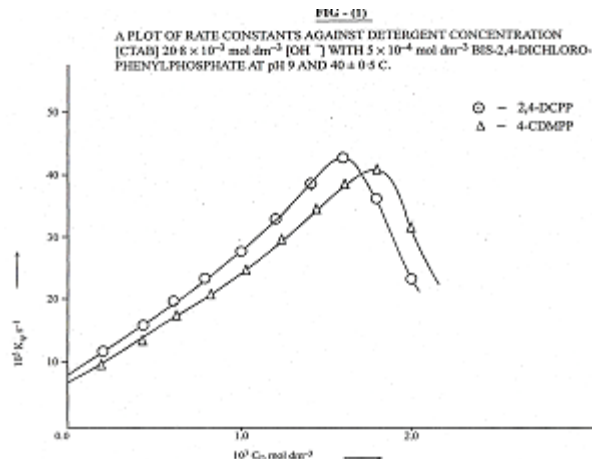
Kinetic study of micellar catalysis of the reaction of bis-2,4-dichloro-phenylphosphate (bis-2,4-DCPP) with hydroxide ion (OH^-) has been carried out at $40 \pm 0.5^\circ\text{C}$ using aqueous dioxan (v/v 20 : 80) mixture in presence or absence of cationic, anionic and nonionic detergents at pH 8.0, 9.0 and 10.0 using borate buffer. The compositions of buffers used have been described in experimental section. Effect of cationic cetyltrimethylammoniumbromide (CTAB) and anionic detergent sodiumlaurylsulphate (SLS) and nonionic polyoxyethylenedodecylether on the rate of hydrolysis of bis-2,4-DCPP in presence of hydroxide ion has been studied spectrophotometrically. Rates of hydrolysis have been measured by rate of appearance of inorganic phosphate during hydrolysis using systronics spectrophotometer. Concentration of bis-2,4-DCPP in all kinetic runs was kept $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ (unless otherwise specified), pseudo first order rate coefficients have been determined at different pH zones of reaction medium. pH was measured directly in solutions and maintained constant throughout the investigation. Effect of the factors which influence the rate of reaction such as hydroxyl ion concentration, pH of the reaction medium, substrate concentration, solvent composition, buffer effect, effect of (HO_2^-) anions, presence of organic and inorganic salts have been studied in detail. Arrhenious parameters have been determined by carrying out kinetic runs at different temperatures using Arrhenious equation.

Pseudo first order rate constants in water have been compared with first order rate constants for the reaction of hydroxyl ion (OH^-) with bis-4-CDMPP in micelles of cationic (CTAB), anionic (SLS) and nonionic (POEDE) detergents.

To examine the validity of pseudophase ion exchange model, the consistent values of ion exchange parameters such as K_{Br}^{OH} , the ion exchange constant m_{Oh}^S the second order rate constant and β , the ratio of counterions to the ionic head groups in the micelles, should be applicable to the reactions of structurally similar substrates in both micellar and aqueous pseudophases.

Effect of cationic micelles of ctab on the reaction of bis-2,4-dichlorophenylphosphate with hydroxide ions:

The reaction of hydroxide (OH^-) ion with bis-2,4-DCPP has been investigated in presence and absence of detergent 10^3 [CTAB] mol dm^{-3} in aqueous dioxan mixture (v/v 20 : 80) at $40 \pm 0.5^\circ\text{C}$. Pseudo first order rate constants have been determined at different concentrations of CTAB, which strongly catalyse the reaction. TABLE-(I) summarises the effect of micellar catalysis of cationic micelles on the rate of hydrolysis at constant hydroxide ion concentration with bis-2,4-DCPP.



Reaction Rates of Bis-2, 4-Chlorophenylphosphate with $20.8 \times 10^{-3} \text{ mol dm}^{-3}$ (OH^-) In Presence of Different 10^3 [CTAB] at pH 9.0 and $40 \pm 0.5^\circ\text{C}$

S.No.	10^3 [CTAB] mol dm^{-3}	Rate constants $10^5 K_w \text{ s}^{-1}$	
		2, 4-DCPP	4-CDMPP
1	0.2	8.79	6.03
2	0.4	11.91	7.51
3	0.6	14.87	9.12
4	0.8	19.03	10.98
5	1.0	23.09	14.45
6	1.2	30.21	18.10
7	1.4	33.62	22.06
8	1.6	45.92	29.53
9	1.8	34.31	20.07
10	2.0	22.29	12.09

K_w (2,4-DCPP) = $6.95 \times 10^{-5} \text{ s}^{-1}$; K_w (4-CDMPP) = $4.54 \times 10^{-5} \text{ s}^{-1}$

3. Conclusion

Bis-2, 4- dichlorophenyl phosphate was prepared and their structure was determined by systronics spectrophotometer. IR spectra and NMR techniques. Effects of cationic micelles and reaction rate of Bis-2, 4-dichlorophenyl-phosphate with $20.8 \times 10^{-3} \text{ mol dm}^{-3}$ hydroxide ion was found approximately equal to theoretical value. As the concentration increases the rate constant also increases at the maximum point the effect of micellar catalysis of cationic micelles on the rate of hydrolysis at constant hydroxide ion concentration with bis-2, 4-DCPP.

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