



MICELLAR EFFECT UPON DEPHOSPHORYLATION OF MONO PHOSPHATE ESTER BY PEROXY ANIONS

A. P. SINGH^{*}, R. C. VERMA, S. RAGHAV^a and RAVI PRAKASH^b

Department of Chemistry, Janta College, Bakewar, ETAWAH (U.P.) INDIA

^aDepartment of Chemistry, K. K. D. C. ETAWAH (U.P.) INDIA

^bDepartment of Chemistry, B. S. A. College, MATHURA (U.P.) INDIA

ABSTRACT

The micellar catalysed reactions between hydroxide or hydroperoxide anion and mono phosphate ester of 4-CMPP has been examined in buffered medium (at pH 8.0-10.0) with borate ions. First order rate constant (K_p) for the reaction of OH^- with 4-CMPP go through maxima increasing with the concentration of cetyl trimethyl ammonium bromide (CTABr). The micelles of CTABr are very effective catalysts to the reactions of phosphate mono ester. Rate enhancement depends upon the hydrophobicity of the nucleophile for the reactions of mono phosphate ester. Rate constants measured with HO_2^- ions are approximate.

Key words: Micelles, Micellar catalysis, 4-CMPP, CTABr.

INTRODUCTION

Micellar catalysis on the hydrolysis of phosphate esters has been reported in literature¹ but little attention has been devoted to the micellar catalysis of hydroperoxy anion assisted hydrolysis of phosphate esters. Recently, Bunton et al.² reported that micelles of [CTABr] catalysis of the hydrolysis of p-nitrophenyl phosphate with [OH] ion accelerate the rate of hydrolysis by added hydrogen peroxy anions, which has interested us to investigate the micellar catalysed hydrolysis of mono 4-CMPP with [OH] ions and peroxy anions.

The interfacial region at a micellar surface can act as a reaction medium, which can be regarded as a pseudophase³⁻⁵ distinct from bulk solvent e.g. water⁶⁻⁹. Quantitative analysis of bimolecular reactions in terms in pseudophase model require estimation of local concentration of both reactants in the micellar and aqueous pseudophases and second order rate constants in each region¹⁰⁻¹⁵. Micellar effects on many biomolecular rate constants have been treated by the quantitatively in terms in this model, which shows that micellar

* Author for correspondence; E-mail: pal_abendra@rediffmail.com

accelerations of counting ionic reactions are, largely due to concentration of reactants in the small volume of the interfacial region. Cationic micelles effectively promote bimolecular attack by anion or nonionic bases or nucleophiles in water, and these reactions have been studied widely.¹⁶⁻²⁰ The charge of ionic micelles is partially neutralized by counter ions that are attracted to the surface and the fractional micellar charge, α , which decreases from approximately 0.4 for small high charge density ions to 0.2 for low charge density ions e.g., Br^- .²¹⁻²⁵ Although CTABr micelles carry no net charge, they attract anions because positive charge density is higher than the anionic charge density and there are specific interactions between the ammonium ion centres and polarizable, low charge density anion e.g., Br^- and ClO_4^- .

An interest rests in the use of cationic agents in hair dyeing and has recently described. The cationic detergent is applied to the hair, which is subsequently treated with an acid dye. The dye stuff form and adhere insoluble lake with the absorbed detergent and thus, fix to hair. The cationic surface active sites are general order of toxicity towards fungi as bacteria.

EXPERIMENTAL

Material and methods

Mono ester of 4-chloro-3-methyl phenol has been prepared by treating excess of phosphorylating agent (phosphorus oxy trichloride POCl_3) with 4-chloro-3-methyl phenol in dry benzene. Pure 4-chloro-3-methyl phenol (14.25 g) was dissolved in dry benzene (100 mL) in a round bottom flask. Phosphorus oxy trichloride (9.03 mL) was added drop by drop with constant stirring to the ice cooled phenol in about half an hour with the help of a separating funnel. After addition of POCl_3 , mixture was refluxed for about 18 hours on the Soxhlet heater at constant temperature 65°C in order to ensure complete reaction and then distilled at reduced pressure. The first reaction of benzene and unreacted POCl_3 , was removed by distillation at b.p. 120°C . The second reaction of a pungent smelling liquid, which was supposed to be 4-chloro-3-methyl phenyl phosphate dichloride and it was distilled at b.p. $120-140^\circ\text{C}$. It was dissolved in ice cooled water (100 mL) and kept at low temperature over night. The 4-chloro-3-methyl phenyl phosphate dichloridate was converted to 4-chloro-3-methyl phenyl phosphate dihydrogen, which was extracted with solvent ether. After removing the solvent ether, a light brown coloured crystalline solid was obtained, which, on recrystallisation with absolute ethyl alcohol gave a white crystalline solid and it was identified to be as mono 4-chloro-3-methyl phenyl phosphate.

Cetyltrimethyl ammonium bromide was purified by the given method. 4-Chloro-3-methyl phenyl phosphate was washed with anhydrous ether-acetone until no amine is

detected in the eluent recrystallised from methanol and then at least 4 times from methanol with addition of anhydrous ether. Amidol (1.4 g) in conical flask covered with carbon paper, activated charcoal (2 g) and water (10 mL) was added into the conical flask and then it was shaken thoroughly for 15-20 min. The colourless, amidol solution so obtained was filtered into a solution containing 100 mL solution of sodium metabisulphate (20%). The reagent obtained was kept in dark at low temperature (0°C). This solution gradually decomposed and turned yellow after 6-8 days. Then it was of no use and hence, discarded each time. Amidol was purified before use.

Substrate in solution has the specific property of absorbing light of wave length characteristic of that particular substance. The basic principle of absorption is utilized in the measurement of various concentrations. The spectrophotometer instrument utilizes a source of radiant energy, a means to isolate a band of radiant energy, which is focused to on the solution and then measured with a detector. Kinetic study for the hydrolysis of all the mono-, di-, and tri ester was followed spectrophotometrically. This method involved the quantitative estimation of inorganic phosphates formed from the hydrolysis of phosphate esters. The inorganic phosphate reacts with the ammonium molybdate and forms a phosphate molybdate complex $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$, which is reduced to molybdenum blue, a soluble complex by addition of mixture of 2,4-diaminophenyl hydrochloride (amidol, diamol or nerol). Phosphate mono esters were prepared by standard methods purified by recrystallisation from absolute ethyl alcohol and examined by IR, CTABr used was of analytical grade. Various strengths of borate buffer were prepared and purified by standard methods.

RESULTS AND DISCUSSION

Micellar effect of [CTABr] on phosphorylation of mono-4-CMPP by the anions of hydrogen peroxide is markedly speeded up in presence of the hydroxide ion of $(20.8 \times 10^{-3} \text{ mol dm}^{-3})$ at higher pH (9.0-10) in borate buffer and at temperature $40 \pm 0.5^\circ\text{C}$. First order rate constant k_p passes through maxima with increasing [CTABr]. With added hydrogen peroxide $1.6 \times 10^{-3} \text{ mol dm}^{-3}$ and [CTABr] $1.2 \times 10^{-3} \text{ mol dm}^{-3}$, the rate increases more than three times than that of with [CTABr] only. This indicates that H_2O_2 , is slightly a better nucleophile than OH^- hydroxyl ion. But α effect is not well marked in $[\text{H}_2\text{O}_2]$ assisted hydrolysis of phosphoric acid ester. Hydrogen peroxide anion $[\text{HO}_2^-]$ complete with hydroxyl ion $[\text{OH}^-]$ pseudo first order rate of both hydroxyl ion assisted hydrolysis in presence of CTABr were estimated and the result have been summarized in Table 1. The rate maxima in presence of [CTABr] and $[\text{H}_2\text{O}_2]$ as in typical micelle catalysed bimolecular reactions, increase in hydrogen peroxide ion concentration. Acceleration of the catalysis takes place over that of at lower detergent concentration otherwise turbidity is formed at

higher concentration, so micellar catalysed reaction with $[H_2O_2]$ could not be studied at higher detergent concentrations. However, the trend of the curve is shown in Fig. 1.

Table 1: Pseudo first order rate constants for reaction of (20.8×10^{-3}) mol dm^{-3} in borate buffer with (5×10^{-4}) mol dm^{-3} . Mono-4-chloro-3-methylphenyl phosphate in presence of [CTABr] and $[H_2O_2]$ at pH-9.0 and $40 \pm 0.5^\circ C$

S. No.	10^3 [CTABr] mol. dm^{-3}	10^3 K_{ψ} s^{-1} In presence of CTABr		
		Without H_2O mol. dm^{-3}	$[H_2O_2]$ 0.8×10^{-3} mol. dm^{-3}	$[H_2O_2]$ 1.2×10^{-3} mol. dm^{-3}
1	0.2	6.54	25.67	40.97
2	0.4	7.60	49.20	72.11
3	0.6	9.35	69.85	101.02
4	0.8	11.45	87.05	120.95
5	1.0	15.12	101.32	136.01
6	1.2	20.59	110.15	147.95
7	1.4	23.95	114.85	153.15
8	1.6	33.45	117.15	156.03
9	1.8	29.75	101.75	142.02
10	2.0	25.55	82.85	116.92

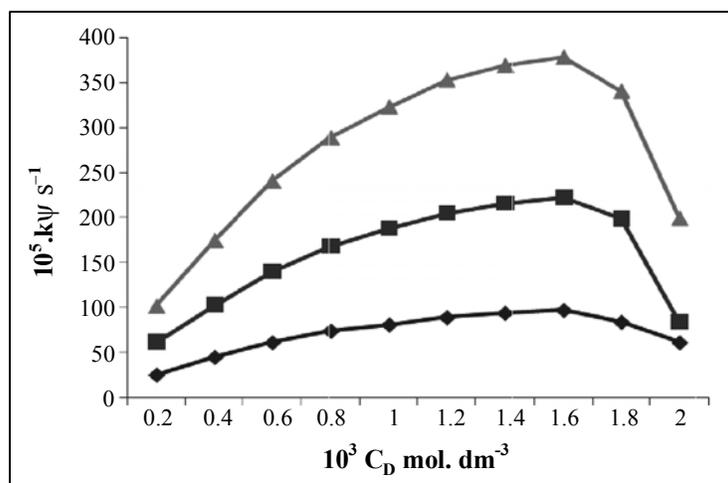


Fig. 1: Effect of H_2O_2 upon reaction rate of mono-4-CMPP of 10^3 [CTABr] at pH-9.0 and temperature $40 \pm 0.5^\circ C$

The effect of pH on the reaction of mono-4-CMPP with $[\text{OH}^-]$ indicates that increasing the pH of the reaction medium from 8.0-10.0 increases the rate constants to the maximum at pH 9.0. Rates increase in [CTABr] detergent with $[\text{H}_2\text{O}_2]$ but further increase in pH of solution shows insignificantly change in the rate constants (Table 2). Effects on rate constants by the medium of detergent [CTABr] with $[\text{H}_2\text{O}_2]$ with inhibition of the reaction rate of mono-4-CMPP in Fig. 2 shows that the relation of dependence of rate constant on the pH of the solution.

Table 2: Effect of pH upon reaction rates of mono 4-CMPP in [CTABr] and in presence of $1.2 \times 10^{-3} \text{ mol dm}^{-3} [\text{H}_2\text{O}_2]$ at $40 \pm 0.5^\circ\text{C}$

pH	$10^5 k'$ w S^{-1}	$10^3 \text{H}_2\text{O}_2$ mol.dm^{-3}	$10^5 k\psi \text{s}^{-1}$ in presence of CTABr									
			0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
8.0	4.17	12	25.13	44.88	61.25	74.06	81.09	89.20	94.11	97.26	84.01	61.21
9.0	5.67	12	36.21	58.02	78.75	94.11	107.05	115.87	122.05	125.12	114.75	22.52
9.0	5.67	-	6.54	7.61	9.38	11.45	15.12	20.59	23.95	33.95	29.75	25.52
10	8.14	12	40.97	72.13	101.03	129.87	135.03	147.98	153.12	156.03	142.02	115.91

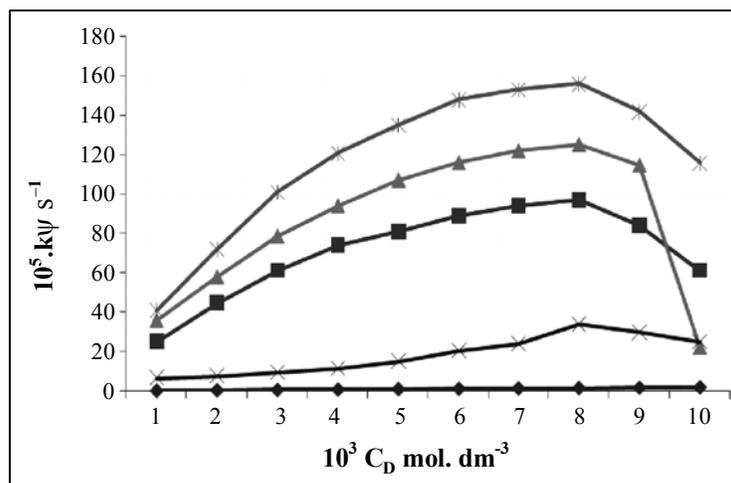


Fig. 2: Effect of pH upon reaction rates of mono-4-CMPP in presence of [CTABr] at pH-9.0 and temp. $40 \pm 0.5^\circ\text{C}$

Effect of buffer on the micelles of [CTABr] was observed on the above reactions

out the reaction of mono-4-CMPP at constant $[\text{H}_2\text{O}_2]$ anions by varying concentration of $[\text{OH}^-]$ anion in presence of micellised $[\text{CTABr}]$ using borate buffer. Rate constants of varying concentration of $[\text{OH}^-]$ anions and $[\text{CTABr}]$ at $1.2 \times 10^{-3} \text{ mol dm}^{-3} [\text{H}_2\text{O}_2]$ have been summarized in Table 3. Fig. 3 indicates the maximum in rate enhancement. Since there is competition between (HO_2^-) and $[\text{OH}^-]$ anions towards biomolecular nucleophilic substitution reactions, analogues mechanism (HO_2^-) ion may be formulated shown in Scheme 1.

Table 3: Effect of borate buffer upon reaction rates of $(5 \times 10^{-4}) \text{ mol.dm}^{-3}$ mono-4-CMPP in 10^3 , $[\text{CTABr}]$ and in presence of $1.2 \times 10^{-4} \text{ mol.dm}^{-3} [\text{H}_2\text{O}_2]$ at $40 \pm 0.5^\circ\text{C}$

pH	$10^5 k'$ w S^{-1}	$10^3 \text{H}_2\text{O}_2$ mol.dm^{-3}	$10^5 k\psi \text{s}^{-1}$ in presence of CTABr									
			0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
8.0	4.17	12	25.13	44.88	61.25	74.06	81.09	89.20	94.11	97.26	84.01	61.21
9.0	5.67	12	36.21	58.02	78.75	94.11	107.05	115.87	122.05	125.12	114.75	22.52
10	8.14	12	40.97	72.13	101.03	129.87	135.03	147.98	153.12	156.03	142.02	115.91

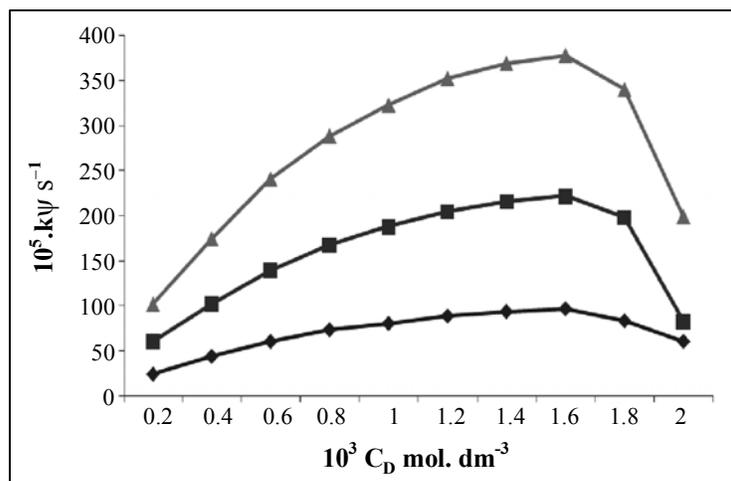
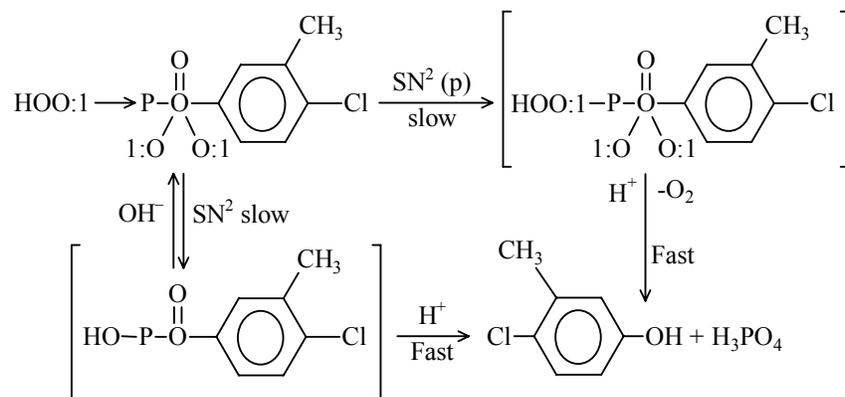


Fig. 3: Effect of borate buffer upon reaction rates of mono-4-CMPP in presence of $[\text{CTABr}]$ and $1.2 \times 10^3 \text{ mol dm}^{-3} [\text{H}_2\text{O}_2]$ at different pH and temp. $40 \pm 0.5^\circ\text{C}$

Mechanism of micellar catalysed hydrolysis of mono-4-chloro-3-methyl phosphate in presence of hydroperoxy anion is –



Scheme 1

The mechanism of micellar catalyzed hydrolysis of 4-chloro-3-methyl phenyl phosphate in presence of hydroperoxy anion on the basis of above kinetic results may be formulated as under:-

- (i) Hydrolysis of 4-chloro-3-methyl phenyl phosphate at pH 8.0-10.0 occurs in two steps. Selection of suitable condition, allowed the investigation of the micelles on k_1 and k_2 Where $k_2 > k_1$ where k_1 and k_2 , respectively are the rate constant for hydroxide and peroxide anions and rate appearance of phosphate ions obeying first order kinetics. This is also supported by the substrate concentration effect and iso-kinetic phenomenon. The ranges of Arrhenius parameters i.e. energy of activation and entropy of the reaction support bimolecular nucleophilic attack of hydroxyl anion with 'P-O' bond fission.
- (ii) Low concentration of mono-4-CMPP in presence of a slight excess of monomeric [CTABr] formed the stable suspension due to interaction between mono anionic substrate and cationic surfactant. The turbidity decreases with increasing [CTABr] concentration and above cmc, a clear solution was obtained. Formation of sparingly soluble ion pairs between the detergent cation and mono-4-CMPP mono anion or other sub micellar aggregates have been postulated as cause of turbidity.
- (iii) Charge densities are important for the inhibition by salts, the order is benzoates $>$ $\text{Cl}^- >$ Br^- .
- (iv) The basic hydrolysis of mono-4-CMPP involves attack of the hydroxyl or hydroperoxy ion on the phosphorus atom of phosphate group of neutral esters, forming anionic phosphate, which then undergoes base catalysed hydrolysis. More slowly intermolecular proton shift has also been suggested for the reaction.

CONCLUSION

The comparative study of rate constants for the reaction of mono-4-CMPP with hydroxides and hydroperoxy anions in presence of 10^{-3} [CTABr] detergent besides the effect of pH and borate buffer has been examined. There was negligible effect of pH and on the rate of reactions. It was postulated that hydro peroxy anions are better nucleophile than hydroperoxide ion.

REFERENCES

1. C. A. Bunton, L. Robinson and L. Sepulveda, *J. Org. Chem.*, **35**, 108 (1970).
2. C. A. Bunton, M. M. Mhala, J. R. Maftall, D. Monarres and G. Saveli, *J. Org. Chem.*, **49**, 426 (1984).
3. A. P. Singh and G. C. Yadav, *Proc. Nat. Conf. Current Concept. Sci. Educational Research- T. D. C. Jaunpur*, 41-45 (2011).
4. A. P. Singh, R. C. Verma and R. S. Kushwaha, *J. Ultra Chem.*, **9(1)**, 23-30 (2012).
5. A. P. Singh, R. C. Verma and R. S. Kushwaha, *Res. J. Chem. Sci.*, **3(8)**, 63-67 (2013).
6. J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley-Interscience, New York (1982).
7. R. Zana (Ed.), *New Methods of Investigation in Surfactants Solutions*, Dekker, New York (1985).
8. M. Gratzel and K. Kalyanasundaram (Ed.), *Kinetics and Catalysis in Micro Heterogeneous Systems*, Dekker, New York (1991).
9. K. Martinek, A. K. Yatsimirski, A. V. Levashov and I. V. Berezin, in K. L. Mittal (Ed.), *Micellization, Solubilization and Microemulsion*, Plenum, New York, **2** () pp. 489-508.
10. S. Tascioglu, *Tetrahedron*, **52**, 11113-11152 (1996).
11. L. S. Romsted, C. A. Bunton and J. Yao, *Curr. Opin. Colloid Interface Sci.*, **2**, 622 (1997).
12. L. S. Romsted and K. L. Mittal (Ed.), *Micellization, Solubilization and Microemulsions*, Vol. 2, Plenum, New York (1997) pp. 509-530.
13. L. S. Romsted, K. L. Mittal and B. Lindman, (Ed.), *Surfactants in Solution*, Plenum, New York, Vol. 2 (1984) pp. 1015-1068.
14. L. S. Romsted, *J. Phys. Chem.*, **90**, 5107.

15. L. S. Romsted, *J. Phys. Chem.*, **90**, 5113 (1985).
16. C. A. Bunton and J. R. Moffat, *J. Phys. Chem.*, **90**, 538 (1986).
17. C. A. Bunton and J. R. Moffat, **92**, 2896 (1988).
18. E. Ortega and E. Rodenas, *J. Phys. Chem.*, **91**, 837 (1987).
19. J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecule System*, Academic Press New York (1975).
20. E. H. Cordes, *Pure and Appl. Chem.*, **50**, 617 (1978).
21. C. A. Bunton, *Catal. Rev. Sci.-Eng.*, **20** (1979).
22. C. A. Bunton, F. Nome, F. H. Quine and L. S. Romsted, *Acc. Chem. Res.*, **24** (1991).
23. C. A. Bunton, M. M. Mhala and J. R. Moffatt, *J. Org. Chem.*, **52**, 3832 (1987).
24. P. DiProfio, R. Germani, G. Savelli, G. Cerichelli, M. Chiarini, G. Mancini, C. A. Bunton and N. D. Gillitt, *Langmuir*, **14**, 2662 (1998).
25. I. M. Cuccovin, L. S. Romsted and H. Chaimovich, *J. Colloid Interface Sci.*, **220**, 96 (1999).

Revised : 03.09.2013

Accepted : 06.09.2013