

EFFECT OF SURFACTANT MICELLES ON THE REACTIVITY OF PEROXY ANIONS TOWARD BIS (4-CHLORO-3,5-DIMETHYLPHENYL)PHOSPHATE

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Abstract

The rate enhancement depends on the hydrophobicity of the nucleophile. The micellar catalyzed reaction between bis-4-chloro-3,5-dimethylphenylphosphate ester and hydroxide or hydroperoxide anions has been examined in buffered medium (pH 8-10). First order rate constant (K_{app}) for the reaction of hydroxide ion with bis-4-CDMPP go through maxima with the increasing concentration of cetyltrimethylammoniumbromide (CTABr). Micelles of CTABr very effective catalyst to the reactions of phosphate diesters. Rate constants measured with OH_2^- ions are approximately twice and thrice than that of OH^- ions in presence of CTABr.

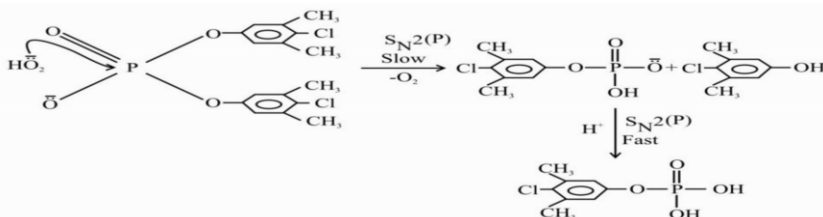
Keywords: CTABr, Micelles, Micellar Catalyses, 4-CDMPP.

Introduction

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 (OH_2^-) assisted hydrolysis. Bunton and Mhala^[4] recently reported that micelles of CTABr catalyse the reaction of hydrolysis by adding OH_2^- ion which interested us to investigate the micellar catalysed hydrolysis of 4-CDMPP diester with OH^- and OH_2^- ions.

The effect of ionic strength^[5] was studied by carrying out kinetic runs at different ionic strengths. In most of the micellar catalyzed reactions, the substrate is incorporated into the micellar pseudophase and is attacked by an external reagent or decomposes spontaneously^[6]. On taking into the consideration, the above mentioned observations, following scheme has been suggested for the mechanism of the hydrolysis of 4CDMPP and OH^- ions.

Scheme:



II. Experimental

2.1 Material-

Diester of 4-Chloro-3, 5-dimethylphenylphosphate (4-CDMPP) is synthesized by the method of Auger and Dupius^[7] and recrystallised by absolute EtOH. The compound 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]

2.2 Kinetics-

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 $40 \pm 0.5^\circ\text{C}$.

2.3 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 OH₂⁻ 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.

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

pH	103 [OH ⁻] mol dm ⁻³	105 K'w s ⁻¹	105 K ψ s ⁻¹ in 103 [CTABr] 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

The rate constants for the reactions of OH₂⁻ ions with diesters of 4-CDMPP increase sharply with the increase of [CTABr] (summarized in table 2). They rise to the maxima and then decrease steadily. This is common for bimolecular micellar catalyzed reactions.

TABLE- 2: Rate constants for reaction with H₂O₂ in presence of CTABr at pH 9 and $40 \pm 0.5^\circ\text{C}$.

S.No.	$10^3[\text{CTABr}]\text{mol dm}^{-3}$	$10^5 K_{\psi} \text{ s}^{-1}$ 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

First order rate constants determined for OH^- and OH_2^- assisted reactions which go through maxima at $1.6 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{CTABr}]$ is $29.86 \times 10^{-5} \text{ s}^{-1}$ with $20.8 \times 10^{-3} \text{ mol dm}^{-3}$ OH^- ions and $114.26 \times 10^{-5} \text{ s}^{-1}$ with $1.2 \times 10^{-3} \text{ mol dm}^{-3}$ OH_2^- ions as shown in Fig. 1&2. Acceleration of the rate constants are more than three times in case of the reactions with OH_2^- ions indicates that OH_2^- is slightly better nucleophile than OH^- . It may be envisaged that probably reacts in competition with OH^- in direct nucleophilic attack at phosphorus centre of ester molecule.

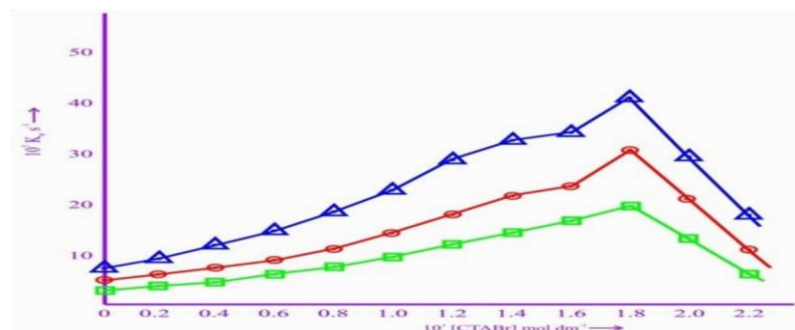


Fig. 1. Reaction of 4-CDMPP with OH^- ions in presence and absence of CTABr at $40 \pm 0.5^\circ\text{C}$.

Δ 10^{-3} 10^{-3} 10^{-3} - $43.8 \times 10^{-3} \text{ mol dm}^{-3}$ OH^- at pH 10, $\circ$ $20.8 \times 10^{-3} \text{ mol dm}^{-3}$ OH^- at pH 9, $\square$ $3.9 \times 10^{-3} \text{ mol dm}^{-3}$ OH^- at pH 8

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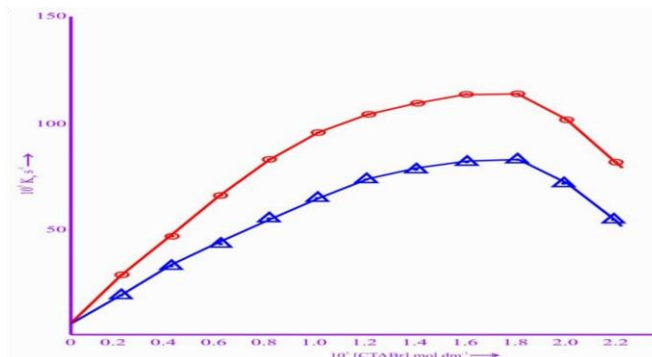


Fig. 2. Reaction of bis-4-CDMPP with H_2O_2 in presence of CTABr.



- $0.8 \times 10^{-3} \text{ mol dm}^{-3} \text{ OH}_2^-$ at pH 9.



- $1.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ OH}_2^-$ at pH 9.

From the results presented in Tables 1 and 2, it is evident that maximum rate enhancement occurs in the region of [CTABr] at which bulk of substrate is incorporated into the micelle. The region for relatively greater enhancement may also be envisaged as due to the hydrogen bonding¹¹ between OH_2^- and P-O groups of ester. The observed rate enhancement can be explained by considering direct involvement of OH_2^- in nucleophilic attack on phosphorous atom as shown in above scheme.

III. Conclusion

Micellar catalysis has a great potential to explore the condition for enzymatic reactions and collection of data is useful for the development of industries such as leather processing, dye technology, photographic emulsions and pharmaceutical formulations.

References

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