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Micellar catalysis on the hydrolysis of mono-2-methoxy phenyl phosphor amide by hydroxide and hydro peroxide ions in buffer medium

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Abstract
The micellar catalysis on the rate of hydrolysis of 2-methoxy phenyl phosphoramide by hydroxide and hydroperoxide ions in Buffer medium of pH 9.0 has been investigated. A cationic surfactant cetyl trimethyl ammonium bromide (CTABr) catalyse were used in the reaction in presence of hydroxide ions and more strongly in presence of hydroperoxide ions. The reaction is catalysed by CTABr more strongly in presence of hydroperoxide ions than hydroxide ions. Anionic surfactant sodium lauryl sulphate {$[CH_3(CH_2)_{15}]$ (NalS)} has little effect on the reaction rates probably because ionic micelles strongly inhibit the nucleophilic attack of OH^- ions on phosphorus atom of dianions of phenyl phosphoramide. Addition of NaCl, KCl or NaBr inhibits reaction because CI^- and Br^- displaces OH^- ions from the micelle. A systematic approach to investigate the mechanistic changeover of these effects have been accounted quantitatively in terms of pseudo phase ion exchange model. The support of isokinetic relationship, bond fission and reaction path will be suggested for the hydroxyl (OH^-) and hyproperoxide ($O.OH^-$) ions on 2- methoxy phenyl phosphoramide.

Keywords: hydrolysis, mono-2-methoxy phenyl phosphoramide, micellar catalysis, hydroxyl, hydroperoxide, Buffer medium

Introduction
Recent progress in the field of micellar catalysis upon organic reactions, in particular hydrolysis of esters, amide and anilide have been extensively investigated [1-5]. Because of the obvious importance of the micellar catalysis in many natural and industrial processes, there have been numerous studies on the micellar catalysis on the hydrolysis of phosphate esters [6-8]. Ionic micelles in water concentrate counterions at their surface and repel co-ions due to coulombic interactions. But non-coulombic are also important because hydrophilic high charge density counterions are bound less strongly than polarisable, low charge diversity counterions. The concentration of reactants of micellar surface is the major source of enhancement of the rates of biomolecular reactions involving counterions.
These are kinetic and equilibrium evidences for binding both hydrophobic [9-12]. and hydrophilic co-ions to ionic micelles. Many hydrophobic organic cations bind readily to cationic micelles because dispersive and hydrophobic attraction overcome coulombic repulsion Hydrophilic anions OH- are not completely excluded from anions micelles of the solution is concentrated in electrolyte. This partial binding could also be explained by ion exchange model or it could also be understandable in terms of an electrostatic model, because electrolytes in solution sharply reduce the surface electrical potential of ionic colloid and repulsion of co-ions. We are interested in the use of rate of effects as probes of ion binding to micelles and in the qualitative interpretation of these rate effects.
Recently the micellar catalysis and effect upon dephosphorylation of methoxy phenyl phosphoramide by peroxy anions in Buffer medium [13], effect of cationic micellar catalysis on the hydrolysis of mono-2-methoxy phenyl phospnoramide ester [14], and micellar effect of anionic of sodium lauryl sulphate on hydroxide ion with mono-2-methoxy phenyl phosphoramide ester [15] have already been studied.

Materials and Methods
a. Substrate: Mono-phosphate ester of 2-methoxy raniline have been prepared by the quatative organic analysis method [16] in which phosphorusoxytrichloride ($POCI_3$) directly react with 2-methoxy aniline in presence of benzene and product always contains mixture of mono-, di- and tri-esters. Mono-ester was extracted and recrystallised, which was characterized by IR-spectra and directly compared with authentic specimen. All reagents used were of analytical grade.

b. Detergents: Cetyl trimethyl ammonium bromide (CTABr) and sodium lauryl sulphate (NaLS) detergents were commercially available (BDH), and there were purified by standard method [17].

Kinetics Measurements: Kinetic measurements were made using the spectrophotometric method (systronics spectrophotometer) Kinetic runs were performed using purified distilled water. Concentration of mono-2-methoxy phenyl phosphoramide was kept at 5.0 x 10^{-4} mol dm^{-3}. All kinetic runs were carries out in water jacketed cuvettes at 40±0.5°C.

Results and Discussion

Effect of Cationic Micelles

Effect of cationic micelles of CTABr, anionic micelles of NaLS on the reaction of mono-2-methoxy-phenylphosphoramide by OH- and O.OH- ions was studied in borate and carbonate Buffers. The experimental pseudo-first order rate constants $K\psi$, for the investigated reactions in micellar solutions of [CTABr] and [NaLS] shown in Table-1. The first order rate constants $K\psi$ go through maxima with increasing in [CTABr] at fixed [O.OH-] and [OH-] as in typical micelle catalyzed biomolecular reactions.

Under comparable conditions observed rate constants of mono-2-methoxy-phenyl phosphor amide have been found to be 2.71 x 105 (S-1) in 2.2 x 10-2 (mol dm-3) [OH]-, 12.41 105 CS-1) at 1.8 103 (mol dm-3) in [CTABr] in (2.2 x 10-2) (mol dm-3) [OH-], and 47.58 x 105 (S-1) in 1.8 x 103 (mol dm-3) [CTABr] and 1.2 x 103 (mol dm-3) [HO2-] concentration at pH 9.0.

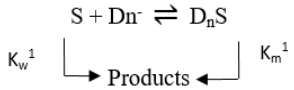
Rate constants against detergent concentrations shows these maximum rate constants. There is insignificant effect of micellar catalysis at very low concentration of the detergent, but once micelles begins to form the rate increases as the reagents are incorporated in the micellar pseudo phase till all desions of phenyl phosphor amide virtually incorporated to maximum at the detergent concentration, Addition of further detergent mearly gives new micelles which attract and therefore deactivate the hydroxide and hydro peroxide ions [18].

Based on the above experimental observations, a probably mechanism of the micellar catalysed hydrolysis of mono-2-methoxy phenyl phosphoramide in presence of OH- and HO2- ions.

Analysis of Rate Constant in Presence of CTABr

Micellar catalysis upon reaction rates are generally analysed in term of the aqueous pseudo phase ion exchange model [19-20]. We have concluded Kinetic rate data of (OH^-) reaction for quantitative analysis. Due to complex behavior of H_2O_2 and difficulty in determining the rate data, HO_2^- ($O.OH^-$) reaction is explained only qualitatively.

The variation in rate constant with addition of surfactant is generally treated on the assumption that substrate 'S' between the aqueous and micellar pseudo phase, designated by subscripts w and m respectively and can react in each pseudo phase, with the first order rate constants being Kw^1 and Km^1 as shown in the following reaction.



Where DnS is the micellar substrate complex. The micellised surfactant (detergent) is designated as Dn, and its concentration is that of the total surfactant concentration, less than that of monomeric surfactant ([Dn]=[CD]-cmc). The concentration of monomeric surfactant should be the critical micelle concentration (cmc) under kinetic conditions.

The plots of K ψ -Kw/m8 on [Dn] versus K ψ /m8 OH for runs at different (CTABr] with (OH-) are linear and yield have been summarized. It is evident that maximum rate enhancement occurs in the region of (CTABr) at which bulk of the substrate is incorporated into the micelles. The OH' being hydrophilic in nature enters the micellar pseudophase at lower concentrations and causes decrease in second order rate constant (K2m) in micellar pseudophase compared to that (Kw) in water. The region for relatively smaller enhancement in HO2 catalysis may probably be due to comparatively weak binding of H2O2 onto the micellar surface [21].

Buffer effects on reaction H_2O_2

The first order rate constants in borate and carbonate buffer at (pH=9.0) were determined and results are shown in Table-1. The decrease in critical micellar concentration (cmc) in carbonate Buffer [22]. can be explained in terms of increase in micellar binding of substrate caused by salt effect. Added borate ion accelerates the HO_2^- reaction rates in the presence and absence of CTABr. The observed rate maxima may be attributed to the formation of reactive peroxy borate ion. Further increase in borate ion reduces the rate due to competition between borate and peroxyborate ion onto the micellar surface.

Salt Effect

In discussing the way in which salts inhibited the reaction of muno-2- methoxy phenyl phosphoramide at constant concentration of OH^- ion in presence of [CTABr] are shown in Table-2. The head groups of cationic detergent attract OH^- and other ions from aqueous region. The ions binding to cationic micellar head groups is due to both specific coulombic attraction.

which are largest for polarizable, low charge density ions. Very hydrophilic ions OH^- are largely coulombically bound, whereas specific interactions are important with Br^- anion to lesser extent to Cl^- ion. These specific Interaction between anion and quaternary NH_4 of CTABr should also be present, but coulombic attraction should relatively small, therefore added Br^- and Cl^- ions inhibit the reaction more than coulombic attracted OH^- ion.

Effect of Temperature in Presence of Cationic Micelles

The plot of log $K\psi$ versus 1/T for the reaction in the presence of 1 x 10^{-3} M of CTABr has been found to be linear. Arrhenius parameters of the reactions were determined by studying the hydrolysis at different temperatures (30°C, 40º C and 50° C). The Arrhenius parameters were obtained by least square method.

Effect of Anionic Micelles

Anionic micelles of NaLS have very small inhibitory effect on the reaction rates probably because anionic micelles strongly inhibit the nucleophilic attack of OH^- ion phosphorous- atom of ion of Phenylphosphoramide (PPA) because hydrophobic interaction of ions of the PPA must overcome the coulombic repulsions between dianions and counterions in the stern layer, but absence of detergent the dianions of PPA are more reactive. The micellar effect at very low concentration of detergent [NaLS], there is insignificant inhibition which increases as the concentration of detergent increases as shown in Table 1 and Table 2. The Salt effect are too small for any quantitative analysis.

Table 1: Pseudo first order rate constants for reaction of 2.2 x 10^{-2} mol dm^{-3} NaOH 2-methoxy phenyl phosphoramide in 5.0 x 10^{-2} mol dm^{-3} Borate buffer solution with pH 9.0 at 40 ± 0.5^0C in presence NaLs.

10^5 K(S^{-1}) at 10^3[NaLS] [mol dm^{-3}]									
0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
Reagent: Borate Buffer									
11.47	8.29	6.10	4.93	4.18	3.21	2.39	1.87	1.82	1.76
Reagent: Carbonate Buffer									
8.43	5.99	5.34	5.11	4.94	4.86	4.51	3.97	3.26	2.81

Table 2: Effect of inhibiting salts upon the hydrolysis of mono-2-methoxy phenyl phosphoramide with 2.2 x 10^{-2} mol dm^{-3} NaOH in Borate Buffer pH 9.0 at 40 ± 0.5^0C in presence of CTABr [1.6 x 10^{-3}].

Salt [mol dm^{-3}]	**Rate Constants Kψ 10^5 sec^{-1}**		
	NaCl	**KCl**	**NaBr**
0.1	6.24	5.50	4.75
0.2	5.31	4.65	3.93
0.3	4.07	3.31	2.74
0.4	3.52	2.84	2.21
0.5	3.11	2.36	1.76
0.6	2.68	1.99	1.42

Conclusions

On the basis of our kinetic studies,it appears likely that the magnitude of micellar catalysed reaction is strongly accelerated by the cationic micelles [CTABI) and inhibited by anionic micelles (NaLS) and addition of salts. The reaction indicates that hydroperoxy ion ($O.OH^-$) is better nucleophile than hydroxide ion $(OH)^-$.

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