



Cationic micellar catalyzed hydrolysis effect on reaction mechanism of mono 2-methoxy phenyl phosphoramidate (MPPA) ester

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Abstract

Reaction of hydroxide ion with mono 2-methoxy phenyl phosphoramidate (mono ester) in presence of micellar of cationic (cetyltrimethyl ammonium bromide) detergent have been investigated at pH 8.0 to 10.0 at $40 \pm 0.5^\circ\text{C}$ in a aqueous solution, Pseudo first order rate constant k and K have been measured spectrophotometrically by rate of appearance of inorganic phosphate during hydrolysis. The concentration of the substrate was maintained $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ for all kinetic runs (Unless otherwise specified) and that of detergents varied in between 10^{-3} to $10^{-4} \text{ mol dm}^{-3}$. Effect of substrate concentration, pH & temperature etc.

Keywords: CTABr, CMC value, Synthesis mono 2-methoxy phenyl phosphoramidate ester

Introduction

Reaction kinetics deals with the rate of chemical reactions and all such factors which influence the reaction rate. It further provides a satisfactory explanation for the reaction rate in terms of the possible mechanism steps, through which the overall reaction proceeds. The most interesting aspect of the study of reaction rates is the insight it provides into the mechanism of a reaction. The dependence of reaction rates on the concentration of reactants temperature and various other factor.

The presence of the aromatic substituents in the detergent enhances the micelle- substrate binding constants and the magnitude of catalysis but did not appreciably alter the rate constants for the hydrolysis in the micellar phase [1, 2]. Micelles has attracted considerable attention as means of controlling the rates of chemical reaction of Industrial effect for the hydrolysis of esters, amides, anilides and acetals etc [3-7].

A numerous phospholipids exist in both α and β forms as well as in different stereochemical configuration which can be isolated in phospholipids [8], diols, lipids [9], sphingolipids, an interesting use of cationic agents in hair dyeing has recently been described. The cationic detergent in applied to the hair which is subsequently treated with an acid dye. The dye stuff forms and adherent insoluble take with the absorb detergent and thus fixed to hair

Materials and Methods

The mono 2-methoxy phenyl phosphoramidate esters have been prepared by the general method in which phosphorus oxytrichloride (POCl_3) directly reacts with methoxy phenyl phosphoramidate. 28.8 gm of mono 2-methoxy phenyl phosphoramidate was taken with 0.13gm. of MgCl_2 in a round bottom flask, 15.9 ml of phosphorus oxytrichloride was slowly added with constant stirring, keeping the temperature of the reaction mixture at about 5.0°C the reaction mixture was refluxed 12 hours at 180° , on oil bath and allowed to cool and then distilled at reduced pressure after adding

10ml. of benzene. The first fraction consisting of benzene and unreacted phosphorus oxytrichlorides (POCl_3) was removed by distillation at 120°C . The second fraction of a pungent smelling liquid was supposed to be 1-naphthyl phosphorus dichloride distilled at $200-210^\circ\text{C}$. It was dissolved in 20ml of ice-cold distilled water and kept at low temperature over night. The 1-naphthyl phosphorodichloridate was converted into mono 2-methoxy phenyl phosphoramidate monoester, which was extracted with solvent ether. After removing the solvent ether, a light brown coloured crystalline solid was obtained which on recrystalline from absolute ethyl alcohol gave a white crystalline solid.

Results and Discussion

Kinetic investigation of micelle induced hydrolysis mono 1-NPE with hydroxide ions in presence or absence of detergent [10^{-3} to 10^{-4}] mol dm^{-3} have been carried out at pH 8.0 -10.0, using borate buffers and at $40 \pm 0.5^\circ\text{C}$ the compositions of buffer used have been described in experimental section, concentration of mono 2-methoxy phenyl phosphoramidate ester in all kinetics runs was kept $5.0 \times 10^{-4} \text{ mol dm}^{-3}$. Effect of cationic micelle cetyltrimethyl ammonium bromide by on the rate hydrolysis in presence of hydroxide ions has been measured by spectrophotometrically by the rate of appearance of Inorganic phosphate using spectrophotometer.

The cationic surfactants (CTABr) reduce the rate considerable as high concentration which non-ionic surfactants play no role at the rate [10]. Cetyl triphenyl phosphonium bromide is more reactive than cetyl trimethyl ammonium bromide. The kinetics of reactions of oximate α - nucleophile with α - nitro phenyl acetate tri alkyl triphenyl phosphonium bromide micelle [11] and results are shown in table-1 to 4.

Table 1: Pseudo first order rate constants for reaction of $[3.9 \times 10^{-3}]$ and 20.8×10^{-3} mol dm⁻³ NaOH with (5.0×10^{-4}) mol dm⁻³ mono 2-methoxy phenyl phosphoramidate ester in presence of 10^{-3} [CTABr] at pH 8-9.0 of Borate Buffer and temperature $[40 \pm 0.5^\circ\text{C}]$

S.No.	CTABr $\times 10^3$ mol dm ⁻³	K_ϕ 10^5 s ⁻¹ α -NPP pH - 8.0 (observe)	K_ϕ 10^5 s ⁻¹ α -NPP pH - 9.0
1.	0.2	6.33	9.12
2.	0.4	11.12	12.54
3.	0.6	14.29	16.99
4.	0.8	19.86	21.50
5.	1.0	23.99	26.99
6.	1.2	29.06	35.73
7.	1.4	34.66	43.59
8.	1.6	41.47	50.62
9.	1.8	36.35	45.78
10.	2.0	34.86	41.39

$K'w = 7.12 \times 10^{-5}$ Sec⁻¹, at pH 8 for 1- NPE

Table 2: Relation between reaction rate and mucle concentration in borate Buffer for mono 2-methoxy phenyl phosphoramidate - at pH- 8.0 and temperature $40 \pm 5^\circ\text{C}$

CD 10^5 mol dm ⁻³	K_ϕ 10^5 Sec ⁻¹	(CD - CMC) 10^5 mol dm ⁻³	$\frac{10^{-5}}{(\text{CD} - \text{CMC})}$ mol dm ⁻³	$(K_\phi - K'w) 10^5$ S ⁻¹	$\frac{10^{-5}}{(K_\phi - K'w) S^{-1}}$
100	26.99	20	0.05	19.87	0.0503
120	35.73	40	0.025	28.61	0.0349
140	43.59	60	0.017	36.47	0.0274
160	50.62	80	0.013	43.50	0.0229

$K'w = 7.12 \times 10^{-5}$ Sec⁻¹, CMC = 80×10^{-2} , N=01

Table 3: Relation between $\frac{K_\phi - K'w}{M_{\text{OH}}^s(D_*)}$ and $\frac{-K'w}{M_{\text{OH}}^s}$ for reaction of mono 2-methoxy phenyl phosphoramidate at different (CTABr) in borate buffer at pH 8.0 and temp. $40 \pm 0.5^\circ\text{C}$

S. No	K_ϕ 10^5 S ⁻¹	$\frac{-K'w \times 10^2}{M_{\text{OH}}^s} \text{ S}^{-1}$	$\frac{K_\phi - K'w \times 10^2}{M_{\text{OH}}^s(D_*)}$
1	09.12	20.222	05.54
2	12.54	27.8048	15.02
3	16.99	37.6718	27.35
4	21.50	47.6718	39.85
5	26.99	59.8447	55.07
6	35.73	79.2239	79.29
7	43.59	96.6518	101.08
8	50.62	112.2394	120.56
9	45.78	101.507	107.15

Table 4: Temperature effect on reaction of mono 2-methoxy phenyl phosphoramidate with (20.8×10^{-3}) mol dm⁻³ NaOH in 5×10^{-2} mol dm⁻³ Borate. Buffer at different temperature in absence & presence of CTABr at pH 9.0.

	t ^o C	T ^o K (abs)	$10^{-5}/T^{\circ}\text{K}$	$K_\phi \times 10^5$	log K_ϕ
Absence of detergent	30	303	330.0	4.15	0.6182
	40	313	319.5	7.12	0.8525
	50	322	309.6	12.86	1.10924
Presence of detergentg	30	303	330.0	33.53	1.5234
	40	313	319.5	50.62	1.70432
	50	322	309.6	67.34	1.8594

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