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Effect of cationic micellar catalysis on the hydrolysis of mono-2-methoxy phenyl phosphoramide ester

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Abstract

Hydrolysis of mono-2-methoxy-phenyl phosphoramide (mono-2-MPPA) was studied in micellar solutions of cetyl trimethyl ammonium bromide (CTABr) at pH 9.0. The hydrolysis was carried out by first order kinetics with respect to mono-2-MPPA concentration. At the concentration of critical micelle concentration (CMC), the rate of hydrolysis was increased with increasing the CTABr concentration. The binding constant of micelle for mono-2-MPPA and the rate constant in micellar pseudo phase were determined from kinetic data using the pseudo phase model.

Keywords: Micellar catalysis, mono-2-MPPA, pseudo phase, hydrolysis

Introduction

Lot of the imperative in living processes are the phosphate esters. These including the inherited substances like DNA and RNA in addition to cyclic AMP. The moving of phosphate groups were among ATP and ADP of indispensable substances in the living systems [1]. The bioactivatable protecting groups represent an enormously powerful tool to increase bioavailability or to generally help deliver drugs to cells. This approach is particularly valuable in the case of biologically active phosphate because of the high intrinsic hydrophilicity and the multitude of biological functions phosphate esters exhibit inside the cells [2].

Aminophosphonates are analogues of amino acids in which a carboxylic moiety is replaced by phosphoric acid. Acting as antagonists of amino acid, they inhibit enzymes involved in amino acids metabolism and thus effect the physiological activity of cells. These effects may be exerted as antibacterial plant growth regulatory of neuromodulatory [3]. All parts of the heritable reactions involving configuration and hydrolysis of these phosphate esters and polyphosphates are inflated by enzyme catalysis. Suitable to significance of such substances and hydrolysis of phosphate esters has reputable original study. Phosphates esters are tremendously very important biologically and most occurring phosphorus compounds contain a terminal unsubstituted –PO (OH)$_2$ groups. Introduction of these groups into molecule is known as phosphorylation [4] then polymers containing the P-O-P linkages are obtained. The magnitude of such substances and process as these immediately mention and hydrolysis of phosphoramide has accepted much critical study [5]. The largest part of work has implicated macrobiotic reactions, commonly in water, mediated by organic micelles which attract reactants, on that a reaction region dissimilar from the bulk solvent [6].

The orthophosphoric acid being a tribasic acid will form a series of esters with phenols, alcohols, aryl amines and their derivatives. Orthophosphoric acid intracts with 2-methoxy aniline to form mono-phosphoramides esters [7]. The hydrolysis of mono-phosphoramide depends upon the experimental conditions. In the most kinetic studies of micellar catalysed reactions, in the case of substrate into the micellar phase brings pull to the micelle by the electrostatic force [8]. Interaction between phosphoramide in finding the conditions in which micelles would the hydrolysis of mono substituted phenyl phosphoramide. The mono-2-MPPA was the preferred substrates because with mono-2-MPPA, the mono anion is the most reactive species [9]. At pH 9.0, the mono-2-MPPA reacts also with hydroxide ion and therefore appropriate choice of a substrate. It is possible to examine the micellar effects upon three mechanism of mono-2-MPPA hydrolysis [10]. The cationic micelles of CTABr was catalysis of the hydrolysis of mono-2-MPPA mono anion.

Materials and methods

The preparation of phosphate mono-2-methoxy phenyl phosphoramide (mono-2-MPPA) esters has been described by standard method [11] and was purified by recrystallization from ethyl alcohol. The kinetics investigation of micellar catalysis in reaction of mono-2-MPPA with hydroxide ion has been carried out at 40 ± 0.2^0C. Kinetics runs were performed by using double distilled water. Reactions were followed by Spectrophotometrically 12] at using the wavelength (λ) 680 nm by the rate of formation of inorganic phosphate [13].

Results and Discussion

Reactions of phosphate mono-2-methoxy phenyl phosphoramide (mono-2-MMPPA) ester were strongly catalysed at different concentration of cetyl trimethyl ammonium bromide (CTABr) at which pseudo first order rate constants were obtained. Investigation of micellar catalysed hydrolysis [14] of mono-2-MPPA with hydroxide ion have been carried out at 40 ± 0.2^0C in presence or absence of detergent [10^{-3} to 10^{-4} mol^{-1}dn^{-3}] at pH 8.0-10.0 using borate buffers solution. Effect of cationic cetyl trimethyl ammonium bromide (CTABr) detergent on rate of hydrolysis of mono-2-MPPA in presence of hydroxide ion has been measured Spectrophotometrically by the rate of appearance of inorganic phosphate [15]. The rate increases sharply at CTABr concentration greater than the critical micelle concentration (CMC) for CTABr at pH 9.0 in 2.5 × 10^{-3} mol, borate buffer, CMC=80×10^{-3}M determined by dye method[16]. The pseudo first order rate constant for mono-2-MPPA has been carried out in presence of detergent. It has been observed that whether the increasing detergent concentration, the rate increases to a maximum value of 30.14×10^{-5} sec^{-1} at 1.6×10^{-3} mol. dn^{-3} CTABr respectively. This maximum rate has been carried in the rate constant against detergent concentration and results are shown in Table-1.

The neutral phosphoramide of the mono-2-MPPA the bend obtained by rates constants against detergent concentration was through due to the result of the maximum protonation which is common in amide system [17]. Unless the heat of protonation is small and the difference in activation energies should result at points, before and after the bend. This view, the kinetic runs were made at maximum where substrate is fully micellar bound at 1.6×10^{-3} mol. dn^{-3} CTABr where maximum rates K=30.14×10^{-5} s^{-1} for the hydrolysis of mono-2-MPPA with micelles of CTABr in buffer solution. The hydrolysis was studied in absence and presence of surfactant. Investigations of Arrhenius parameters for the hydrolysis of mono-2-MPPA are shown in Table-2. The rate of enhancement arises almost completely from a lowering of activation energy in absence of CTABr-ΔE = 17.62K. cals /mol and entropy of –ΔS ≠ 58.34(e.u.) and in presence of CTABr-ΔE= 26. 20 cals/mole and entropy of -ΔS ≠ 54.82 (e.u.).

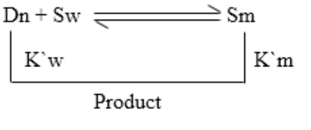
Table 1: Reaction of mono-2-MPPA in presence of cationic surfactant

S.No.	[CTABr] x 10^{-3} mol.dn^{-3}	KΨ10^5 S^{-1}
1.	0.2	4.61
2.	0.4	5.69
3.	0.6	6.93
4.	0.8	7.89
5.	1.0	8.62
6.	1.2	9.37
7.	1.4	10.40
8.	1.6	10.98
9.	1.8	9.86
10.	2.0	8.75

Table -2: Arrhenius parameters for the hydrolysis of mono-2-MPPA

S. No.	Ester	ΔE Kcal/mol	λsec^{-1}	ΔS≠(e.u.)
1.	Mono-2-MPPA without CTABr	3.75	470.11×10^5	-68.35
2.	Mono-2-MPPA with CTABr	4.11	716.31×10^5	-65.68

Where Sw and Sm are substrates in aqueous and micellar pseudo phase respectable K\`w and K\`m are the related first order rate constants and Ks are the binding constant [18].



Reactions in the water makes minor contribution to the observed rate constant [19]. The first order rate constant for hydroxide (OH^-) ion is given by the following equation:

$$K\Psi = \frac{K'w + K'm\ Ks\ [Dn]}{1 + Ks\ [Dn]}$$

The value of K\`m can be obtained by analysis of the variations of Ks with Dn or by choosing conditions such that substrate is essentially fully micellar bond [20].

The main features of mechanism of micellar catalysed hydrolysis of with the hydroxide ion in presence of (CTABr) detergent [21] may be concluded pointwise as under:

1. The study of substrate concentration effect found in significant increases in rates. Hence the reaction may be considered kinetically of first order.
2. The higher rate of mono-2-MPPA are in consistent in our observations, suggesting the intra molecular transfer of a protonation to the leaving group by concerted mechanism Sn^2.
3. Since the only reactive species of mono-2-MPPA in the pH region 8.0-10.0 appears to favour nucleophilic attack by the hydroxide ion on the phosphorous atom of the group of phosphoramide. However, KΨ the pseudo first order rate coefficient does not increase linearly with the increase of CTABr. Suggesting that the dianion of phenyl phosphoramide intramolecularly involved in proton transfer to the leaving group in the transition state forming a meta phosphoramide ion in bimolecular hydrolysis, which is more probable due to high negative value of entropy and energy of activation.
4. The nucleophile hydroxide (OH^-) anions bind strongly to the micelles in which dianion of mono-2-MPPA is buried in the interior of the micelles and suitably exposed to the nucleophilic attack of (OH^-) ions.

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