

Effect of Added Polymer on the Hydrolysis of ACYL BZBT

D.Mohanambal¹, S.Arul Antony², S.Bangaru Sudarsan Alwar¹

Department Chemistry, Sriram Engineering College, Perumalpattu, India¹

P.G & Research, Department of Chemistry, Presidency College, Chennai, India².

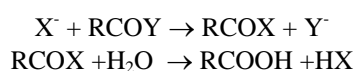
Department of Chemistry, Dwaraka Doss Goverdhan Doss Vaishnav College, Chennai, India³

ABSTRACT: Kinetics of the hydrolysis of amide in the presence of polymer polythene glycol (PEG) 6000 by hydroxide ion in varying solvent media has been carried out conduct metrically. The results obtained through light on the role of catalysis in the mechanism of hydrolysis of amide. Further the presence of polymer is found to after the role of solvent while the course of the reaction. These preliminary results are important for predicting the nature of attack by enzymes on various substrates in biochemical reaction.

KEYWORDS: Polymer, Catalysis, Acyl transfer

I. INTRODUCTION

Acid, bases and enzymes catalyze the hydrolysis of esters. A nucleophilic attack takes place on the carbonyl carbon and Electrophilic attack takes place on the alcoholic oxygen atom in the hydrolysis of BZBT in aqueous medium. The study of these reactions are important of predicting the mechanism of several biological reaction^{1,2}. The interaction between a nucleophile and amide is a depicted in the following scheme.



Where X^- is a nucleophile, which replaces Y^- from the amide forming an acyl intermediate which will be attacked upon latter by water to give final products.

Solvent plays an important role in these reactions. The solvent water apart from or provides proton for attacking the carbonyl oxygen or polarize the carbonyl group of the amide or stabilize the acyl intermediate or solvates the leaving group. A polar aprotic solvent such as DMSO is added and the effect of polarity change on the reaction rates has been studied. Further role of added polymer i.e., polyethylene glycol during the hydrolysis also has been studied. In the present study the variation of the rate of hydrolysis of amide and its derivative in varying solvent medium has been studied.

Addition of surface-active material in the solvent exhibit unusual variation in the physical properties such as surface tension, osmotic pressure, etc³. In dilute solution, the surfactant acts as a normal solute. At fairly high concentration abrupt changes in physical properties have been observed. McBain pointed out that this anomalous behavior could be explained in terms of organized aggregates, or micelles of the surfactant ions in which the lipophilic hydrocarbon chains are oriented towards the interior of the micelle, having the hydrophilic groups in contact with the aqueous medium.

In the hydrolysis of esters by benzotriazole acting as nucleophile, acyl intermediate formation is proposed as initial step by several scientists. For a clear understanding one requires a study of fate of such intermediates during hydrolysis. In the present work (p-substituted) benzoyl acid chlorides are treated with benzotriazole and corresponding

tertiary amides are synthesized. later hydrolysis of the various amides synthesized in binary solvent mixtures of various compositions are followed conductometrically under the second order condition. further the reactions are carried out in the presence of polymer (PEG 60000). The rate constant obtained are compared.

II. EXPERIMENTAL METHODS

2.1 Materials

Pure samples of p-Nitro benzoic acid and Benzotriazole were purchased from Otta Kemi chemical limited and used as such. p-chlorobenzoic acid, p-bromo benzoic acid were purchased from Aldrich chemical and used as such. Pure sample of polythelene glycol (PEG 6000) purchased from Merck is used as such. The purity of the each solid compound was checked by TLC (a single spot was obtained). Melting points were determined using the Toshinwal melting point.

2.2. Conductivity water

Water used in all the experiments was obtained initially purifying ion exchange and then distilling with alkaline permanganate in all glass apparatus. This water boiled to expel any dissolved carbon dioxide before use.

2.3. Sodium hydroxide

Concentrated sodium hydroxide was prepared in degassed conductivity water and allowed to stand for 24 h. the clear supernatant liquid was decanted carefully and quickly into a pyrex glass bottle and stoppered. The solution is standardized using a standard oxalic acid solution. From the standardized sodium hydroxide solution, the solution required composition is prepared in degassed conductivity water and used for studying kinetics.

2.4 Experimental Technique

The kinetic study of the hydrolysis of the Benzoylbenzotriazole and substituted benzoylbenzotriazoles by hydroxide ion chosen in the present investigation were followed conductometrically by taking the benzoylbenzotriazole and hydroxide ion in equal concentration ($1 \times 10^{-3} \text{ mol/dm}^3$) in aqueous DMSO medium and constant ionic strength is maintained by adding required quantity of KCl conductance was measured using the digital conductivity bridge by dipping a conductivity cell in the reaction mixture at various time intervals. Conductivity of the blank solution, C_0 and the conductivity of the reaction mixture at infinite time, C_∞ were also determined. From these values the second order rate constant for the hydrolysis of the amide were determined according to the equation:

$$K_2 = (1/at) (C_0 - C_t) / (C_t / C_\infty) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Where 'a' is the initial concentration of the amide in mol dm^{-3}

Rate constant were also determined graphically by dividing the slope of the plot $(C_0 - C_t) / (C_t / C_\infty)$ against time in seconds by the initial concentration of the reactant.

III. RESULTS AND DISCUSSION

The kinetic data obtained during the study of the hydrolysis of different amide by hydroxide ion at 303k (Tables 1-4)

TABLE – 1
KINETIC DATA FOR THE HYDROLYSIS OF BENZOYL BENZORIAZOLE IN VARIOUS SOLVENT MEDIA

[OH⁻] = 1x 10⁻³ mol dm⁻³,
 [KCl] = 1x 10⁻³ mol dm⁻³

[BenzoylBenzoriazole] = 1x 10⁻³ mol dm⁻³
 Temperature 303k

Solvent composition : (% V/V)		K ₂ /dm ³ mol ⁻¹ s ⁻¹
DMSO	Water	
10	90	1.6633 x 10 ⁻³
20	80	1.9560 x 10 ⁻³
30	70	2.7296 x 10 ⁻³

TABLE – 2
KINETIC DATA FOR THE HYDROLYSIS OF [p-Cl-BENZOYL BENZORIAZOLE] IN VARIOUS SOLVENT MEDIA

[OH⁻] = 1x 10⁻³ mol dm⁻³,
 [p-Cl-BenzoylBenzoriazole] = 1x 10⁻³ mol dm⁻³

[KCl] = 1x 10⁻³ mol dm⁻³
 Temperature 303k

Solvent composition : (% V/V)		K ₂ /dm ³ mol ⁻¹ s ⁻¹
DMSO	Water	
10	90	3.376 x 10 ⁻³
20	80	3.5091 x 10 ⁻³
30	70	3.6261 x 10 ⁻³

TABLE – 3
KINETIC DATA FOR THE HYDROLYSIS OF [p-Br-BENZOYLBENZORIAZOLE] IN VARIOUS SOLVENT MEDIA

[OH⁻] = 1x 10⁻³ mol dm⁻³,
 [KCl] = 1x 10⁻³ mol dm⁻³

[p-Br-BenzoylBenzoriazole] = 1x 10⁻³ mol dm⁻³
 Temperature 303k

Solvent composition : (% V/V)		K ₂ /dm ³ mol ⁻¹ s ⁻¹
DMSO	Water	
10	90	5.5135 x 10 ⁻³
20	80	5.5751 x 10 ⁻³
30	70	5.8620 x 10 ⁻³

TABLE – 4
KINETIC DATA FOR THE HYDROLYSIS OF [p-NO₂-BENZOYL BENZOTRIAZOLE] IN VARIOUS SOLVENT MEDIA

$[\text{OH}^-] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{p-NO}_2\text{-BenzoylBenzotriazole}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$
 $[\text{KCl}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ Temperature 303k

Solvent composition : (% V/V)		$K_2 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
DMSO	Water	
10	90	0.5942×10^{-3}
20	80	6.8859×10^{-3}
30	70	7.3557×10^{-3}

As the percentage of organic solvent increase the rate of hydrolysis of the amide increases. This may be due to the salvation of metal ion by the organic solvent resulting in OH⁻ ion which attacks in a facile manner.

TABLE – 5
VARIATION OF HYDROLYSIS OF SUBSTITUTED BENZOYL BENZOTRIAZOLE BY HYDROXIDE ION IN THE PRESENCE OF PEG 6000 AT 303K

p-Cl BZBT, p-Br BZBT, and p-NO₂ BZBT in the presence of PEG

$[\text{OH}^-] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ Solvent: DMSO: H₂O (2:3)
 $[\text{BenzoylBenzotriazole}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{KCl}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$
 $[\text{p-Cl-BenzoylBenzotriazole}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ Temperature 303k
 $[\text{p-Br-BenzoylBenzotriazole}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$
 $[\text{p-NO}_2\text{-BenzoylBenzotriazole}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$

[PEG] mol dm ⁻³	$K_2 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \times 10^{-3}$			
	BZBT	p-Cl-BZBT	p-Br-BZBT	p-NO ₂ -BZBT
1×10^{-7}	1.6481	3.0135	4.0064	7.1286
1×10^{-6}	4.8957	6.5079	6.5579	8.0883
5×10^{-6}	3.1972	4.1702	3.8939	6.7179
1×10^{-5}	2.1570	3.4823	3.5479	5.3181
5×10^{-5}	1.3656	2.7734	3.2373	4.8129

It is found that the rate of hydrolysis of BZBT, p-Cl-BZBT, p-Br-BZBT, and p-NO₂-BZBT increases linearly as the concentration of the polymer increases. This may be as due to the decrease in the polarity of the medium Table 5. As the Concentration of the polymers increase. It is found that the rate of hydrolysis of p-Br-BZBT, and p-NO₂-BZBT increase and then decreases. This may be attributed to the change in the role of the polymer at higher concentration when if may solvate the amide (being smaller than amide derivate) thereby retards the hydrolysis.

The rate of hydrolysis of benzoylbenzotriazole by hydroxide ion is found to obey second order kinetics with a dependence of first order on each of the reactant amide and the hydroxide ion at 303K in various solvent media studied. The rate equation for the hydrolysis may be given as rate = k [amide] [hydroxide]. The Bronsted β values for the leaving

International Journal of Innovative Research in Science, Engineering and Technology

An ISO 3297: 2007 Certified Organization

Volume 4, Special Issue 1, February 2015

THIRD NATIONAL CONFERENCE ON ADVANCES IN CHEMISTRY (NCAC – 2015)On 18th February 2015

Organized by

Department of Chemistry, Easwari Engineering College (SRM Group of Institutions), Chennai-600089, India.

group variation is obtained as -0.5 to -0.72 in presence of solvent medium of varying polarity. This indicates the reaction involves symmetrical bond formation and bond cleavage in the transition state. This indicates the solvent polarity play an important role in the cleavage of living group. Hydrolysis rate constant increase with increase in mole fraction of the DMSO initially and later decreases in all the amides studied expecting in the case of nitro were initial increase is not significantly seen. This is due to a probable solvation of Na^+ ion by the medium thereby hydroxide ion is made to attack freely. When the composition of DMSO increases the medium becomes less polar and solvate the bigger amide thereby the attack by the hydroxide ion is made difficult, resulting in the decrease in the rate constant. Hammett ρ value obtained for the hydrolysis of amides in various solvent media of varying polarity varies between 0.58 to .78. This indicates change in the sensitivity at the reaction center due to variation in solvent polarity. Positive ρ value indicates electron rich transition state as expected resulting in the development of negative charge in the transition state. The hydrolysis constant of N-benzoylbenzotriazole and p-substituted benzoylbenzotriazoles increase with increasing the concentration of polyethyleneglycol and then decrease. This may be due to the formation of clusters by the polymer in which the amide gets trapped at higher concentration of polymer and thereby the reaction rate decrease. When the polymer concentration is very less, probably such a cluster formation may not occur and hence the above trend is observed. Hammett ρ value obtained is +1 in the case of hydrolysis of benzoylbenzotriazole in the presence of polymer. The value is slightly greater than the value obtained in the case of reaction carried out in the absence of polymer. This indicates increased electron flow in the case of reaction in the presence of polymer. The studied indicate both the solvent polarity and the presence of polymer as a role on the development of negative charge on the acyl intermediate which is also influenced by the presence of substituent in Para position. The studied reveals the cleavage of the acyl group occur to the same extent as that of attacking by the hydroxide ion. This plays an important role in the formation acyl intermediate in the ester hydrolysis by the heterocyclic unit of the enzyme and the hydrolysis of intermediate in the subsequent step.

IV. CONCLUSION

The various parameters obtained during experimental studies revealing the role of substituent, solvent polarity and presence of polymer in altering the rates of hydrolysis of acylbenzotriazoles. The results indicate symmetrical transition state involving the attack of hydroxide and cleavage of benzoyl group simultaneously to the same extent.

REFERENCES

1. T.C.Bruice and S.J.Benkovic, Bioorganic Mechanisms, Benjamin, New York, Vol.1 (1966)
2. G.Yashodha and V.Thiagarajan, Indian J. Chem., **23B**, 146 (1984).
3. E.H.Fendler and E.H Fendler, Catalysis in macromolecules and Micellar systems, Academic Press, New York (1975)