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The Effect of Various Factors on Hydrolysis of Thiophosphate

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Abstract: The nucleophilic hydrolytic reactions of Mono-isobutyl phosphate ester & Mono-2,4,6 tribromo thiophosphate ester have been discussed in this paper. Study of the hydrolysis of these monoesters have been made in the region .1 to 8 mol dm⁻³ HCl acid & p^{H} 1.24 to 7.46 at 65^oC & 50^oC respectively. Detailed study of the hydrolysis has been made at constant ionic strength, temperature, effect of solvent & concentration etc. The concept such as Hammatt acidity function¹, Bunnet Parameters², Zucker-Hammett hypothesis, isokinetic relationship³etc. have been applied to determine the probable reactions. It is clear from the experiment that the reactivity of monoesters is more than di- & tri- esters but di-negative sps. of monoester have very less contribution to the overall rate of hydrolysis.

Key words: Nucleophilic, hydrolytic reactions, monoesters, bunnet parameters, isokinetic relationship.

I. INTRODUCTION

Hydrolysis of an ester⁴ may proceed either through uni-molecular nucleophilic substitution $[SN_1]$ path depending on the structure & the set of experimental conditions used.

There are a no. of solvents may be used as nucleophilic reagents.

The following main factors required to be determined for studying the most suitable mechanism of hydrolysis of an ester.

[1] Reactive species

[2] Molecularity

[3] Bond rupture

There are four reactive species:

Conjugative, neutral, mono-negative & di-negative.

H O
l ll

$$R-S^+-P-OH$$
 conjugative form
OH R= isobutyl or 2,4,6 tribromo
O
ll
 $R-S-P-OH$ neutral form
l
OH
OH
OH
O
ll
 $R-S-P-O^-$ mono-negative form
O
ll
OH

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 $R - S - P - O^{-}$ di-negative form 1

0

Molecularity may be either uni or bi, even though hydrolysis is basically a double decomposition reaction between substrate ester & water.

Bond rupture may either be C-S or P-S depending upon the point of attack of nucleophile , can be shown by figure:

O O 11 11 R-|-S--P--OH, R--S-|-P--OH 1 1 OH OH [C-S bond fission] [P-S bond fission]

Berreau, M.L.⁵ examine a binuclear Zinc hydroxide complex for thio-ester hydrolysis reactivity. The result suggest that a terminal Zn-OH moity may be required for hydrolysis reactivity with a thio-ester substrate, also⁶ catalyze the hydrolysis of a thio-ester substrate & have been found to coordinate a variety of di-methyl combinations including Fe, Zn within the enzyme active site. Donald⁷ examine the hydrolysis of S-N-butyl phosphoro-thioate in aqueous solution at constant ionic strength has a rate maximum at $p^{H}3.25$ as the acidity is increased to 10 M perchloric acid & at 8 ml HCl the rate decreases. Chlebowsk, F.J.⁸ studied the hydrolysis of phosphate & O-phosphoro-thioate monoesters by Zn & Co , Although the rate of hydrolysis of O-phosphoro-thioate is slower than phosphate ester.

II. RESULT & DISCUSSION

Keeping up the various factors the possible reaction pathways for the hydrolytic breakdown of monoester can be summarized as below:

A. Mechanism of Hydrolysis of conjugative sps

Hydrolysis of the conjugative sps. Whether uni-molecularily or bi-molecularity would involve a transition state[T.S.].

Thus analysis of experimentally observed rate values and all the above mentioned consideration show the following possible mechanism via conjugative sps in mono ester:

Bimolecular P-S bond fission:

H O H O
l ll slow l ll

$$R-S^+-P-OH === [R-S^+....P....OH]-R-SH$$

 $\downarrow OH OH T.S.$
 $H-O-H O$
 ll
 $+ H-O^+-P-OH$
 l
 H
 $O O$
 $ll fast ll$
 $H-O^+-P-OH ===OH-P-OH + H^+$
 l

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B. Mechanism of Hydrolysis of neutral sps Arrhenius parameters support the bimolecular hydrolysis of these monoesters:

Bimolecular P-S bond fission:



C. Mechanism of Hydrolysis of mono-negative sps

A hydrogen bond structure formed with water for the mono-negative form of the monoester.



The following is the most suitable pathway of the mechanism of present monoester via the mono-negative sps with P-S bond cleavage.

Rapid formation of cycle intermediates out of mono-negative sps & water molecule:

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