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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 Hammett acidity function¹, Bunnet Parameters², Zucker-Hammett hypothesis, isokinetic relationship³ etc. 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 [SN₁] path depending on the structure & the set of experimental conditions used.

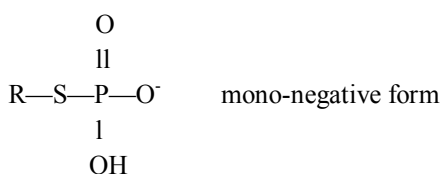
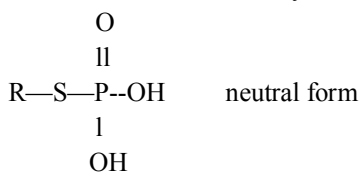
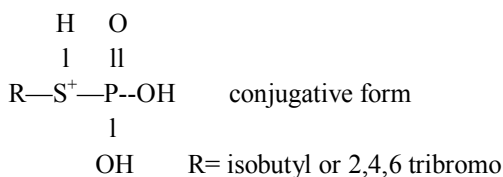
There are a no. of solvents may be used as nucleophilic reagents.

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

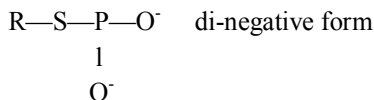
- [1] Reactive species
- [2] Molecularity
- [3] Bond rupture

There are four reactive species:

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

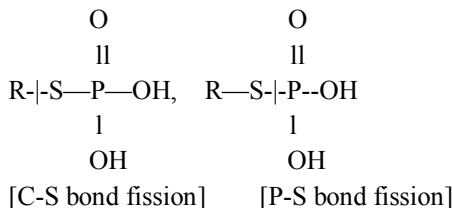


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Molecularity may be either uni or bi, even though hydrolysis is basically a double decomposition reaction between substrate ester & water.

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



Berreau, M.L.⁵ examine a binuclear Zinc hydroxide complex for thio-ester hydrolysis reactivity. The result suggest that a terminal Zn-OH moiety 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 pH 3.25 as the acidity is increased to 10 M perchloric acid & at 8 ml HCl the rate decreases. Chlebowski, 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

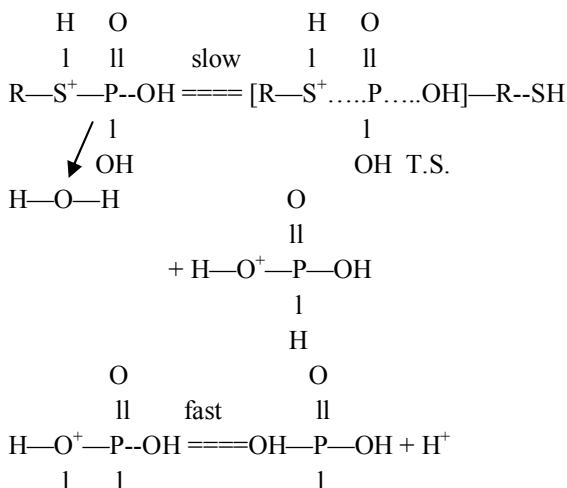
Keeping up the various factors the possible reaction pathways for the hydrolytic breakdown of monoester can be summarized as below:

A. Mechanism of Hydrolysis of conjugative sps

Hydrolysis of the conjugative sps. Whether uni-molecularly or bi-molecularly 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:



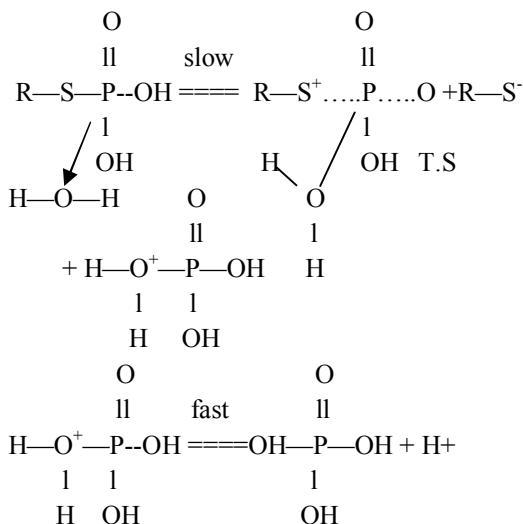
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H OH OH

B. Mechanism of Hydrolysis of neutral sps

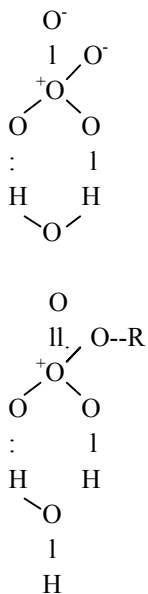
Arrhenius parameters support the bimolecular hydrolysis of these monoesters:

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.

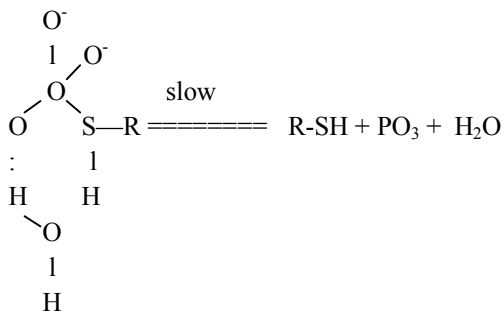
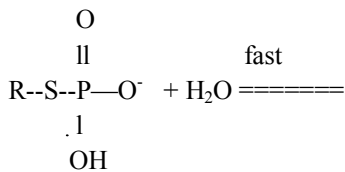


More convenient structure

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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