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Hydrolysis of Mono-S- Isobutyl -Phosphoro- Thioate: A Kinetic Study

Nimisha Misra

Abstract: Kinetic study of the Hydrolysis of Organic phosphate is gaining a great importance due to their vast industrial applications & investigations in the field of Bio-chemistry. The Kinetic study of hydrolysis of phosphate esters having C-S-P linkages is very limited & there is much scope for the systematic study in the field. Therefore Kinetic study of hydrolysis of Mono-s-isobutyl Phosphoro-thioate has been undertaken as a part of said project.Their rate of hydrolysis was measured by determining the rate of appearance was measured by determining the rate of appearance of inorganic phosphate by Allen's modified colorimetric methods .Aqueous medium was chosen & the factors such as ionic strength, temperature etc. that govern the rate , have been included in kinetic study .Mono phosphate ester has been kinetically studied in the range 0.1mold m^{-3} to 8mold m^{-3} HCl & in p^H buffer solution 1.24 to 7.46 in aqueous medium at 65^0C. All neutral, mono-negative & conjugate acid species has been found to be reactive.

Key Words: K inetic study, Hydrolysis, Organic Phosphate , C-S-P linkages , Allen's modified method .

I. INTRODUCTION

Hydrolysis via conjugate species: It was observed that the rate of hydrolysis increases with the increase in acidity up to 7 mol dm-3 HCl & then falls off. The rise in rate of the reaction in the acid solution from 1mol dm-3 to 7mol dm-3 due to the incursion of reaction via conjugate acid species rate laws may be formulated as:

Mono-S-Isobutyl Phosphoro-thioate ester-

$K_e = {}^kH_0^+ C_H^+ . \exp. bH^+ \mu + K_{Na} . \exp. b'N.\mu$

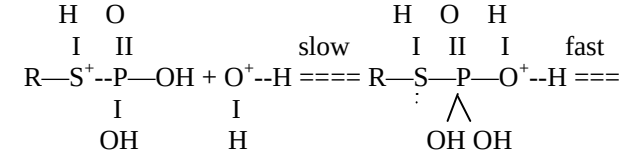
$K_e = .955 \times 10^{-3} C_H^+ . \exp.[2.303 \times 0.00] \mu + 2.37 \times 10^{-3}, \exp.[2.303 \times 0.2]\mu$

The agreement between calculated & observed rates proves the validity of above rate equations by considering second empirical term of Debye- Huckel equation .The Kinetic study of constant ionic strength shows that hydrolysis via conjugate acid species is subject to positive slope increases with the increase in acidity. Ionic strength data shows that the maximum at 7 mol dm^{-3} HCl is due to salt effect. The specific acid catalyzed rates are constant in the compound. The effect of concentration shows that the rate coefficients are independent of initial ester concentration.

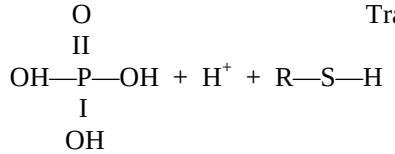
Hydrolysis may therefore be taken to be of kinetically first order & bimolecular. It shows that during hydrolysis a transition state is formed in which dispersion of charges has take place.

Probable mechanism of hydrolysis may formulated under:





Transition state



Hydrolysis via neutral species: In the region p^H 1.24 TO 4.17 neutral & mono negative species are reactive. At minimum p^H -

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1.24 only neutral specie is present .The rate laws governing the hydrolysis in different regions of p^H are given below:

i] p^H 0.30 to1: $K_c = K_H^+, C_H^+ + k_N$

$$= K_H^+, C_H^+ + 2.358\times10^{-3}\ N/N+M\ [min^{-3}]$$

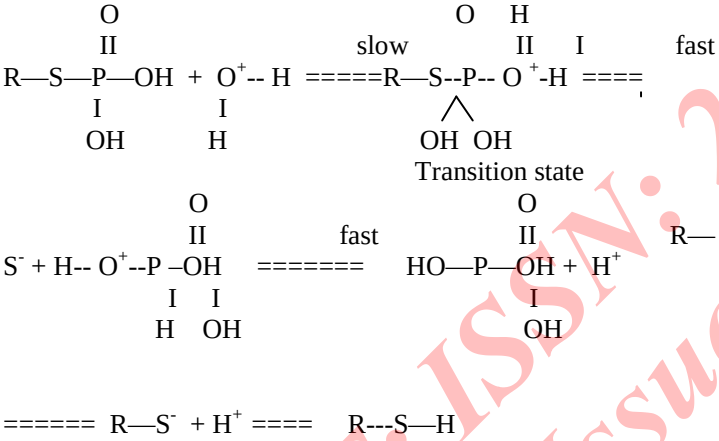
ii] p^H 1.24 to7.46: $K_c = K_H^+, k_m + k_N$

$$= 36.48 \times 10^{-3}\ .\ M/M+N\ [min^{-1}] + 2.358\times10^{-3}\ N/N+M\ [min^{-1}]$$

Contribution by neutral rates to the overall rate of hydrolysis in increasing order with respect to salt efect . Concentration effect shows pseudo first order reaction in respect to substrate.

The reaction path way has been formulated as:

Bimolecular P-S bond fisson [SN^2] [P-S]:



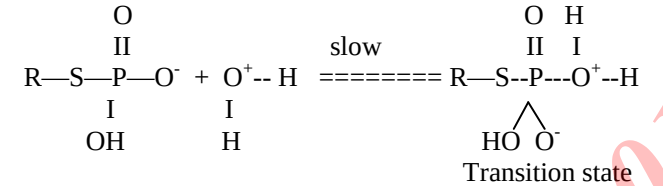
Hydrolysis via mononegative species:

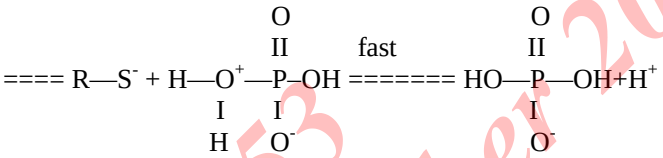
Reaction via mononegative species has been shown to be operative in the region p^H 1.24 TO 7.46. In this region the reaction is governed by the following equation:

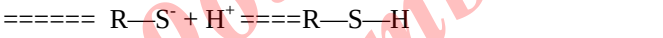
$K_m = k_m\ M/M+N + k_{N0}\ N/N+M$

The theoretical rates so calculated have been found to agree well with the experimental rates showing the validity of the above equation. The rate rises with the increase in p^H up to 4.17 is due to the incursion of more reactive mono-negative species.

The mechanism is shown below:







II.REVIEW

The resistant nature of mono-esters towards alkaline media have reported by Cavalider[1] [1998] ,Plimmer & Scott [2] [1908] , Malengreaue & Prigent[3][1911], Fleury & Curtius [4][1942] etc. When carbonyl group is present to the phosphorous atom, withdrawl of electron by the carbonyl function exposes the carbon atom to the nucleophile attack. As aresult hydrolysis progresses easily in the alkaline medium. The hydrolysis of simple monoalkyl phosphates accelerated more by halogen hydro-acids than by mineral acids, the order of reactivity being;

$$HI > HBr > HCl$$

Two French workers Bailly & Desjobert [5,6]studied the kinetics of hydrolysis of monoesters of phosphoric acid [H_3PO_4]. Chanley & Feagson [7] carried out kinetic investigation of α & β $-$ $naphthyl\ phosphate$, $phenyl-m-$ carbonyl, phenyl – p-carbonyl phosphate etc. These esters obey I_{st} order kinetics & exhibited a maximum rate in an intermediate p^H range. Kinetic study of hydrolysis of glucose -1-phosphates showed that the rate to be almost nil at p^H 8, increased gradually to p^H 4 & than increased quite rapidly in going from p^H 4 to 1.

Further Oldham[8] studied the hydrolysis of methyl di-hydrogen phosphates & glucose -1-phosphate & determined the reactive species, molecularity & bond fission in various zones of p^H log rate profile. The O^{18} tracer technique used by Cohn[9] & Bending

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[10]for the acid hydrolysis of glucose -1- phosphate at 37^0 C & Acetyl phosphate at 25^0& 85^0 conducting P-O & C-O bond fission respectively. Silver[11] [1957] kinetically studied the hydrolysis of phenyl , P-tolylphosphate exhibited acid catalyzed hydrolysis in more acidic media than p^H1. Swoboda[12] & Mhala[13,14] studied hydrolysis & rearrangement of Glycero-phosphate Kinetically. Mhala & coworkers[15] studied the hydrolysis of substituted aryl phosphates with the substituent of graded observed that the magnitude of acid catalysis follows the order of the polarity of the polarity & substituent.Ghosh K.K.[16]& coworkers studied the rates of hydrolysis of PNPDPP, Paraoxan & Parathion spectra photo-metrically with varying concentrations of N- hydroxyl amides in micelle media at 27^0C under pseudo- first order conditions. The reaction rate increases with increasing concentration of N -hydroxy amide Jan F. chlebowski & Joseph E. Coleman [17]studied the mechanism of hydrolysis of O-phosphoro-thioates &. Inorganic Thio-phosphates. The rate of hydrolysis of the O-phosphoro-thioate by the Zn[II] enzyme is -100-fold slower than the hydrolysis of phosphate esters . Milena Trimcic & David R.W. Hodgson[18] focus on kinetic studies & prediction on the hydrolysis & aminolysis of esters of 2-S-phosphorylacetates & founds cross linking between uridine 5- monophosphorothioate & D-glucosamine using N-hydroxybenzotria-infective. Extra potation of the data for hydrolysis use of readily accessible trifluro ethyl 2-S-[5^i- thiophosphoryl uridine] acetate with leaving group p^{KOH} of 12.4 showed afford better selectivity while maintaining reasonable reaction time.

Some important features of kinetic study of hydrolysis of monoesters are given below:

1] None of the monoesters has been found to posses all theoretically predicted reaction paths through neutral , mono-negative, di- negative & conjugate acid species.

2] All the monoesters react fast at about p^H 4 leaving aside few exceptions such as di-nitro-phenyl phosphate monoesters involving P-O bond fission.

3] The mono-anion of the monoester is more reactive in nature due to the formation of readily decomposable intermediates formed out of the mono-anion & water, but there is no experimental evidence for such hydrogen bonding.

III. RESULT & DISCUSSION

Kinetic behavior of the Mono-phosphate ester during Hydrolysis:

Hydrolysis of an ester[19] may proceed either through uni-molecular nucleophilic substitution [SN^1] or Bimolecular Nucleophilic Substitution [SN^2] path depending on its structure & the set of experimental conditions used. Kinetic study of the hydrolysis of mono-S- iso- butyl phosphoro-thioate has been made in the region 0.1 to 8 mol dm^{-3}HCl. Hydrolysis was studied by determining the rates which were measured from the rates of appearance of inorganic phosphates by Allen's method[20]. Concentration of the ester used in kinetic run was 5×10^{-4}mol dm^{-3}as a result of which first order rate coefficient was obtained. It is shown that mostly monoester show optimum rates at about 4mol dm^{-3} HCl, but this monoester show maximum rates at 7mol dm^{-3} HCl. Monoester on acid hydrolysis in the range 0.1 to 8mol dm^{-3}HCl shows an enhancement in the rate with the increase in acid molarity up to7moldm^3. It may noticed , however that the entire acid range is not solely governed by the conjugated acid form of the monoester calculated rates indicates that the substrate do not show complete protonation up to high acid molarity[7 mol dm^{-3}], where the maximum appears. Kinetic runs was made at different ionic strength which was maintained by a proportionate mixture of NaCl & HCl .

Some interesting result of effect of ionic strength on the rate of hydrolysis reactions are summarized below :

1] Monoester under goes hydrolysis in the acid region via both neutral & conjugate acid species.
2]The specific acid catalysis is constant.
3] Contribution by neutral rates to the overall rate of hydrolysis is in increasing order.
4] The effect of ionic strength is large, positive.
5] Rate law may be formulated as:

$$K_e = .955 \times 10^{-3}\ C_H^+.\ \exp.[2.303\times 0.00]\ \mu + 2.37\times 10^{-3},\exp.[2.303\times 0.2]\mu$$

Table-1: Hydrolysis of Mono-S-isobutyl phosphoro-thioate [65^0C] at constant ionic strength:

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Ionic strength [μ]	Composition, HCl/NaCl	$10^3 k_e$[absd.] min^{-1}
1	.2/.8	4.100
1	.4/.6	4.250
1	.6/.4	4.500
2	.4/1.6	6.550
2	.6/1.4	6.750
2	.8/1.2	6.950

Table-2: The rates of hydrolysis are shown to be changed in increasing order when a series of kinetic runs were made at different temperature:

Temperature,T^0K [abs.]	3moldm^{-3}, $10^3 k_e$ [min^{-1}]	5 moldm^{-3}, 10^3[min^{-1}]	
328	2.400	4.416	
338	3.820	7.120	
348	6.383	11.61	
358	10.00	17.78	

IV. EXPERIMENTAL SECTION

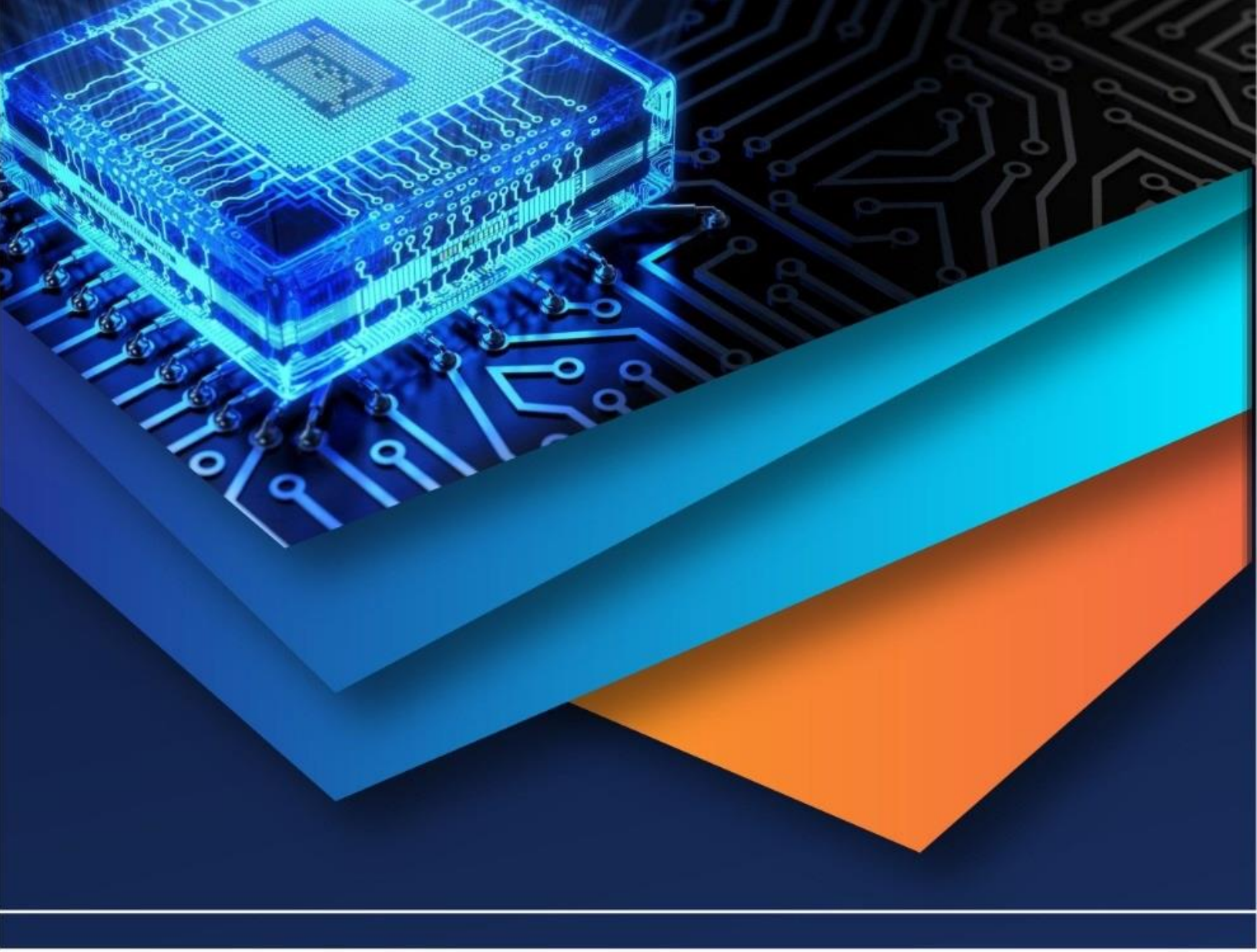
The experimental methods of preparation of thiophosphate of ortho phosphoric acid under taken for kinetic study have been operated under following operations:

1]Preperation of Mono-S-isobutyl phosphoro-thioate ester.
2] Colorimetric estimation of inorganic phosphate.
3] Kinetic measurement.

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