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Kinetic Study Of Mono-3-Chloro-2-Methyl-Aniline Phosphate In Buffer Medium

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Abstract :- The kinetics of hydrolysis of Mono-3-Chloro-2-methyl aniline phosphate has been carried out in buffer solution at 50°C in the pH range 0.00 to 7.46. The rate of reaction increases with increase in pH up to 4.17. The maximum value at pH 4.17 is due to hydrolysis via mononegative and neutral species . The neutral and monoanion have been found to be reactive . The experimental and theoretical rate values are in good agreement .The nature of molecularity of hydrolytic reaction has been decided on the basis of temperature and solvent effect . The monoester involves P-N bond fission, which is strengthened by comparative kinetic rate data .
Keyword:-Kinetics,Buffer medium,hydrolysis,P-N bond fission Mono 3-Chloro-2-Methyl aniline.

Introduction :-

Organophosphorus compounds are the essential constituents of protoplasm and play important role for maintenance of life, e.g.nucleotide, genetic informations, metabolic intermediate phosphates, photosynthesis, saccharide synthesis, nucleic acid helicesand involvement in co-enzyme system.Organophosphorus compounds play a key role in life processes, in living organism for growth, development and maintenance of all plants and animals.These compounds have been used for the veriety of purposes as fertilizers,smoke generation,additives for petroleum and corrosion inhibitors, selective extractants for metal salts from ores and chemical warfare agents .They play a vital role in photosynthesis and conversion of sugar in to starch in plants and also involved in nitrogen fixation . Many organophosphorus compounds are commonly used as insecticides even through they display extreme toxicity to humans. Phosphates and phosphoramidates are widely used as prodrug moieties to enhancewater solubility or therapeutic potential of a parent drug.Recently two nucleoside anologus 3-azidotoxithymidic(AZT) and 2-3,dideoxycytidin(DDC), havebeen therapeutically used for the treatment of acquired immune deficiency syndrome (AIDS) patients.

Experimental -:

Mono-3-Chloro-2-Methyl aniline phosphate (Ba-Salt) has been prepared from 3-chloro-2-methyl-nitro aniline and phosphorus pentaoxide by the method described earlier.Kinetic study of the hydrolysis of Mono-3-chloro-2-methyl aniline phosphate is carried out 50°C employing $5x10^{-4}$ mol dm^{-3} solution of the monoester in aqueous medium. The buffer solutions were maintained using appropriate mixture of KCl ,COOH C_6H_4.COOH NaOHand H_3BO_3. Allen's modified method was used for spectrophotometric determination of inorganic phosphate . All the chemical during work used were of A.R. grade .

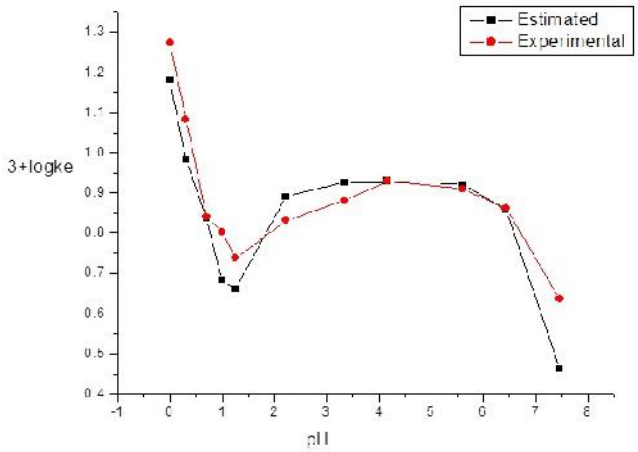


Fig-: pH log rate profile for the hydrolysis Mono-3-chloro-2-methyl-aniline phosphate at 50^{o}C

Results and Discussion -:

Hydrolysis of Mono-3-chloro-2-methyl aniline phosphate has been studied at 50^{o}C in the pH range 0.00 to 7.46 using suitable buffers . **Fig. 1** shows the pH log rate profile in which theoretical rates closely agreed with those observed rates. The rate of reaction increases with the increase in pH up to 4.17. The maximum value at pH 4.17 is due to hydrolysis via mononegative species and dissociation of neutral species After pH 4.17 the fall in rates is due to the inertness of the dinegative species.A slight deviation of the experimental rate in pH range 0.00 to 2.00 has been found to be due the incursion of the neutral species Similar nature of hydrolysis observed in the case of ortho and p-methoxy phenyl dihydrogen phosphate, p-ethoxy phenyl dihydrogen phosphate monoester.Neutral & mononegative rates can be represented as :

$k_N = k_{No}\, N / N + M$ ……(1)
$k_M = k_{Mo}\, M / M + N$ ……..(2)

where k_{NO} is specific neutral rate , k_{Mo} (specific mononegative rate) is experimental rate at pH 4.17 and N/N+ M and M/M+ N are the fraction of neutral and mononegative species respectively .The results summarized in Table -1show that there is close agreement between calculated and experimental rates . The value of specific neutral rates (k_{NO}) was determined from the relation:

$k_e = k_{MO}\,.\, M/M + N + k_{NO}\,.\, N/ N + M + k_H^{+}.\, C_H^{+}$ …… (3)

Where k is experimental rate. There is a good agreement between values of specific neutral rate k_{NO} determined by equation (3) is1.21x 10^{-3} min^{-1} at different pH from 0.00 to 1.00 and from ionic strength data 1.21 x10^{-3} min^{-1} .

It is clear from Table -1 that in the pH range 0.00 to 1.00; hydrolysis governs by neutral conjugate and mononegative species. In the pH range 1.00 to 1.24, the reactions are via neutral and mono negative species. In the pH range 1.24 to 7.46 only mononegative species are reactive.

Kinetic rate laws for the hydrolysis of Mono-3-chloro-2-methyl aniline phosphate may be represented as :

(1) In the pH range 0.00 to 1.00
$k = k_H^{+}.C_H^{+} 8.51 \times 10^{-3}\ M / M + N + 1.21 \times 10^{-3}\ N / N + M$

(2) In the pH range 1.00 to 1.24
$k = 8.51 \times 10^{-3}\ M / M + N + 1.21 \times 10^{-3}\ N / N + M$

(3) In the pH range 1.24 to 7.46
$k = 8.51 \times 10^{-3}\ M / M + N$

A change over from water to aqueous dioxane increases the rate showing dispersion of changes in the transition stateas shown is Table -1 Arrhenius parameters for hydrolysis via neutral and mono-negative species summarized in Table-2 are in favour of a bimolecular reaction. A comparative kinetic rate data for the hydrolysis of some phosphate monoesters via neutral and mononegative species as shown in Table - 3 and 4 also supports the bimolecular nature of hydrolysis involving P-N bond fission .

The probable reaction mechanism for the hydrolysis of mononegative species and neutral species of Mono-3-chloro-2-methyl-aniline phosphate has been represented.

Table-1 Estimated and Experimental Rates of the Hydrolysis of Mono-3-chloro-2-methyl aniline Phosphate (Ba-Salt) via Neutral and Mononegative Species at Different pH values at 50°C

pH	M/M+N	N/N+M	k_M10^3 (min^{-1})	k_N10^3 (min^{-1})	$k_H+C_H+10^3$ (min^{-1})	k 10^3 (min^{-1}) (Estd.)	k 10^3 (min^{-1}) (Expt.)	3+logk (Estd.)	3+logk (Expt.)
0.00	0.063	0.937	0.536	1.133	14.51	15.43	18.82	1.180	1.274
0.30	0.119	0.881	1.012	1.066	8.63	9.55	12.15	0.981	1.084
0.70	0.253	0.747	2.153	0.903	3.21	6.87	6.93	0.836	0.840
1.00	0.403	0.597	3.429	0.722	2.19	4.84	6.36	0.684	0.803
1.24	0.540	0.450	4.595	0.544		4.59	5.46 15.66* 17.82+ 21.17*	0.661	0.737
2.20	0.915	0.085	7.786	0.103		7.78	6.79	0.891	0.831
3.33	0.993	0.007	8.450	0.008		8.45	7.62	0.926	0.881
4.17	0.999	0.001	8.501	0.001		8.50	8.51 18.35* 22.68+ 31.49**	0.929	0.929
5.60	0.980	-	8.339	-		8.33	8.11	0.921	0.909
6.43	0.850	-	7.233	-		7.23	7.29	0.859	0.862
7.46	0.340	-	2.893	-		2.89	4.33	0.461	0.636

*10% dioxane , + 20% dioxane,** 30% dioxane.

Table-2 Arrhenius Parameters for the Hydrolysis of Mono-3-chloro-2-methyle aniline Phosphate (Ba-salt) via Neutral and Mononegative Species at 50°C

pH	E (Kcal/mole)	A (Sec^{-1})	$-\Delta S^{\neq}$ (e.u.)
1.24	7.321	$3.86x10^6$	43.25
4.17	5.948	$5.38x10^7$	47.17

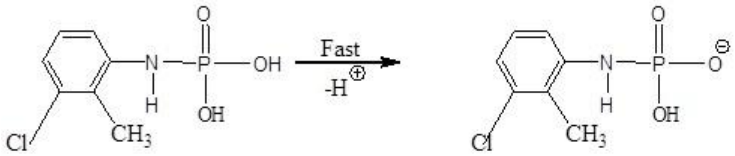
Table-3 Comparative Kinetic Rate Data for The Hydrolysis of Some Phosphate Monoesters via Neutral Species .

Sr. No.	Phosphate monoesters	Medium pH	E (Kcal/mole)	$-\Delta S\neq$ e.u.	molecularity	Bond fission
1	2-chloro-5-nitroaniline	1.24	3.38	48.52	2	P-N
2	3-chloro-2-methyle aniline	1.24	7.321	43.25	2*	Present work
3	p-nitro aniline	1.20	11.44	69.57	2	P-N
4	DinitroDiphenyl Amine	1.24	7.59	57.40	2	P-N
5	2,5-Dichloro aniline	1.24	5.03	64.77	2	P-N

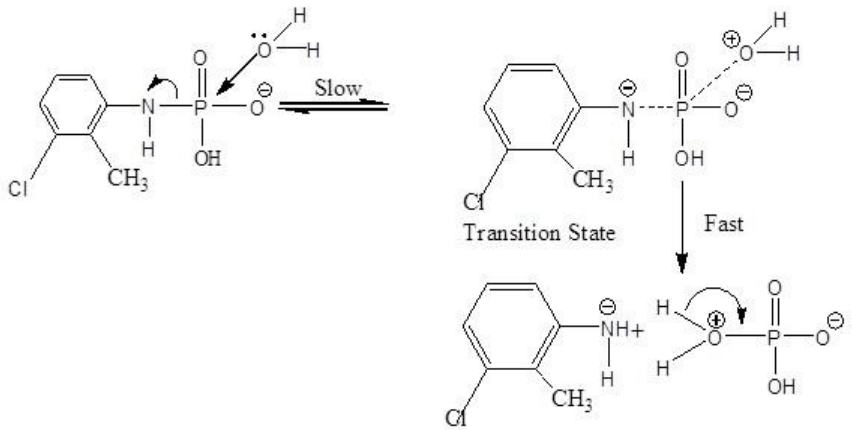
Table-4 Comparative Kinetic Rate Data for the Hydrolysis of Some Phosphate Monoesters via Mononegative Species

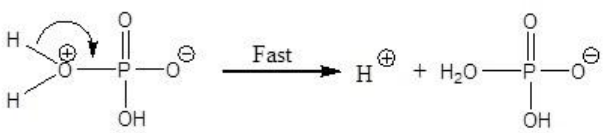
Sr. No.	Phosphate monoesters	Medium pH	E (Kcal/mole)	-ΔS≠ e.u.	Molecularity	Bond Fission
1	Di-isopropyle Aniline	4.17	8.69	54.74	2	P-N
2	p-toluidine	4.17	12.26	31.56	2	P-N
3	O-toludine	5.20	10.05	40.52	2	P-N
4	3-chloro-2-methyl	4.17	5.94	47.17	2	Present Work
5	2-4-dinitro aniline	4.17	13.30	44.40	2	P-N

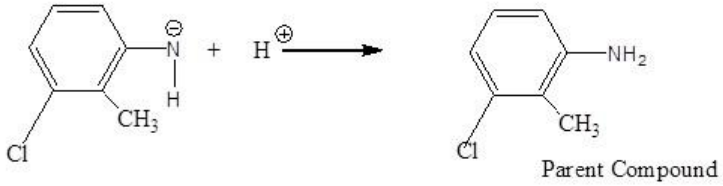
Formation of mononegative species



Bimolecular nucleophilic attack of water on phosphorus via mononegative species SN^2 (P)

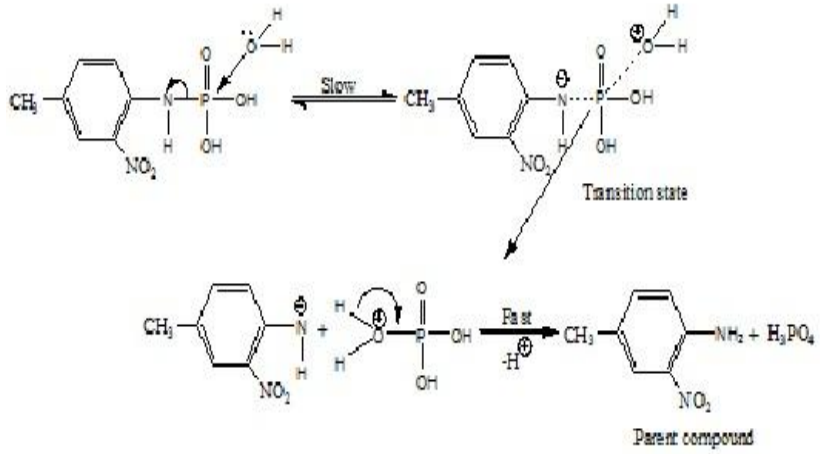






Mechanism via neutral species

Bimolecular attack of water on phosphorus atom of the neutral species SN^2 (P)



Conclusion

The neutral and mononegative species are found to be reactive in Mono-3-chloro-2-methyl-aniline phosphate.The rate of reaction increases with increase in pH up to 4.17 . It may be due to conversion of neutral species into mononegative species.The theoretical rates have been found to be in good agreement with experimental rates.Comparative kinetic rate data and isokinetic relationship plot suggests bimolecular hydrolysis with P-N bond fission.The SN_2 (P) mechanism has been suggested for hydrolysis via neutral and mononegative species.

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