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Kinetics Of Phosphate Esters; A Review

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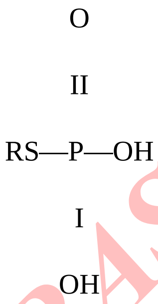
Abstract: Basically the Phosphate esters are synthesized by unified methods of Phosphorelation. The detailed kinetic study of hydrolysis of mono-, di- & tri-esters of ortho-phosphoric acid & their characteristic features could be out lined only after 1950 by the research workers of London, Harvard, Cambridge & California Universities, Even though the kinetic studies had begun in 1940. It was only after this that the hydrolysis of orthophosphates was investigated kinetically. In this paper I present the kinetic details & result of various thiophosphates.

INTRODUCTION

Thiophosphates or phosphorothioate are tetrahedral anions with the phosphorous at the center of the tetrahedran. These Hetrobifunctional crosslinking agents are used widely in protein science for forming covalently –bonded protein- protein complexes & protein small molecule system[1].These can be discuss as;

MONO-ESTERS: Mono-phosphates of o-phosphoric acid are expressed by a general formula;



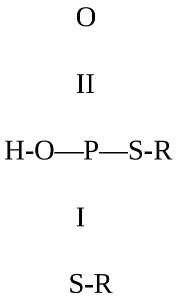
$$\begin{array}{c} O \\ \text{II} \\ RS—P—OH \\ \text{I} \\ OH \end{array}$$

A group of workers namely Bailey and Desjobert examined 1&2 glycerophosphate[2], methyl[5], ethyl as well as hydroxy ethyl phosphates. They found characteristic of monoesters which have maximum rate of P^{H} 4 and are reactive via their mononegative species. The decrease in rate in more acidic region has been taken to indicate the conversion of mono anion in to less reactive neutral species while in alkaline region formation of less reactive dianion has been proposed.

Butcher and Westheirmer[6] the American research workers further carried out studies on 1-methoxy propyl-2-phosphate by ^{18} O Tracer technique and optical methods. Bunton has reviewed reaction of monoesters[8] and the mechanism of different reactive species in variety of conditions. Other aryl esters with proper substituents in their aryl part[10], some allyl [12] and substituted benzyl[13] phosphates have also been kinetically studied. Kinetic study of the modification reactions that generate monothiophosphate disulphide linkages with either 5^{I}-GMPS alone or 5^{I}-GMPS primed RNA as the substrate revealed that the II_{nd} order rate constants increased as the p^{H} was decreased[30].

The ion – conductivity & ion- exchange properties of the unique monothiophosphate solid Zr[HPo35]2.1.5H2O were measured as a function of temp. & the data were evaluated using the model of Boyd. The solid was found to decomposed at higher temp. to form ZrP207, Proton, Sodium ion & Zinc ion mobility & exchange were examined[31].

DI-ESTERS: Diesters are represented by the general formula –



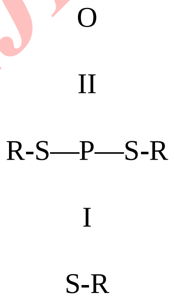
$$\begin{array}{c} O \\ \text{II} \\ H\text{-}O—P—S\text{-}R \\ \text{I} \\ S\text{-}R \end{array}$$

Kinetic study of the diesters of ortho phosphoric acid has not been made much compared to that of monoesters. The first compound studied in detail [7] in University college, London was 'Dimethyl phosphate' molecularity , bond fission and reactive species have been determined to propose various rection path. Disubstituted esters were found to be reasonably stable towards alkali and could be hydrolysed only under drastic conditions. Acid hydrolysis however, was found to proceed more readily.

Plimer& Burch[14] showed the dialkyl phosphates hydrolyse in acid but not in alkali, while diaryl phosphates undergo hydrolysis in both acid and alkaline media. Brown and Todd [15] stressed the presence of a hydroxyl function in proximity to the phosphoryl group as a pre- requisite for alka- liability in dialkyl phosphates, Recently Mhala & coworkers have also studied the hydrolysis of substituted Benzyl[8], Aryl[13]& Allyl phosphate esters[12]. They found acid catalysis in substituted aryl diesters with electron attracting substituents, while the same was absent in mono substituted electron repelling aryl phosphates. After detailed study of disubstituted aryl diesters [10] the observed acid catalysis and also discovered a new reactive species. [16]

The sonolytic degradation of aqueous solution of dimethoate, O,O-Dimethyl S-[2-[methylamino]-2-oxoethyl] dithiophosphate, wasexamined. More than 90% toxicity of dimethoate was reduced with in 45 min. ultrasonic irradiation.Fe^{++} at micro molar level can significantly enhance the sonolytic degradation of dimethoate & effectively reduce the yields of toxic intermediate omethoate[32].

TRIESTERS: Triesters are represented by the general formula –



$$\begin{array}{c} O \\ \| \\ R\text{-}S\text{—}P\text{—}S\text{-}R \\ | \\ S\text{-}R \end{array}$$

The recent investigation on the hydrolytic reaction of trimesters by Cavallier,Plimmer and Burch & Bailly[14] and scott showed the triesters are readily hydrolysed in alkali at room temperature. Blumental and Herbert[18] were the first to study P-O bond cleavage of alkaline hydrolysis of trimethyl phosphate.On this compound the detailed study has given by Vernon, Bunton and Coworkers[19]. They found the rate of hydrolysis of this ester to be much faster than of trimethyl phosphate in 75% dioxan at 35^{0} C. Thian[20] pointed out the first order rate constant for the neutral & acid catalysed hydrolysis of trithiolate & triphosphate ester in 60% aqueous dioxin at 82 ^{0}C. He suggested that there is the involvement of P-S bond fission in the hydrolysis of thiol ester & showed acid catalysis. The unexpected P-S bond rupture of the thio- ester and showed acid catalysis. The unexpected P-S bond rupture of the thio-ester in the acid medium was shown to be due to the greater & smaller bond energies of the C-S & P-S respectively.Synthesis of C-Glycosides from S-Glycosyl phosphorothioates was done by W-Kudelska[22-23].Kinetics of phosphatidylionsitol specific phospholipase C with vericles of a Thiophosphate analogue of phosphatidylinasital was successfully studied by H-Stewart Hendrickson & co –workers[24-25].The new lead potassium thiophosphate KPbPS4 was synthesized by reacting Pb with an in situ formed melt of K2S3,P2S5 & S[26].Synthesis and reaction of O,O-Dibutyl S-alkyl Thiophosphates with cholinesterase was done by G.G.Ol, khovayaR.S.& Others[27-29].

REFERENCES

1.Cavalier, compt. Rend.,127,60[1898]

2. Bailey, M.C. Bull, Soc. Chim., France., [1947],9,340,405.

3. Desjobert,A.Bull Soc. Chim., France., [1947],14,809

4. Desjobert,A. Compt., rend., [1947],224,575.

5. Desjobert,A.Bull Soc. Chem., Bio., 1951,33,42.

6. Westheimer F.H., J. Amer. Chem.. soc. 1955,77,2420.

7. Bunten, C.A.Mhala, M.M., Oldham, K.G. & Vernon, C.A.J. Chem., Soc., 3292[1960].

8. Atherston, F.R. Special Publication no. 8, The chemical soc. London 66, [1957]

9. Mhala, M.M. Patwardhan, M.O. & Kasturi G., India J. Chem. 7[1969] 149

10. Mhala M.M. Holla, C.P. Kasturi, G & Gupta K. Indian J. Chem. 8, 51-56, 336 [1970]

11. Prabha S. Ph. D. Thesis, Jiwaji University, Gwalier[1971]

12. SaxenaS.B. Ph.D. Thesis Jiwaji University, Gwalier[1968]

13. Mhala N.M. & Kavadiker, V.M. Unpublished data.

14. Plimer & Burch, J. chem.. soc. [1959], 279,292.

15.Brown, D.M. & Todd, A.R. J. chem.. soc. [1952]52.

16. M.M.Mhala & Sashiprabha, J.I.C. , Vol.8 Nov. 1970, PP. 972-76

17. Baily & Gaume, Ibid [1936] 3

18. Blumenthal & Herbert, Trans, Faraday soc. [1945]41, 611

19. Barnard, P.W.C. Bunton, C.A. Liewellyn, D.R., Vernon , C.A. & Welch, V.A.J. Chem. Soc. [1961] 2760

20. Thain, E.M. Private communication.

21. Hudson & Keay, J. Chem. Soc. [1956], 3629

22. Z. Natar forsch 57b, 243-247 [2002]

23. W. Kudelska, Cabohydrs. RES, 329[3] , 687[2000]

24. St. Olaf Collage, Nortelfeld, MN 55057-1098, USA[1999]

25. I.A.S.B.S. Gava Zanjan 45159-195[2002]

26. Solid State Sciences ISSN12293-2558 vol.8 no.1, pp.59-63 [2006]

27. Academy of Sciences of the USSR Mascow no. 1 pp. 194-197[2007]

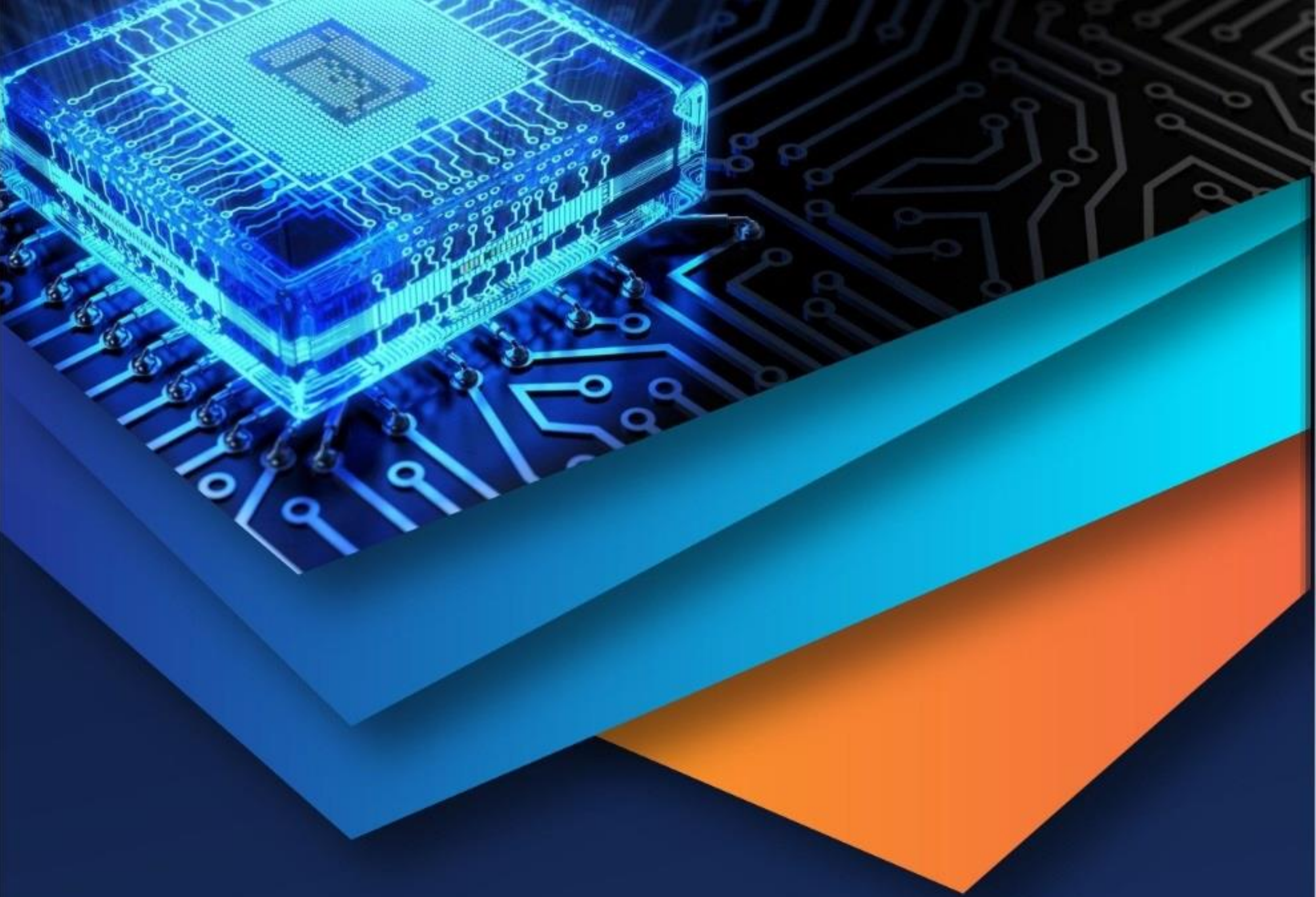
28.W. Kudelska , polish J. of Chemistry71, 1548, [1997]

29. W.Kudelska, Z.Naturforsch, 63b, 1277[2008]

30.WuCw,EderPS, GopalanV, BehrmanEJ: Bioconj. Chem.2001 Nov.-Dec.12[6]842-4

31.I.A.Stanina, A.D. Aliev, P.K.Dorhout & A.B. Yaroslavtsev, Inorg. Chem. 2004,43[22],PW7141-7145

32. Yao JJ, HoffmannMR, GaoNY, Zhang Z, Lil, Water Res.2011 Nov.15, 45 [18] 5886-94



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