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Kinetics Of Phosphate Esters; A Review

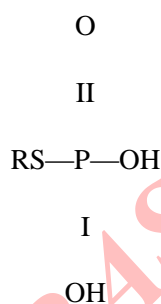
Dr. Nimisha Misra

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 tetrahedron. These Hetrobifunctional crosslinking agents are used widely in protein science for forming covalently –bonded protein- protein complexes & protein small molecule system¹. These can be discuss as;

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

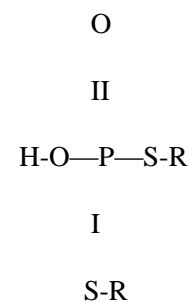


A group of workers namely Bailey and Desjobert examined 1&2 glycerophosphate², methyl⁵, ethyl as well as hydroxy ethyl phosphates. They found characteristic of monoesters which have maximum rate of P^{H} 4 and are reactive via their mononegative species. The decrease in rate in more acidic region has 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 Westheimer⁶ 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 monoesters⁸ and the mechanism of different reactive species in variety of conditions. Other aryl esters with proper substituents in their aryl part¹⁰, some allyl¹² and substituted benzyl¹³ phosphates have also been kinetically studied. Kinetic study of the modification reactions that generate monothiophosphate disulphide linkages with either 5¹-GMPS alone or 5¹-GMPS primed RNA as the substrate revealed that the II_{nd} order rate constants increased as the p^{H} was decreased³⁰.

The ion – conductivity & ion- exchange properties of the unique monothiophosphate solid $\text{Zr}[\text{HPo35}]2.1.5\text{H}_2\text{O}$ 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 examined³¹.

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



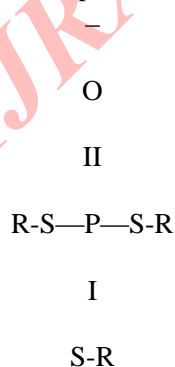
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Kinetic study of the diesters of ortho phosphoric acid has not been made much compared to that of monoesters. The first compound studied in detail⁷ in University college, London was 'Dimethyl phosphate' molecularity, bond fission and reactive species have been determined to propose various reaction 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 & Burch¹⁴ showed the dialkyl phosphates hydrolyse in acid but not in alkali, while diaryl phosphates undergo hydrolysis in both acid and alkaline media. Brown and Todd¹⁵ stressed the presence of a hydroxyl function in proximity to the phosphoryl group as a pre-requisite for alkali-lability in dialkyl phosphates. Recently Mhala & coworkers have also studied the hydrolysis of substituted Benzyl⁸, Aryl¹³ & Allyl phosphate esters¹². 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 diesters¹⁰ 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, was examined. More than 90% toxicity of dimethoate was reduced within 45 min. ultrasonic irradiation. Fe^{++} at micro molar level can significantly enhance the sonolytic degradation of dimethoate & effectively reduce the yields of toxic intermediate omethoate³².

TRIESTERS: Triesters are represented by the general formula



The recent investigation on the hydrolytic reaction of trimesters by Cavallier, Plimmer and Burch & Bailly¹⁴ and Scott showed the triesters are readily hydrolysed in alkali at room temperature. Blumental and Herbert¹⁸ were the first to study P-O bond cleavage of alkaline hydrolysis of trimethyl phosphate. On this compound the detailed study has been given by Vernon, Bunton and Coworkers¹⁹. They found the rate of hydrolysis of this ester to be much faster than of trimethyl phosphate in 75% dioxan at 35°C. Thian²⁰ pointed out the first order rate constant for the neutral & acid catalysed hydrolysis of trithiolate & triphosphate ester in 60% aqueous dioxin at 82°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-Kudelska²²⁻²³. Kinetics of phosphatidylcholine specific phospholipase C with vesicles of a Thiophosphate analogue of phosphatidylcholine was successfully studied by H-Stewart Hendrickson & co-workers²⁴⁻²⁵. The new lead potassium thiophosphate KPbPS4 was synthesized by reacting Pb with an in situ formed melt of K2S3, P2S5 & S²⁶. Synthesis and reaction of O,O-Dibutyl S-alkyl Thiophosphates with cholinesterase was done by G.G.Ol, Khovaya R.S. & Others²⁷⁻²⁹.

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