iJRASET
International Journal For Research in Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 3 **Issue:** IV **Month of publication:** April 2015

DOI:

www.ijraset.com

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Volume 3 Issue IV, April 2015
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

Recent Advances of Reactivity and Importance of Thio-phosphates in Chemical Science

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Abstract: ***The study of various re-activities of organic phosphates is gaining a great importance due to their vast industrial applications in the field of medicine, Lubricants, Bio-chemistry, Agriculture and Engineering. Quantitative reactions of the phosphate esters being often met with in various organo-phosphorus compounds are of interest for many scientific disciplines. This paper focused on various re-activities & importance of Thio-phosphates recently presented in various fields.***
Key words: Organic phosphates, importance, industrial applications, medicine, lubricants, bio-chemistry, agriculture.

I. INTRODUCTION

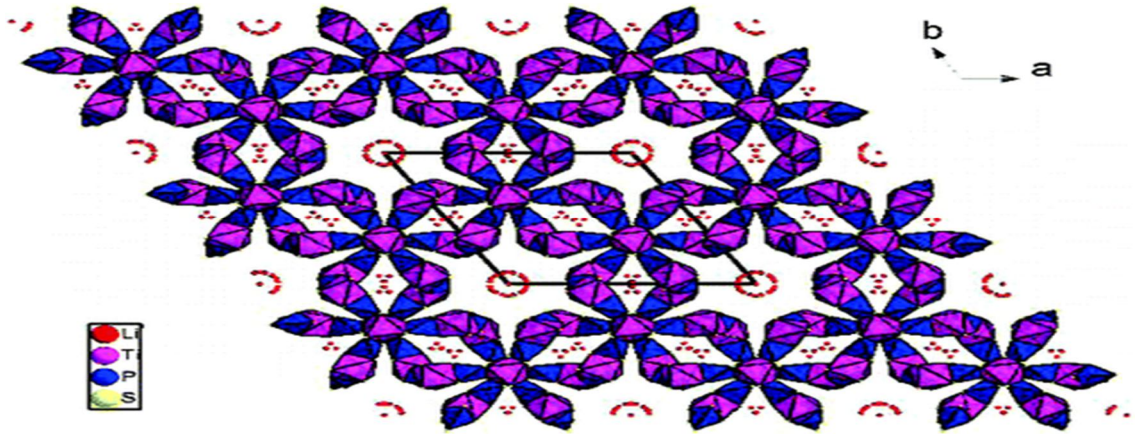
Thiophosphate is a family of compounds and anions with the general chemical formula

$PS_{4-x}O_x^{-3}$ x= 0,1,2,3,

Phosphate esters have found industrial applications due to their overall stability, especially in the presence of oxygen. The ability to exchange oxygen for sulfur and to easily include a variety of substituent groups has led to a wide range of applications as fire retardants, environmentally degradable pesticides, surfactants and brighteners in detergents. The multiple industrial uses have led to the commercial availability of a wide range of phosphates esters with different properties& reactivities. The phosphate esters which were known for many years have been found to play an important role in various chemical reactions particularly in bio-chemical reactions. Recent investigations on nucleotides have added their importance in biochemistry as vital part of the living cell. Thio-phosphates plays an important role in the metabolism & photosynthesis of carbohydrates & in the most important synthesis of nucleotides. Due to their large practical applications in the field of medicine, agriculture , engineering & various other areas the reactivities of phosphate esters have been the subject of intensive studies.

II. REVIEW

Y. kim, N.Arumugam, John B.G[1]. Presented a 3D framework structure of a new Lithium Thiophosphate, $LiTi_2[PS_4]_3$, as Lithium Insertion Hosts.

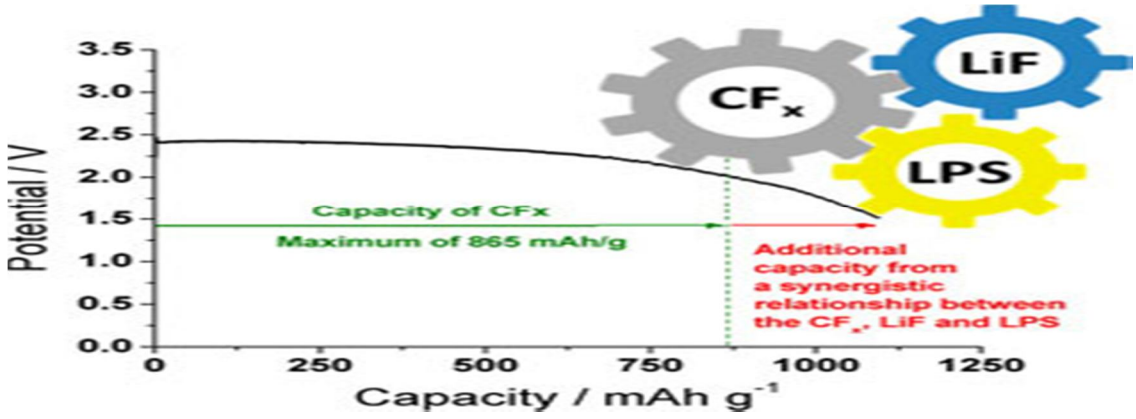


O. Ridge, T.[2] have developed a new & unconventional battery . Chemistry aimed at producing batteries that last longer than previously thought possible. The team demonstrated the new concept in a Lithium carbon fluoride battery considered one of the best single use batteries because of its high energy density, stability & long shelf life.When ORNL researchers incorporated a solid

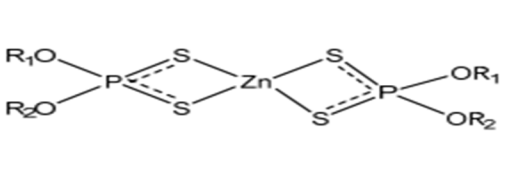
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lithium thiophosphate electrolyte, the battery generated a 26% higher capacity than what would be its theoretical maximum if each component acted independently. The increase explaine Liang is caused by the cooperative interactions between the electrolyte & cathode.

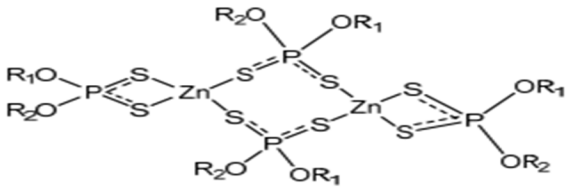
As the battery discharges, it generates a lithium fluoride salt that further catalyzes the electrochemical activity of the electrolyte.



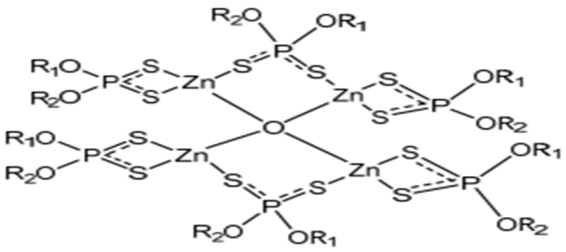
F.Farjadian[3] explain the synthesis of phosphoro-thiols using thio-phosphate salts. Organic phosphates compounds have found a wide range of application in the areas of industrial, agricultural & medicinal chemistry owing to their biological & physical properties as well as their utility as synthetic intermediate & the synthesis of phosphate esters is an important objective in organic synthesis, since they have found use in the preparation of biologically active molecules & also versatile intermediate in synthesis of amides & esters. They report a new method for the preparation of phosphoro- thioates by reaction of diethyl phosphate with alkyl halides in the presence of a mixture of ammonium acetate /s/alumina irradiation which produces high yields of phosphoro – thioates. David W.[4] explain additives in automobile enzines containing esters include aromatic phosphate such as tricresyl phosphate, alkyl phosphate esters such as tributyl phosphate , thiophosphates & metal containing phosphate esters such as Zink di alkyldithio-phosphates [ZDDP] .ZDDP is applicable as antiwear additive.



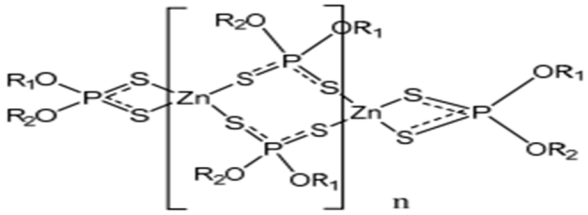
Monomeric ZDDP



Dimeric ZDDP



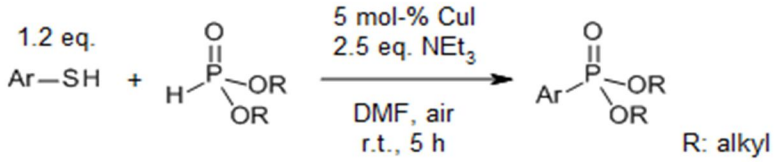
Tetrameric form of ZDDP



Polymeric form of ZDDP

B.Kaboudin[5] launches a simple & efficient method for the preparation of thio-phosphates from benzene-thiols involves Copper [I] iodide catalyzed coupling of thiols with H-Phosphonates in the presence of triethyl amine. The reaction proceeds effectively via an aerobic dehydrogenative coupling to afford the corresponding thio-phosphates in good yields.

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C.Neuhausen & Stephan T. [6] presented a new ternery compoundsUP_2S_6,UP_2S_7,$U[P_2S_6]_2$& $U_3[PS_4]_4$ were prepared from uranium metal, phosphorus pentasuphide & sulfur at 700^0C. It consist of central uranium [IV] atoms coordinated by $[P_2S_6]^{-4}$ anions.

The mono thio-phosphate analog[7] was synthesized some yrs ago & was shown to be a highly potant activator with a high stability to enzymatic degradation. All seven diastereomers of these analog have been separated and purified, stereochemistry of the two diastereomers of the mono-thioate analog was assigned by enzymetic digestion of the linear dimer as well as direct enzymetic degradation of the cyclic dimers. In addition, the same linear dimer was cyclized to produce a cyclic dimer of known configuration. The correlation between stereochemistry & 31 PNMR chemical shift of the two diastereomers of the mono- thioate was then used to assign configurations of the di-, tri- thio-phosphate analogs. It is difficult to overestimate the importance of nucleoside triphosphates in cellular chemistry . They are the building blocks for DNA , RNA & important sources of energy modifications. These biologically important organic molecules with fluorine[8] are of great interest to chemists & biologists because the size & electro negativity of the fluorine atom can be used to make defined structural alterations to biologically important molecules. The progress in the field of modified tri-phosphates was limited by the lack of synthetic methods allowing to access bisCF_2 substituted nucleotide analog , one of the most interesting classes of non hydrolysable nucleotides, These compounds have correct polarity & the smallest possible steric perturbation compared to natural nucleotides , No other known nucleotide have these advantages , making bisCF_2 – substituted analogs unique. They report a concise route for the preparation of Litherto unknown highly acidic & polybasic bis[difluoro methylene] triphosphoric acid. New synthesis & reactions of phosphonates presented by Rebekah M.R. [9] . phosphonate moieties in particular have broad applications including their use as reagents in the Horner- Wads worth –Emmons Olefination reactions, a widely used synthetic strategy. As an alternatives to the often harsh conditions required for phos-phonate synthesis , a mild & versatile one flask protocol has been developed in which a benzyl alcohol can be directly converted to the diethyl benzyl phosphate ester The new phos-phonate methodology has been utilized successfully on allylic, heterocyclic & both electron poor & rich benzylic systems. It provide good yield.[P-based methodology]

N.V. Venkatraman [10] explained the functionalization of the internal surfaces of layered cadmium thiophosphate with cationic surfactants. Ion exchange intercalation of the cationic surfactant acetyl tri-methyl ammonium in layered $CdPS_3$ leads to the formation of an intercalated bilayer within the galleries, there by converting several uncharged organic guest molecules were found to be solubilized in the intercalated bilayer host.

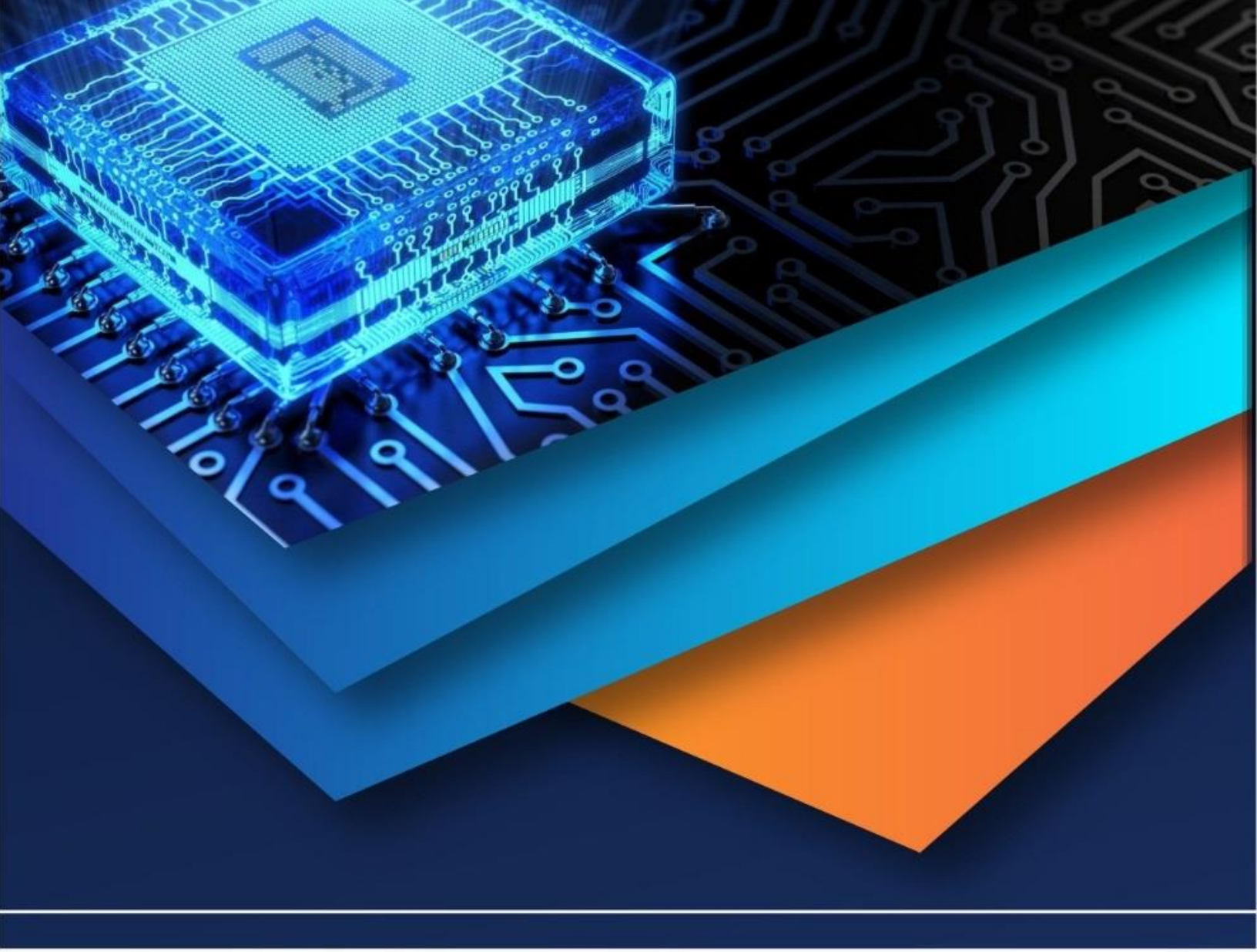
III. CONCLUSIONS

In the recent studies of thiophosphates the stress is laid on the reactivity & applications of the Thio-esters. We also get the knowledge of structure & synthesis of various thio-phosphates & more information of involvement of thiophosphates in various fields, which could be a revolutionary mile stone to future inventions.

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