

PREPARATION AND PROPERTIES OF THE LAYERED ORGANIC DERIVATIVES OF
 γ -ZIRCONIUM PHOSPHATE, $Zr(CH_3-(OCH_2CH_2)_n-OPO_3)(HPO_4)$ ($n=1-3$)

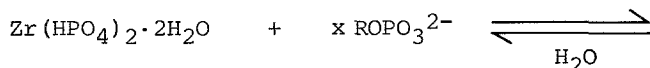
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ABSTRACT. New kinds of organic derivatives of layer structured γ -zirconium phosphate $Zr(HPO_4)_2 \cdot 2H_2O$ are prepared by the exchange of the interlayer phosphate groups with phosphoric ester groups having oxyethylene chains, $CH_3-(OCH_2CH_2)_n-OPO_3^{2-}$ ($n=1-3$). Half of the interlayer phosphate groups are exchanged topochemically, the oxyethylene chains being grafted onto the phosphate layers through the ester bonds in the resulting derivatives. The derivatives behave like crown ethers, and form complexes with alkali salts of soft base anions such as SCN^- and I^- . Alkali salts of hard base anions such as Br^- and NO_3^- do not form complexes with the derivatives. The alkali iodide complexes of the organic derivatives can be used for the halogen exchange reaction. *n*-Butyl bromide is converted into *n*-butyl iodide in the presence of the alkali iodide complexes. The reactivities for the halogen exchange reaction increase with the number of the oxyethylene units.

1. INTRODUCTION

Zirconium bis(monohydrogen orthophosphate) dihydrate, $Zr(HPO_4)_2 \cdot 2H_2O$, hereafter referred to as γ -zirconium phosphate, is an insoluble inorganic ion exchanger with a layer structure. As shown schematically in Figure 1, the phosphate layer consists of ZrO_6 octahedra lying on a plane and $PO_3(OH)$ tetrahedra situated above and below the ZrO_6 plane. Each tetrahedron shares its oxygen atoms with three different ZrO_6 octahedra. (1)
(2) The hydrogen ions of the interlayer hydrogen phosphate groups are exchangeable with various cations. The water molecules reside in the interlayer space.

In a series of previous papers, we have reported that the interlayer $PO_3(OH)^{2-}$ groups are exchangeable with various phosphoric ester ions of the type $ROPO_3^{2-}$ where R is an organic group such as phenyl, (3) (4) *n*-alkyl, (5) (6) glycol, (7) and others:



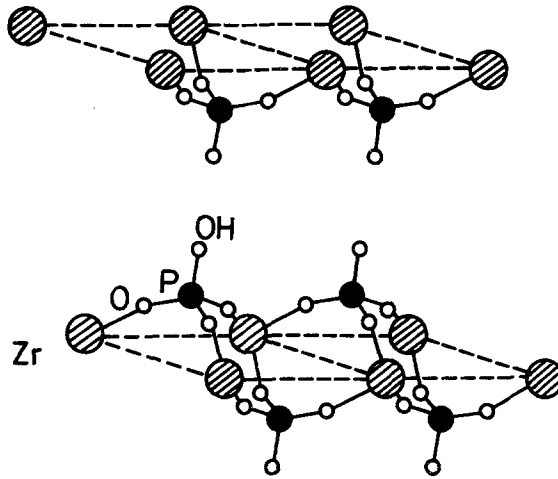


Figure 1. A schematic structural model of γ -zirconium phosphate.

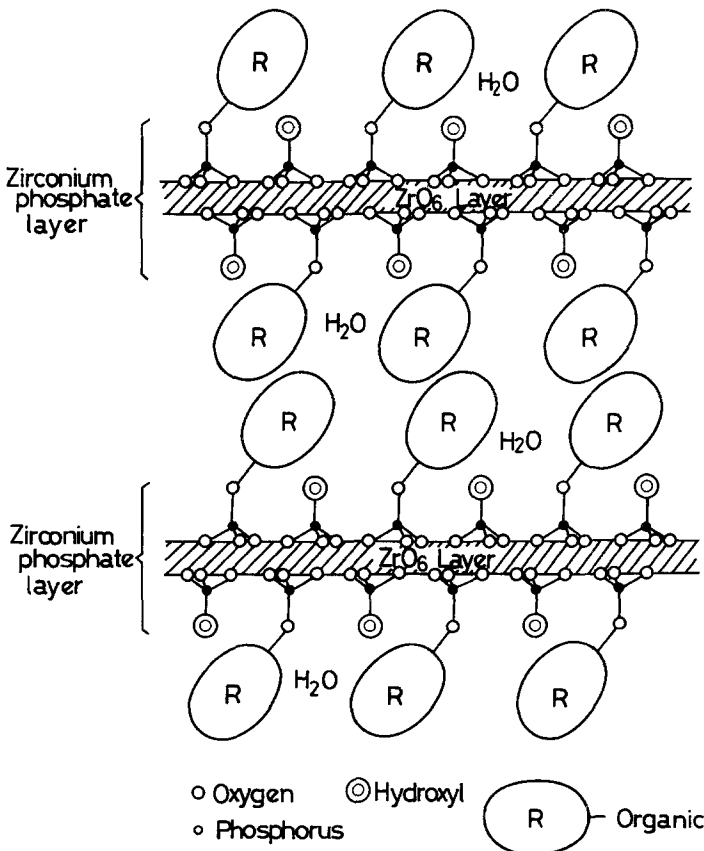
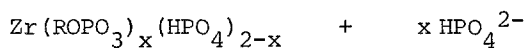


Figure 2. A schematic structural model of the organic derivatives of γ -zirconium phosphate.



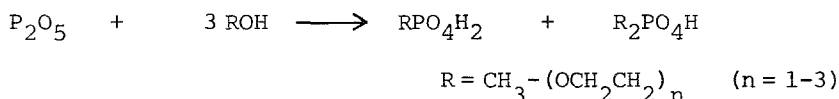
The reaction proceeds topochemically by a diffusion process⁽⁴⁾ and the resulting organic derivatives retain the original layer structure of γ -zirconium phosphate. Such exchange reactions enable us to tailor the interlayer surfaces of γ -zirconium phosphate systematically. A schematic structural model of the organic derivatives is shown in Figure 2.

In the present study, exchanges have been carried out by using phosphoric acid esters having oxyethylene chains, $\text{CH}_3-(\text{OCH}_2\text{CH}_2)_n-\text{OPO}_3\text{H}_2$ ($n=1-3$). It has been found that the resulting organic derivatives of γ -zirconium phosphate behave like crown ethers, forming complexes with various alkali thiocyanates and iodides.

2. EXPERIMENTAL

2.1. Materials

γ -Zirconium phosphate was prepared according to the method described previously.⁽¹⁾ Three kinds of phosphoric acid esters $\text{CH}_3-(\text{OCH}_2\text{CH}_2)_n-\text{OPO}_3\text{H}_2$ ($n=1-3$) were prepared by the reaction of the monomethyl ethers of mono-, di-, and tri-ethylene glycols with phosphorus pentoxide as follows: the respective monomethyl ether (0.33 mol) was diluted with 30 ml of dimethyl ether and added dropwise to 0.11 mol of phosphorus pentoxide (15 g) dispersion in 30 ml of dimethyl ether with stirring and cooling in an ice bath. The mixture was allowed to come to room temperature and to stand for 24 h with stirring, followed by removal of the solvent by evacuation at 40°C. The resulting products were mixtures of the mono- and di-esters with a trace amount of orthophosphoric acid:



Since only the monoester constituent can be involved in the exchange reaction, the resulting mixtures were used without further separation.

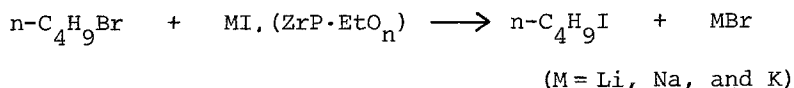
2.2. Exchange Reaction

The exchange of the interlayer phosphate ions with the phosphate ester ions were carried out by a similar procedure described elsewhere:^{(3) (5)} the respective mixture of mono- and di-esters (about 20 g) was dissolved in a 100 ml mixture of equal volumes of acetone and water, into which 2 g of γ -zirconium phosphate was dispersed and heated for 24 h under reflux at a pot temperature of 70°C. The solution was renewed and the refluxing was repeated to assure the completion of the exchange reaction. The dispersed solid was separated by filtration, washed with acetone and air dried. The derivatives obtained by the above exchange reactions with the phosphoric acid esters $\text{CH}_3-(\text{OCH}_2\text{CH}_2)_n-\text{OPO}_3\text{H}_2$ ($n=1-3$) are referred to as $\text{ZrP}\cdot\text{EtO}_n$ ($n=1-3$), respectively.

2.3. Complexes with Alkali Salts

The derivatives $ZrP \cdot EtO_n$ were dispersed in aqueous solutions containing varied amount of alkali salts MX ($M = Li, Na, K,$ and Cs ; $X = SCN, I, Br,$ and NO_3), and then evaporated to dryness at $90^\circ C$ together with the salts. The basal spacings of the dried samples were measured by an X-ray diffractometer with a nickel-filtered $Cu K\alpha$ radiation in comparison with the spacings of the initial $ZrP \cdot EtO_n$.

Usefulness of the alkali iodide complexes of $ZrP \cdot EtO_n$ in the following halogen exchange reaction was investigated.



The organic derivatives $ZrP \cdot EtO_n$ ($n = 1-3$) (about 0.25 g) were separately mixed with the equimolar amount of the alkali iodide in water. Each mixture was evaporated to dryness at $110^\circ C$ and dispersed in 0.2 g of a n-butyl bromide solution in 1 ml of benzene. The dispersion was heated under reflux at $80^\circ C$, the conversion process of the n-butyl bromide to n-butyl iodide being followed by gas chromatography. The column used for separation was 5% silicone SE-30 on chromosorb W AW DMCS (60-80 mesh) from Gasukuro Kogyo Co..

3. RESULTS AND DISCUSSION

The basal spacings and the compositions of the exchanged products $ZrP \cdot EtO_n$ are summarized in TABLE I. The basal spacings increase with the increase of the number of oxyethylene units of the esters. Figure 3 shows the thermal analysis curves of $ZrP \cdot EtO_3$ measured for a heating rate of $10^\circ C/min$. The first weight loss (W_1) is due to dehydration of the water adsorbed in the interlayer space and the second weight loss (W_2) observed in the temperature range of about 200° to $800^\circ C$ consists of the losses due to the decomposition and oxidation of the interlayer

TABLE I. Basal spacings and compositions of the organic derivatives.

Derivative ($ZrP \cdot EtO_n$)	Basal spacing (\AA)	Composition*)	
		x	m
n = 1	14.8	1.02	0.38
n = 2	17.7	0.82	0.43
n = 3	19.4	0.73	0.33

*) Composition in $Zr(CH_3-(OCH_2CH_2)_n-OPO_3)_x (HPO_4)_{2-x} \cdot mH_2O$

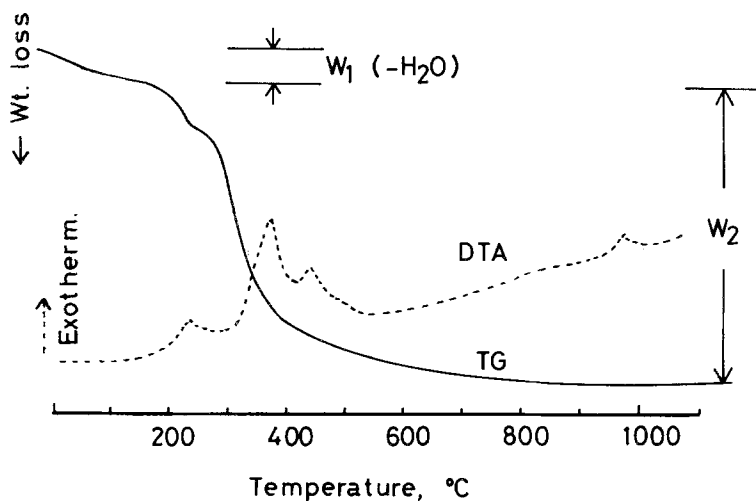


Figure 3. Thermal analysis curves of the organic derivative $\text{ZrP}\cdot\text{EtO}_3$ measured for a heating rate of $10^\circ\text{C}/\text{min}$.

organic groups and the loss due to dehydration accompanied by the conversion of the sample to pyrophosphate ZrP_2O_7 . The other products $\text{ZrP}\cdot\text{EtO}_1$ and $\text{ZrP}\cdot\text{EtO}_2$ also gave similar thermal analysis curves. The compositions in TABLE I were determined on the basis of these weight loss data. The compositions indicate that almost half of the phosphate groups of γ -zirconium phosphate are exchanged with the ester groups as found previously in the other ester exchange reactions of γ -zirconium phosphate, (3)-(7) although in this case there seems to be a tendency that the exchange amount decreases with the increase of the number of the oxyethylene units of the ester groups.

The exchanged products $\text{ZrP}\cdot\text{EtO}_n$ were separately dispersed in aqueous solutions of alkali salts MX ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{and Cs}$; $\text{X} = \text{SCN}, \text{I}, \text{Br}, \text{and NO}_3$) and then evaporated to dryness at 90°C . Figure 4 shows the basal spacings of the samples thus dried with alkali thiocyanates as a function of the molar mixed ratio $\text{MSCN}/\text{ZrP}\cdot\text{EtO}_n$. The basal spacings increase with the increase of the ratio until the ratio approaches about unity except for the case of CsSCN , where the increase of the basal spacing ceases at the lower mixed ratios. This seems to be attributed to the large size of cesium ions. Alkali iodides also formed complexes with $\text{ZrP}\cdot\text{EtO}_n$, the basal spacings similarly increasing with the increase of the mixed ratio $\text{MI}/\text{ZrP}\cdot\text{EtO}_n$. However, the X-ray diffraction patterns of those iodide complexes became broader with the increasing mixed ratios and made it difficult to determine the precise basal spacing values. The basal spacings of the samples dried in the presence of alkali bromides and nitrates were unchanged over a similar range of mixed ratios. This indicates that the alkali bromides and nitrates do not form complexes with $\text{ZrP}\cdot\text{EtO}_n$.

In the derivatives $\text{ZrP}\cdot\text{EtO}_n$, only half of the interlayer phosphate groups are exchanged and the rest of the phosphate groups remain unex-

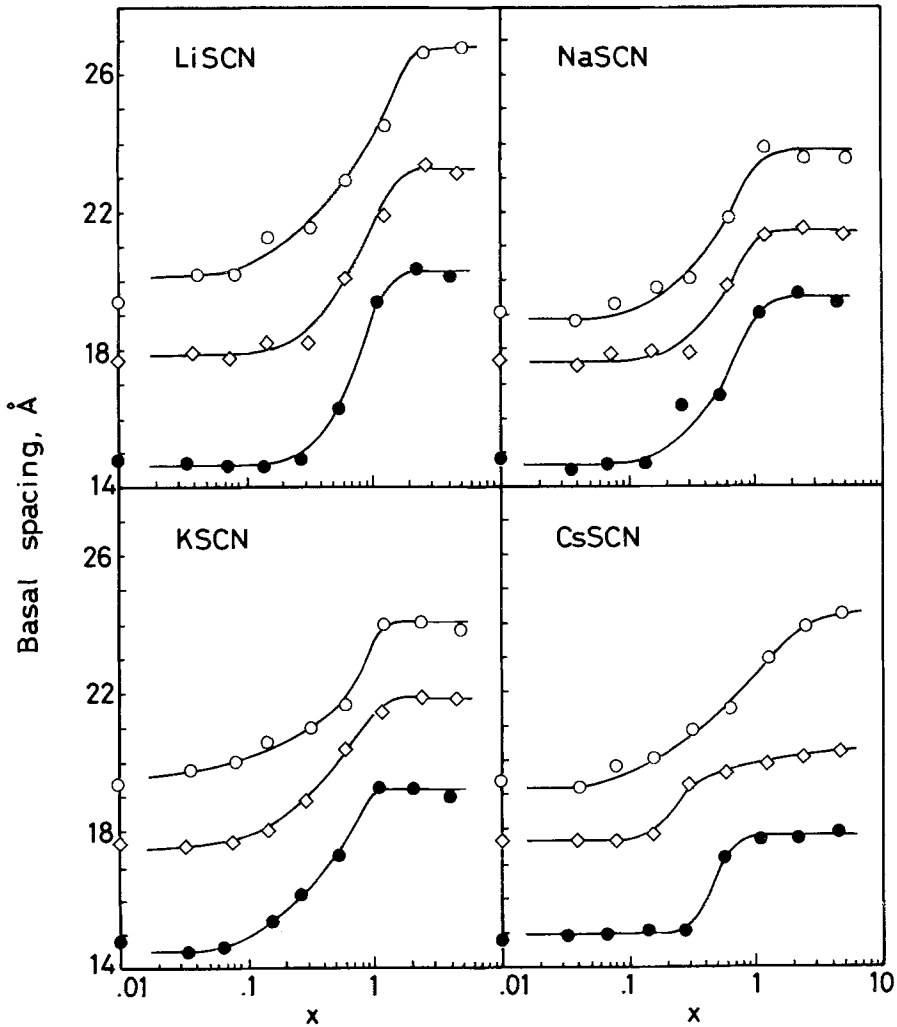


Figure 4. Basal spacings of the derivatives $ZrP \cdot EtO_n$ ($n=1-3$) mixed with alkali thiocyanates MSCN ($M=Li, Na, K, \text{ and } Cs$) in varied molar ratio $x = MSCN/ZrP \cdot EtO_n$.

changed. Although these interlayer phosphate groups remaining bear exchangeable hydrogen ions, an idea that the increase in the basal spacing may be caused by the ion-exchange of the interlayer hydrogen ions with alkali ions is strongly rejected, because the complexes are formed only with the alkali salts of certain kinds of anions. It is evident that the increase in the basal spacing on addition of thiocyanates and iodides can be interpreted in terms of the intercalation of cation-anion pairs, which will induce the configurational changes of the interlayer ether chains, resulting in the increase in the basal spacing of the derivatives.

A schematic illustration of the interlayer arrangement is shown in

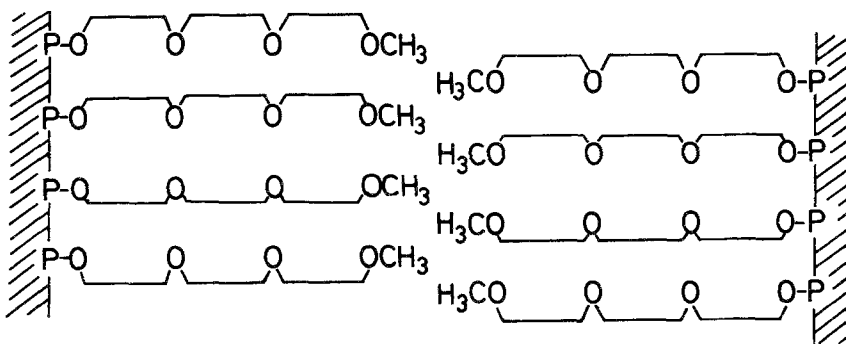


Figure 5. A schematic illustration of the interlayer arrangement of the organic derivatives $ZrP \cdot EtO_n$

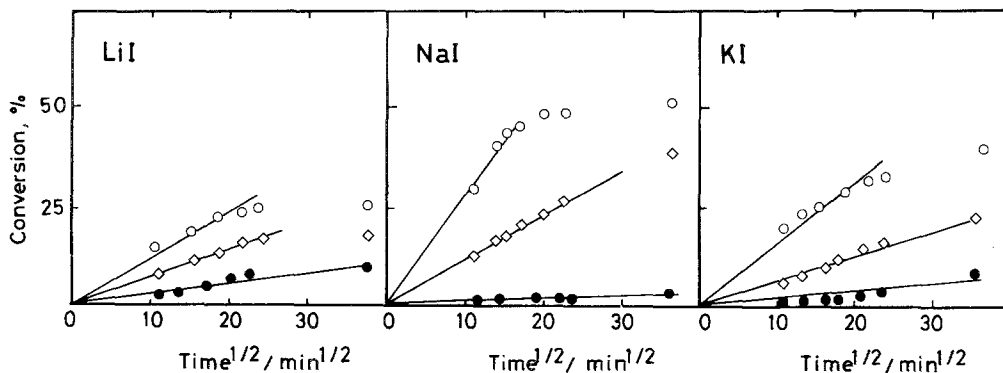


Figure 6. Conversion of *n*-butyl bromide to *n*-butyl iodide at 80°C as a function of the square root of the reaction time (time in minute) in the presence of the complexes of the derivatives $ZrP \cdot EtO_n$ ($n=1-3$) with Li, NaI, and KI: $n=1$ (●), $n=2$ (◇), and $n=3$ (○).

Figure 5. It is likely that the intercalated alkali cations are surrounded by ethereal oxygen atoms like the cations in crown ethers, the iodine and thiocyanate anions being associated with the cations. It is interesting to note that the organic derivatives of γ -zirconium phosphate synthesized in this study can form the complexes only with the alkali salts having soft base anions such as I^- and SCN^- , but not with the salts having hard base anions such as Br^- and NO_3^- .

Halogen exchange reaction of *n*-butyl bromide to the corresponding iodide was investigated by heating *n*-butyl bromide in the presence of alkali iodide complexes of $ZrP \cdot EtO_n$ ($n=1-3$). Figure 6 shows the fraction converted as a function of the square root of the reaction time. Since these reaction systems contain only half the molar

quantity of the respective alkali iodide required for the complete conversion of n-butyl bromide to n-butyl iodide, the figure shows that almost all of the iodide ions added are effectively used in the system of $ZrP \cdot EtO_3 - NaI$. The reactivity in the halogen exchange reaction is in the order of $ZrP \cdot EtO_3 > ZrP \cdot EtO_2 \gg ZrP \cdot EtO_1$ as for the number of the oxyethylene units, and in the order of $NaI > KI > LiI$ as for the kind of alkali iodide. The order in the reactivity seems to indicate that the derivatives having larger number of oxyethylene units are more strongly coupled with alkali cations, and consequently the iodide ions can be in more activated states for the halogen exchange reaction.

The linear relations observed between the fraction converted and the square root of the reaction time indicate that the rate-determining step of the exchange reaction is a diffusion process. It seems reasonable to assume that only the alkali iodides located at the edge sites of the crystallites can take part in the exchange reaction. The rate controlling process is the diffusion of the alkali iodide through the interlayer spaces to the outer edges in order to react.

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