Zirconium Phosphate Ester Interchange Reactions

C. Yolanda Ortiz-Avila and Abraham Clearfield *
Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.

α-Zirconium phosphate was demonstrated to undergo ester-interchange reactions with alkyl phosphate groups. Partial interchange was found to occur in neat alkyl phosphate solutions. However, complete exchange is possible if the interlayer spacing of α-zirconium phosphate is first enlarged by intercalating an amine. The phosphate groups in α-zirconium phosphate are also labile and the supposed lack of reactivity previously reported is due to the inaccessibility of the organic phosphate groups to the interlayer spaces. Ethyl and butyl phosphates were prepared by both ester-interchange and direct precipitation methods. The reagents used contained considerable amounts of dialkyl phosphates and these are incorporated into the products along with monoalkyl phosphate. The β-phosphoglyceric acid (2-hydroxy-3-phosphono-oxypropionic acid) derivative could only be prepared by direct precipitation. This compound exhibits interesting chelation behaviour.

Zirconium bis(hydrogenorthophosphate) hydrate, $Zr(HPO_4)_2{\cdot}H_2O$, is a crystalline, insoluble ion exchanger with a layered structure.[1,2] It has an interlayer spacing of 7.6 Å. A second form of zirconium phosphate, with an interlayer spacing of 12.2 Å, is also known.[3] This compound has the composition $Zr(HPO_4)_2{\cdot}2H_2O$, and while its structure is unknown, the layers are structurally different to those of the monohydrate.[4] This compound will be referred to as γ-ZrP whereas the monohydrate is termed α-ZrP.

Yamanaka and co-workers[5,6] have reported that the hydrogenphosphate groups in γ-ZrP are exchangeable with various phosphate ester ions of the type $ROPO_3^{2-}$ where R is an organic group such as phenyl, n-alkyl, *etc.* [equation (1)].

$$Zr(HPO_4)_2{\cdot}2H_2O + xROPO_3^{2-} \rightleftharpoons Zr(ROPO_3)_x(HPO_4)_{2-x}{\cdot}mH_2O + xHPO_4^{2-} \quad (1)$$

α-ZrP does not behave in a similar fashion. However, Barret *et al.*[7] have shown that facile exchange of the layer phosphate groups of α-ZrP with HPO_4^{2-} takes place in dilute solutions. Thus, theoretically α-ZrP should exhibit ester interchange type reactions, but may be prevented from doing so by virtue of the narrow interlayer spacing which prevents diffusion of the organic phosphate ion to the exchange site.

We have previously demonstrated[8] that ethylene oxide will react with the P–OH groups of α-ZrP as well as with those of γ-ZrP.[9] The supposed lack of reactivity in α-ZrP is in reality lack of access to the exchange sites as its narrow interlayer spacing prevents all but the smallest molecules from diffusing into the crystal interior. The present study was designed to determine conditions under which organic phosphates and phosphonates could be made to undergo ester interchange with α-ZrP. The products obtained were then compared with those prepared by the direct precipitation method.[10]

Experimental

Sample Preparation.—α-Zirconium phosphates of different surface areas and crystallinities were obtained by refluxing a gel in H_3PO_4 of varied concentrations for different lengths of time.[1,11] γ-ZrP and θ-ZrP were prepared according to the methods described previously.[3,12] Ethyl phosphate (ICN Pharmaceuticals, Inc.), butyl phosphate (Pflatz & Bauer), and β-phosphoglyceric acid (2-hydroxy-3-phosphono-oxypropionic acid) barium salts (Sigma) were used without further purification. Preparations of amine[13] and alcohol[14] intercalates are described elsewhere.

Exchange Reactions.—(*a*) Zirconium phosphate or the amine or alcohol intercalate (500 mg) was dispersed into an aqueous phosphate ester solution (about 1 mol dm^{-3}), and heated under reflux for 24 h. The solids were separated by filtration, washed with water (or acetone), and air dried. In those cases where the organic phosphate was insoluble in water, a water–acetone (1 : 1) solution was used.

(*b*) Zirconium phosphate or the amine or alcohol intercalate (500 mg) was dispersed in the pure liquid phosphate ester (50 cm^3) and heated in a round-bottom flask fitted with a condenser in an oil-bath at 100 °C for 24 h. The solid was then filtered off, washed with the appropriate solvent (water, acetone, or a combination of both), and air dried.

Preparation of $Zr(ROPO_3)_x(HPO_4)_{2-x}$ *by Direct Precipitation.*—To the phosphate ester (40 mmol), dissolved in water (100 cm^3), zirconyl chloride (10 mmol) in water (25 cm^3) was added very slowly by means of a dropping funnel while the mixture was magnetically stirred. A white solid precipitated during the addition, and upon completion of the addition the mixture was heated at reflux temperature for 15 h. The solid was filtered off, washed with deionized water until the pH of the filtrate was above 4, then air dried.

Analysis and Instrumental.—*X*-Ray powder diffraction patterns were obtained using a Seifert Scintag automated powder diffraction unit (PAD II) with nickel-filtered Cu-K_α radiation (λ = 1.5418 Å). A Cahn electrobalance was used for thermal gravimetric analysis (t.g.a.). Thermograms were obtained in a nitrogen–oxygen atmosphere at a heating rate of 4 °C min^{-1}. The pH measurements were carried out with a Fisher Accumet model 144 digital pH meter fitted with a Fisher Microprobe combination electrode. The solids were analyzed for C, N, and H by the Center for Trace Characterization at Texas A & M University. The ^{31}P n.m.r. spectra were acquired on a Bruker MSL 300, equipped with a cross-polarization magic angle spinning (c.p.m.a.s.) probe, operating at 121.496 MHz. High-power ^1H decoupling was used during data acquisition. Variable spinning speeds of 2.5–3 kHz were used to assign spinning sidebands. The spectra were accumulated using delays of 20, 100, and 300 s, to determine the integration of the different peaks. The reference was 85% phosphoric acid.

Table 1. Results of ester interchange between α-zirconium phosphate (α-ZrP) and phosphate esters $ROPO_3H_2$

Experiment no.	Form of α-ZrP	R	T/°C	x	Interlayer spacing of product (Å)
I-65	9:48	CH_2CH_3	70	0.04	7.6
I-50	BuAm[a] (9:48)	CH_2CH_3	70	0.54	7.6 (15%) + 10.6 (60%) + 8.3 (25%)
I-51	BuAm (9:48)	CH_2CH_3	100	2.0	11.95
I-25	α-ZrP (2.5:15)	$(CH_2)_3CH_3$	70	0.11[b]	7.6
I-29	θ-ZrP (10:100)	$(CH_2)_3CH_3$	70	0.37	15.8 (20%) + 7.6 (80%)
I-33	BuAm (10:100)	$(CH_2)_3CH_3$	70	0.15	10.5 (20%) + 7.6 (80%)
I-36	BuAm (10:100)	$(CH_2)_3CH_3$	100	1.96[c]	15.95
V-96	α-ZrP (9:48)	$(CH_2)_3CH_3$	100	1.11	15.5 (55%) + 7.6 (45%)
V-98	α-ZrP(9:48)	CH_2CH_3	100	1.93	11.7
I-77	BuAm (9:48)	$CH_2CHOHCO_2H$	70	0.02	7.6
I-83	BuAm (9:48)	$CH_2CHOHCO_2H$	90	0.3	7.6

[a] BuAm means the butylamine intercalate of α-ZrP was used. [b] C, 2.15%; $Zr(O_3POC_4H_9)_{0.14}(HPO_4)_{1.86}\cdot 0.81H_2O$ requires C, 2.15%. [c] C, 24.60%; $Zr(O_3POC_4H_9)_{1.94}(HPO_4)_{0.06}$ requires C, 24.45%.

Table 2. X-Ray diffraction patterns of $Zr(O_3POR)_2$-type α-zirconium phosphate esters

R = C_2H_5		$(CH_2)_3CH_3$		$CH_2CHOHCO_2H$	
d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
11.9	100	15.8	100	14.3	100
5.94	5	7.9	25	7.15	20
4.48	35	5.21	5	4.73	7
3.87	45	4.40	20	4.36	20
3.19	10	3.97	50	3.84	10
2.67	13	3.46	15	3.34	5
2.61	10	2.97	8	3.29	5
		2.66	10	2.64	10
		2.62	10		

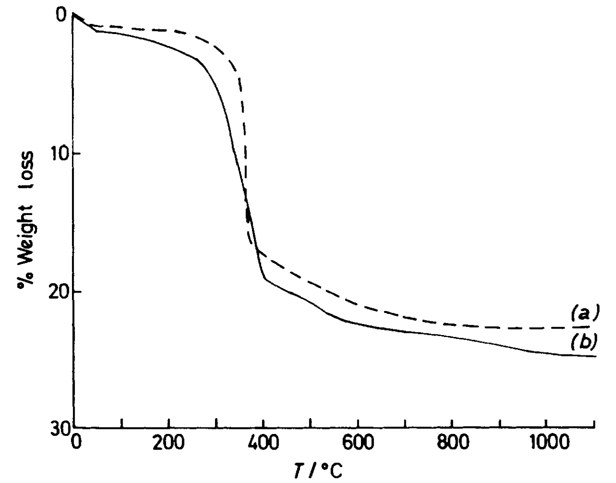

Figure 1. Thermogravimetric weight-loss curves for $Zr(O_3POC_2H_5)_2\cdot xH_2O$ prepared by (*a*) ester interchange in 1 mol dm^{-3} ethyl phosphate and (*b*) direct precipitation

Results

The strategy used to obtain the desired α-ZrP reactivity was to expand the interlayer spacing or increase the surface area of the α-ZrP. This same technique was utilized to obtain polyether derivatives.[8] Higher surface areas can be produced by using less crystalline samples of α-ZrP. For example, if zirconium phosphate in the amorphous gel form is refluxed in 4.5 mol dm^{-3} H_3PO_4 for 48 h the resultant product has a surface area of ~30 m^2 g^{-1} whereas when 12 mol dm^{-3} H_3PO_4 is used the surface area is of the order of 8 m^2 g^{-1}.[11,15,16] In the text and tables, such products will be referred to as α-ZrP(4.5:48).[16] An expanded layer form of α-ZrP, with an interlayer spacing of 10.4 Å, can be prepared by titrating to the half-exchange point with NaOH followed by removal of the Na^+ with acid.[17] The resultant product is a hexahydrate and is generally referred to as θ-ZrP.[18] Another method of expanding the layers is to intercalate a neutral species such as an alcohol[14] or amine.[19] The solids in these various forms were allowed to react with the phosphate esters under conditions indicated in the Experimental section and Table 1. Reactions of γ-ZrP were also carried out for comparison purposes.

The extent of reaction or moles of organic ester bonded to the layers is indicated by the value of x in Table 1. These values were determined from C, H, and N analysis and t.g.a. weight-loss curves. Consider the reactions of ethyl phosphate first. Heating this ester with α-ZrP (9:48) at 70 °C (experiment I-65) did not result in incorporation of ester groups between the layers as the interlayer spacing did not increase. However, the compound as a whole contained 0.04 mol of the organic phosphate. Although the interior of the α-ZrP crystals is not accessible to the phosphate ester, surface phosphate groups are possible sites for ester interchange. The α-ZrP used in experiment I-65 had a surface area of *ca.* 10 m^2 g^{-1} and complete coverage of this surface by ethyl phosphate groups would amount to *ca.* 0.02 mol which is about one half of the observed value. Infrared bands also showed the presence of ethyl groups (2 960, 2 910, 2 940, and 2 880 cm^{-1}).

Ester interchange was facilitated in α-ZrP by first preparing the butylamine intercalate and allowing the intercalate to react with ethyl phosphate. At a reaction temperature of 70 °C (experiment I-50) only 0.54 mol of organic was incorporated and a mixture was obtained. The mixture consisted of some unreacted α-ZrP, about 60% of a partially ester-interchanged product, and *ca.* 25% of an unidentified compound with an interlayer spacing of 8.3 Å. However, upon raising the reaction temperature to 100 °C, complete conversion into the ester phase (I-51) took place. The X-ray diffraction pattern of the ethyl ester phase is given in Table 2 and the t.g.a. curve shown in Figure 1. The first weight loss, which occurred below 100 °C, amounted to 1.45% which is equivalent to the loss of 0.28 mol of water. At about 260 °C organic material began to be lost and this was followed by an abrupt change in slope at about 370 °C signalling the end of this process. The final weight loss, which occurred above 370 °C, is accounted for by the loss of 1 mol of water resulting from the condensation of hydrogenphosphate groups. A small amount of carbon, deposited by the thermal decomposition of the ethyl groups, also burned off at these higher temperatures. The weight losses are summarized by equations (2)—(4) which are in accord with the observed values in Figure 1 to within 1%. Infrared bands for the zirconium ethyl

Table 3. Infrared bands (cm^{-1}) for $Zr(O_3POR)_2$-type α-zirconium phosphate esters

Functional group	R = CH_2CH_3	$(CH_2)_3CH_3$	$CH_2CHOHCO_2H$
H_2O, O–H str	3 650—3 325 w	3 500 w (br)	3 700—3 200 vs
H_2O bend	1 650 w	1 630 w	1 640 s
Alcohol OH	—	—	3 700—3 200 vs
Carboxyl OH	—	—	3 700—3 200 vs
CH_3, C–H, asym	2 979 m	2 965 m	—
CH_3, C–H, sym	2 908 w	2 915 m	—
CH_2, C–H, asym	2 933 w	2 940 m	2 980 w
CH_2, C–H, sym	2 870 w	2 880 m	2 930 w
CH, str	—	—	2 890 w (sh)
CH_3, asym bend	1 445 w	1 468 m	—
	—	1 433	
CH_3, sym bend	1 371 w	1 383 m	—
C=O, str	—	—	1 780, 1 750 s
O–H, bend	—	—	1 325, 1 285, 1 240 s
CH_2, scissors	1 481	1 483 m	1 465 m
		1 478	
CH_2, twist	1 396 w	1 400 m	1 395 s
CH_2, rock	783 mw	748 m	780 s
PO_4 or	1 296 w	1 245 vs	1 200—1 000 vvs
P-OC_2H_5	1 173 s	1 100—910 vs	—
	1 126 vs		
	1 079 vs		
	1 043 vs		

Table 4. Data for organic esters of zirconium phosphate prepared by direct precipitation, $Zr(ROPO_3)_x(HPO_4)_{2-x}$

				x		
Experiment no.	R	T/°C	Time	t.g.a.	*	Interlayer spacing (Å)
V-19A	CH_2CH_3	25	15 h	3.08		12.8
V-19B	CH_2CH_3	100	1 week	1.97		11.8
II-3A	$(CH_2)_3CH_3$	25	15 h	3.69		15.9
II-3B	$(CH_2)_3CH_3$	100	1 week	2.20	2.15	15.9
V-23 or II-86	$CH_2CHOHCO_2H$	25	15 h	1.98	1.93	14.5
V-23 (I-95A)	$CH_2CHOHCO_2H$	70	10 h	1.64	1.63	14.5
I-95B	$CH_2CHOHCO_2H$	100	15 h	1.56		14.4
I-95C	$CH_2CHOHCO_2H$	100	1 week	0.16		7.6

* From elemental analysis.

$$Zr(O_3POC_2H_5)_2{\cdot}0.3H_2O \xrightarrow{50\,^{\circ}C} Zr(O_3POC_2H_5)_2 + 0.3H_2O \quad (2)$$

$$Zr(O_3POC_2H_5)_2 \xrightarrow{260-370\,^{\circ}C} Zr(HPO_4)_2 + 2C_2H_4 \quad (3)$$

$$Zr(HPO_4)_2 \xrightarrow{>370\,^{\circ}C} ZrP_2O_7 + H_2O \quad (4)$$

phosphate are shown in Table 3 and confirm the presence of ethyl phosphate groups in the compound.

In order to confirm that the compound obtained by ester interchange was indeed $Zr(O_3POC_2H_5)_2$ we prepared this same composition by the direct precipitation method (Table 4, V-19B). The *X*-ray powder patterns and i.r. spectra for the ethyl esters prepared by the two different methods were identical. In addition, the t.g.a. curve for V-19B was the same as that shown in Figure 1. However, when the preparation was carried out at room temperature (V-19A) instead of 100 °C a curious result was obtained which will be discussed later.

Zirconium Butyl Phosphates.—A series of ester-interchange reactions was carried out in which the experimental details were similar to those described for ethyl phosphate. In the first example (I-25, Table 1) a high-surface-area α-ZrP was used. At 70 °C only 0.11 mol of butyl phosphate was exchanged presumably for surface phosphate groups. Since the α-ZrP used had a surface area in excess of 100 m^2 g^{-1}, we expect that full coverage would require 0.1—0.14 mol of butyl groups. The result indicates that almost complete surface exchange was attained. When similar experiments were carried out with expandable-layer forms of α-ZrP (I-29 and I-33, Table 1), only partial reaction occurred. Approximately 20% of the θ-ZrP was converted into a butyl phosphate while the remainder reverted to α-ZrP, as shown by the *X*-ray pattern and t.g.a. curve. Even less ester interchange occurred with the butylamine intercalate. The reflection at 10.5 Å is indicative of an amine intercalate with low levels of amine present.[13] Use of alcohol intercalates gave mainly α-ZrP.

Increasing the temperature to 100 °C resulted in a dramatic improvement in the reaction with the butylamine intercalate (I-36). Complete ester interchange was seen to occur (Table 1). The t.g.a. curve, shown in Figure 2(*b*), indicates that no water was present in the compound, probably as a result of the hydrophobic nature of the alkyl chains. A portion of the *X*-ray powder pattern is given in Table 2 and Figure 3(*c*). By way of comparison, a butyl phosphate derivative was prepared at 25 °C by direct precipitation (Table 4, experiment II-3A) from a mixture of zirconyl chloride and butyl phosphate. Its *X*-ray pattern, shown in Figure 3(*a*), indicates a poorly crystallized product. Furthermore, a much greater ratio of organic groups to zirconium than required for $Zr[O_3PO(CH_2)_3CH_3]_2$ was obtained. However, on subsequently heating this derivative on a

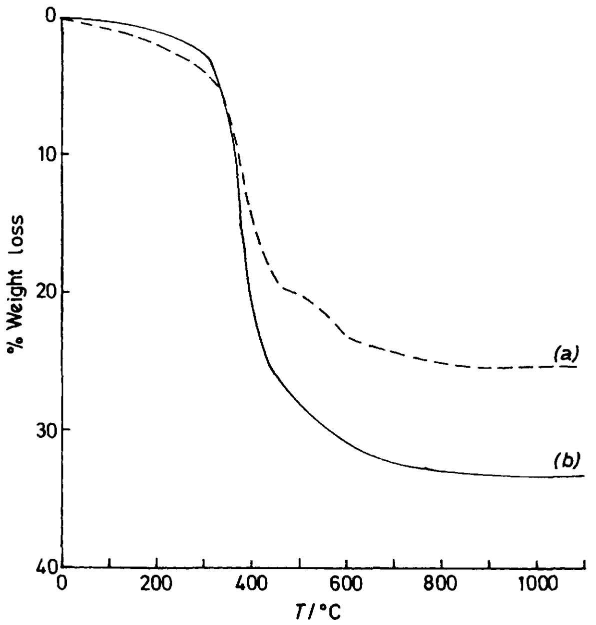

Figure 2. Thermogravimetric weight-loss curves for zirconium butyl phosphate derivatives. Prepared by (*a*) ester interchange of α-ZrP in neat butyl phosphate and (*b*) ester interchange at 100 °C in 1 mol dm^{-3} butyl phosphate from the α-ZrP amine intercalate

water-bath (100 °C) for 1 week, it became more crystalline [Figure 3(*b*)] and the amount of butyl groups approached two per mol of Zr. A similar result was obtained with the ethyl derivative (Table 4, experiments V-19A and V-19B). The probable explanation is as follows. The ethyl and butyl phosphates as purchased contain a considerable amount of dialkyl derivatives. If these preferentially react with the zirconium, a mixed product with a maximum of four alkyl groups per Zr could be obtained. However, on heating for long periods of time in aqueous acidic media, the dialkyl phosphates hydrolyze to yield mainly monoalkyl phosphates and the desired layered products are then obtained.

A listing of the i.r. bands for the 2:1 butyl phosphate derivative (I-36) is given in Table 3. There are very weak bands at 3 500 and 1 630 cm^{-1} for surface water. All the C–H stretching and bending modes of the pendant butyl groups are present as well as the very intense and broad phosphate band.

Several reactions were run in neat alkyl ester media. The one in butyl phosphate (Table 1, V-96) converted about half of the α-ZrP into the butyl ester of α-zirconium phosphate. Its weight-loss curve, Figure 2, yielded three distinct weight losses, while the *X*-ray pattern indicated that a mixture of $Zr(HPO_4)_2 \cdot H_2O$ and $Zr(O_3POC_4H_9)_2$ was present. The weight losses correspond to those expected for a mixture of 45% α-ZrP and 55% of the butyl ester. In contrast, the reaction in neat ethyl phosphate yielded an almost 100% ester-interchanged product (Figure 1).

Glyceric Acid Derivative.—α-Hydroxy acids are excellent chelating agents. It was therefore of some interest to determine whether such a structure could be attached to the layers of zirconium phosphate to provide a powerful, insoluble complexing agent. The required hydroxy acid phosphate was prepared by acidification of the barium salt of β-phosphoglyceric acid, $BaO_3POCH_2CHOHCO_2H$. At 70 °C in an acetone–water solution the reaction with the amine intercalate of α-ZrP resulted in only interchange at the surface (Table 1, I-77). Even at 90 °C, only a small amount of ester interchange occurred (Table 1, I-83). Therefore, resort was made to the direct precipitation method. When carried out at room temperature, a stoicheiometric product, $Zr(O_3POCH_2CHOHCO_2H)_2 \cdot nH_2O$, was obtained. Its *X*-ray diffraction pattern is given in Table 2. The t.g.a. curve, Figure 4, indicates that $n = 2.4$. This water was lost gradually on heating to 150 °C whereupon organic groups began to be lost. The loss of organic material corresponded to almost exactly that expected for the stoicheiometric formula given above. Finally, 1 mol of water was lost above 600 °C as a result of condensation of phosphate groups to form ZrP_2O_7.

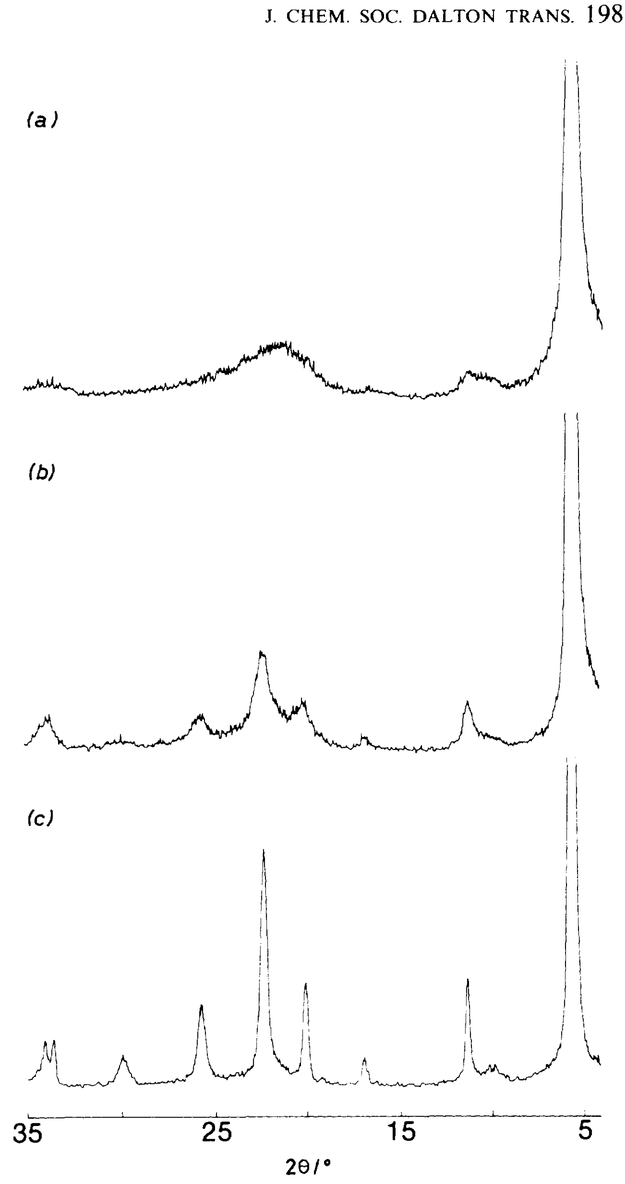

Figure 3. *X*-Ray powder diffraction patterns of zirconium butyl phosphate derivatives prepared under different conditions: (*a*) direct precipitation at 25 °C; (*b*) heating the product obtained in (*a*) at 100 °C for 1 week; and (*c*) as in Figure 2(*b*)

Infrared absorption bands for $Zr(O_3POCH_2CHOHCO_2H)_2 \cdot 2.4H_2O$ are collected in Table 3. A very strong broad band occurs in the O–H stretch region of the spectrum (3 200—3 700 cm^{-1}). That this band represents both water and the organic OH groups is shown by the band for the water-bending motion at 1 640 cm^{-1}, while the OH bend region contains three strong bands. The C=O stretch is represented by two strong bands at 1 750 and 1 780 cm^{-1}.

Attempts were made to obtain a more crystalline product than that produced at room temperature by heating the initial precipitate for different lengths of time in the mother-liquor

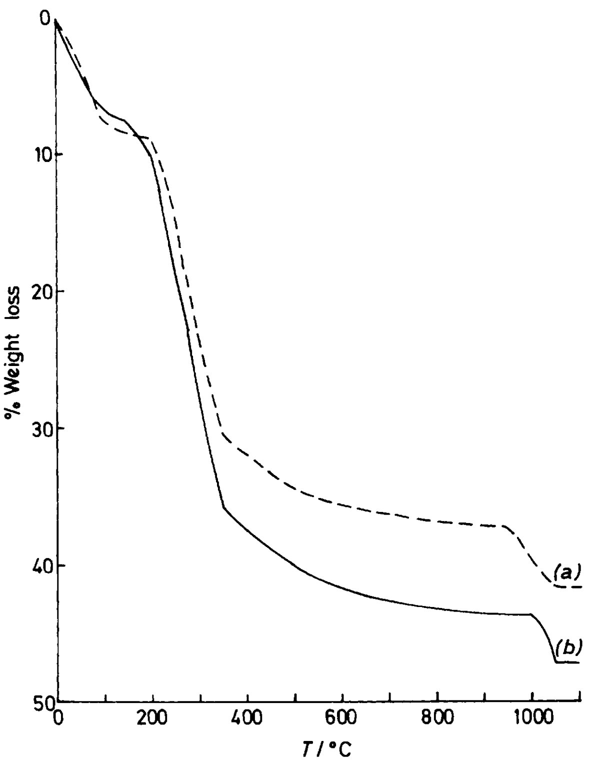

Figure 4. Thermogravimetric weight-loss curves for $Zr(O_3POCH_2CHOHCO_2H)_{2-x}(HPO_4)_x \cdot nH_2O$: (*a*) $x = 0.44$ and (*b*) $x = 0, n = 2.4$

Table 5. Results of ester-interchange reactions between γ-zirconium phosphate and phosphate esters, $ROPO_3H$

Experiment no.	R	T/°C	x	Interlayer spacing of product (Å)
I-29-2	$(CH_2)_3CH_3$	70	1.23	18.4
I-73	$CH_2CHOHCO_2H$	70	0.85	14.2
I-87	$CH_2CHOHCO_2H$	80	1.55	14.4

Table 6. *X*-Ray powder patterns of organo γ-zirconium phosphates obtained by ester interchange

Butyl phosphate		Glycerophosphate	
d/Å	I/I_0	d/Å	I/I_0
18.4	100	14.3	100
9.2	10	7.14	30
6.51	10	4.37	35
5.79	15	2.63	15
4.62	5		
4.04	30		
3.52	10		
3.48	15		
3.30	20		
3.09	2		
2.91	4		
2.67	5		

(Table 4, I-95A-C) but this resulted in continuous hydrolytic loss of glyceric acid. The hydrolyzed products gave the same *X*-ray diffraction pattern as the original precipitate with no reflections for α-ZrP. Thus, the hydrolyzed derivatives are probably of the type $Zr(HPO_4)_{2-x}(O_3POCH_2CHOHCO_2H)_x \cdot nH_2O$. The t.g.a. curve for sample I-95B, which was heated at 100 °C for 15 h, is shown in Figure 4 and the lowered glyceric acid content is evident from the reduced weight loss in the 150—600 °C temperature range. After 1 week of heating, almost all the organic groups were removed and the *X*-ray pattern was that of α-ZrP (Table 4, I-95C).

γ-ZrP *Derivatives*.—Organic derivatives of γ-ZrP can only be prepared by ester interchange reactions as the direct precipitation method leads to α-type structures. Because γ-ZrP has an interlayer spacing of 12.2 Å, it is not necessary first to expand the layers by means of amine intercalation. In the case of butyl phosphate a derivative containing more than 1 mol of organic per mol of zirconium was obtained at 70 °C (Table 5, I-29). The interlayer spacing was 18.4 Å or an increase of 6.2 Å. This increase is smaller than that (8.3 Å) observed with α-ZrP, but may result from the lower number of organic chains per layer which allows closer approach of adjacent layers. This is possible because the chains have more space per group and so may tilt away from the perpendicular to the layers or they may overlap into the intervening spaces.

The t.g.a. curve for I-29 is similar to those in Figure 2 for the α-type compounds. The weight loss to 150 °C amounts to 3.7% and is attributed to the presence of water in the interlamellar space. The bulk of the butyl groups are lost between 250 and 370 °C and the final weight loss results from loss of water together with some additional organic matter. The formula based on this analysis is $Zr[O_3PO(CH_2)_3CH_3]_{1.23}(HPO_4)_{0.77} \cdot 0.76H_2O$. This formula, derived from the t.g.a., requires 16.10% C and 3.65% H. The actual determined values (Galbraith Laboratories) are 16.80% C and 3.75% H in good agreement with the formula. As a means of identification the *X*-ray powder pattern of I-29-2 is given in Table 6. It is further distinguished by its i.r. spectrum which contains all the bands attributable to the butyl groups identified in Table 3 for the α-type derivative. However, the differences that are noted in the two spectra arise from the phosphate groups. For the γ compound a PO–H stretch is observed at 3 570 cm^{-1} and PO_4 vibrations at 1 228, 1 123, and 1 005 cm^{-1} as compared with 1 250, 1 160, 1 040, and 970 cm^{-1} for sample I-29, Table 1.

Clayden[4] examined the magic angle solid-state ^{31}P n.m.r. spectra of α- and γ-ZrP. He observed a single resonance at −18.7 p.p.m. for α-ZrP and two resonances for γ-ZrP at −9.4 and −27.4 p.p.m. Furthermore, both Yamanaka *et al.*[20,21] and Clayden[4] found that a maximum of 1 mol of phosphate groups could be interchanged with alkyl or aryl phosphates. Clayden concluded that half the phosphate groups are bound in the framework and cannot undergo interchange while the other half are dihydrogenphosphate groups which readily exchange. Therefore, it was surprising that we obtained more than 1 mol of butyl groups exchanged. The ^{31}P m.a.s. n.m.r. spectrum for our butyl phosphate-exchanged compound is shown in Figure 5. In this spectrum we observe three resonances at −27.7, −22.07, and −14.4 p.p.m. along with spinning side bands. Clayden also observed three resonances for the phenyl phosphate-exchanged γ-ZrP at −27.4, −19.8, and −14.4 p.p.m. He assigned the peak at −27.4 p.p.m. to the framework phosphate because it was present for both γ-ZrP and the organic compound. The peak at −19.8 p.p.m. was assigned to the phenyl phosphate group and the one at −14.4 p.p.m. to unexchanged dihydrogenphosphate groups. The large shift from −9.4 to −14.4 p.p.m. for this group Clayden attributed to its different environment resulting from the presence of nearby aryl groups. A similar assignment could be made for our compound except that the intensity of the peak at −22.07 p.p.m. is too low to represent 1.23 mol of organic phosphate. Rather we believe that the peak at −14.4 p.p.m. must represent the organic phosphate as well. In fact this peak represents the bulk of the organic phosphorus.

Figure 5. M.a.s. ^{31}P n.m.r. spectrum for butyl phosphate-interchanged γ-ZrP showing the resonance for PO_4 at −27.7 p.p.m. and those for the organic phosphate groups at −14.4 and −22.07 p.p.m.

Integration of the peaks in the n.m.r. spectrum together with their spinning sidebands indicates that the sum of the two resonances at −14.4 and −22.07 p.p.m. equals that at −27.7 p.p.m. This suggests that both monobutyl and dibutyl phosphate groups may replace the dihydrogenphosphates of γ-ZrP. To test this hypothesis we analyzed the butyl phosphate reagent, obtaining 37.40% C, 8.15% H and P. This analysis indicates that the reagent contains approximately 35% of dibutyl phosphate. An n.m.r. spectrum of the neat butyl phosphate reagent yielded two resonances at +0.68 and −0.66 p.p.m. with a 55:45 intensity ratio. We interpret this spectrum in terms of the presence of both the mono- and di-butyl phosphates in the reagent. It is then reasonable to suppose that both types of organic phosphates exchanged with γ-ZrP and that the final product contained 77% monobutyl phosphate and 23% dibutyl phosphate to yield the 1.23 butyl groups in the exchanged solid. Thus, the correct formula is $Zr(O_3POC_4H_9)_{0.77}[O_2P(OC_4H_9)_2]_{0.23}$-$PO_4 \cdot 0.76H_2O$.

Table 6 also lists the *X*-ray pattern for the glyceric (α-hydroxypropionic acid) derivative obtained by ester interchange with γ-ZrP. Both the *X*-ray pattern and the i.r. spectrum are identical with those for the α-ZrP derivative. Thus, the ester-interchange reaction in this case causes a transformation of the γ-type layer into the α-type.

Discussion

Yamanaka and co-workers[5,6,20,21] have shown that phosphate esters react with γ-ZrP in a facile manner through ester interchange to form alkyl or aryl ester derivatives. In contrast α-ZrP was found not to react similarly. Furthermore, ethylene oxide esterified γ-ZrP very readily[9] but appeared to react with α-ZrP in a sluggish manner. However, the present authors demonstrated[8] that α-ZrP in fact did react in a facile manner with ethylene oxide if the interlamellar space was made accessible. α-ZrP has a small interlayer spacing (7.6 Å) compared with γ-ZrP. Thus, the esters are not hindered from diffusing to the P–OH sites in the interior of the γ-ZrP crystals, but are prevented from doing so in the α-layered compound. Since the surface of α-ZrP crystals did in fact react with ethylene oxide under relatively mild conditions,[8] it was felt that the lack of reactivity of the α-phase to ester interchange was a reflection of the inaccessibility of the interior. The present study has amply demonstrated that this is the case. What was found surprising is the fact that under more severe conditions, such as reflux in neat alkyl phosphates, α-ZrP did undergo significant ester interchange without the necessity of first enlarging the interlayer space. We view this as occurring in a layer-by-layer fashion. As the surface layer becomes esterified it swells in the organic ester permitting the ester to diffuse in between the first and second layer and so on. Higher α-ZrP surface areas would be expected to facilitate this process.

Yamanaka *et al.*[21] and also Clayden[4] found that a maximum of 1 mol of phosphate groups was interchanged with alkyl or aryl phosphates. Furthermore, ^{31}P m.a.s. n.m.r. spectra revealed[4] two phosphate resonances for γ-ZrP showing the presence of two types of phosphate groups. Clayden proposed that one type is a framework phosphate which cannot undergo interchange, and another a dihydrogenphosphate group which can. In contrast, we found that more than 1 mol of ester can exchange with γ-ZrP under similar conditions. The fact that one resonance at −27.9 p.p.m. remains unchanged after ester interchange bears out Clayden's assertion that this resonance must represent a framework PO_4^{3-} group. The other peak at −9.4 p.p.m. is totally missing in the spectrum of our butyl phosphate derivative indicating that this dihydrogenphosphate group was totally replaced by butyl-phosphate groups. To account for the stoicheiometry we suggest that 77% of the groups exchanged were $C_4H_9OPO_3H$ and 23% dibutyl phosphate, accounting for the peaks at −14.67 and −22.07 p.p.m., respectively. That dibutyl phosphate groups are present in the butyl phosphate reagent used for the exchange reaction is shown by the n.m.r. spectrum which reveals two peaks close together in an approximate ratio of 1:1 and the high carbon to phosphorus ratio of the reagent. Thus, the most likely explanation for our γ-butyl derivative is the replacement of some of the dihydrogenphosphate by dibutyl phosphate.

We have already found it necessary to propose that diethyl and dibutyl phosphates present in the monophosphate reagents appear to interact with the zirconium(IV) species as well (Table 4, samples V-19A and II-3A). The resultant derivatives in the case of α-ZrP may be mixed ones in which both mono- and di-phosphates are attached to the same layer. Alternatively, mixtures of mono- and di-phosphate derivatives may form. If sufficiently crystalline they can be distinguished by the d_{001} *X*-ray peaks provided they differ by about 0.5 Å.

Assuming a value of 6.6 Å for the layer thickness, and 2.41 Å for the O–C–C portion in the ethyl derivative, the calculated interlayer spacing is 11.4 Å without allowing for hydrogens. Their inclusion adds 1 Å to the total which is slightly more than the interlayer distance observed (12 Å). This indicates that the alkyl chains are tilted at an angle as is the case for intercalated alkylamines.[22] The angle of tilt from the perpendicular necessary to reconcile this difference is less than 10°. However, when three ethyl groups are present in the direct precipitated product (sample V-19A, Table 4) the interlayer spacing is 12.8 Å indicating that the dibutyl groups require a larger interlayer spacing. However, on continued refluxing the interlayer spacing is reduced to 11.8 Å while a 2:1 ratio of ethyl phosphate to Zr is attained. If 2.5 Å is added to the above value to include the additional C–C distances in the butyl derivative, the calculated interlayer spacing is 17.4 Å which is again larger than the experimental value of 15.95 Å. The amount of water in this sample is negligible, so the difference must be due to the alkyl chain inclination, especially since the butyl derivatives contained a greater than 2:1 ratio of organic to Zr.

For the glyceric acid derivative, the calculated distance for the C–C–C–O portion is 4.8—4.9 Å, which gives an interlayer distance of 16.2—16.4 Å, and is also much longer than the actual value of 14.5 Å. The polar nature of the hydroxy and carboxy groups suggests the possibility for strong hydrogen bonding between groups in adjacent layers, thus reducing the distance between the planes, but the calculation already allowed for this by omitting the O–H distances. If the amount of glyceric acid decreases, as in the sample with $x = 1.56$, the amount of water intercalated increases from 1.6 to 2.1 mol. This water probably occupies the free spaces left by the leaving organic groups since the interlayer spacing is also reduced by *ca.* 0.13 Å despite the higher water content. Thus, in all cases the pendant organic groups are inclined by a small angle (10—20°) to the perpendicular to the layers.

Preliminary studies on the ion-exchange and chelating properties of the glyceric acid derivative have been conducted with Na^+, Cu^{2+}, Pd^{2+}, and Ag^+. Complete results will be presented in a subsequent paper.

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