copper in each of the ions listed in Table III. Each ion listed in Table III with m/z less than that of $M^{+\cdot}$, the molecular ion, with the exception of $Cu^{II}LR^+$ would have the copper assigned an oxidation state of +1. If one accepts the oxidation states assigned to ligand moieties as reasonable, then it must be concluded that reduction of the copper from the original Cu(II) to Cu(I) is an important process in the olefin CI-induced reactions of $Cu^{II}L_2$.

Extending the argument to include those ions with m/z greater than $M^{+\cdot}$, two fragments of ion cluster species may be identified as having resulted from an internal redox reaction: $Cu^ICu^{II}L_2^+$ and $Cu^ICu^{II}L_2R^+$.

It is of interest that the observed ratio of ion intensities for Cu(II) to Cu(I) species associated with reagent gas never exceeds 0.85 and is zero in 11 of the 24 examples in Table III. This is consistent with the previous observation that Cu(II) olefin adducts are considerably more labile than those of Cu(I).[12] Salomon and Kochi have observed copper(I) olefin complexes in solution-phase chemistry,[13] and that observation has been supported by Schwendiman and Kutal.[14]

The analogy between macroscopic reaction systems and the microreactor that is the source of a mass spectrometer is continued by noting from Table III the overwhelming predominance of ions in which the ratio of ligand to copper does not exceed a value of 2.

There are basically three types of ions found in the olefin CI mass spectra of these complexes with m/z greater than that of the molecular ion or protonated molecule. These are simple cluster ions formed by CuL_2^+ and CuL_2 to give $Cu_2L_4^+$ and their dissociation fragments, ions formed by the condensation of a prominent hydrocarbon fragment from the reagent gas with CuL_2 to give CuL_2R^+, and ions formed by the condensation of an ion cluster with a neutral reagent olefin. Peaks of the first type have not been noted in previous CI studies but have been observed by Schildcrout in high-pressure mass spectra of $Cu(hfa)_2$.[15] Schildcrout also observed a peak corresponding to $Cu_3(hfa)_4^+$, but the mass of this ion is beyond the range used in this study. The presence of these peaks in the high-pressure mass spectra of the neat complexes is attributed to ion–molecule reactions between the molecular ion and the parent molecule. Presumably, the high pressure of isobutene in the CI source allows a similar process to occur in this system. Even though the absolute concentration of the metal complex is relatively low, its residence time in the high-pressure source is long enough to allow the condensation reaction to occur.

At least two methods have been reported recently for producing metal ions that then are allowed to react with organic additives. The methods used were the generation of Cr^+, Fe^+, Co^+, and Ni^+ from the appropriate neutral metal carbonyl by EI[16] and the laser generation of metal ions via impact of the beam on the appropriate metal foil. Freiser and others have reported the generation and reactions of Cu^+, Ni^+, and Fe^+ ions, using this method and ICR or FT-MS.[17] Our method appears complementary to these techniques.

Registry No. $[Cu(hfa)_2]$, 14781-45-4; $[Cu(tfa)_2]$, 14324-82-4; $[Cu(acac)_2]$, 13395-16-9; Cu, 7440-50-8; ethene, 74-85-1; propene, 115-07-1; allene, 463-49-0; propyne, 74-99-7; 2-methylpropene, 115-11-7; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; 1,3-butadiene, 106-99-0.

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Polyether Derivatives of Zirconium Phosphate

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γ-Zirconium phosphate, $Zr(HPO_4)_2\cdot 2H_2O$, with a 12.2-Å interlayer spacing is known to react with ethylene glycol solutions to form glycol esters of the zirconium phosphate. It has now been shown that the α polymorph with a smaller interlayer distance (7.6 Å) also behaves similarly. With highly crystalline samples of α-zirconium phosphate, reaction takes place only at the surface. However, if the interlayer distance is first increased so that ethylene oxide can diffuse into the interior, complete reaction ensues. Less crystalline samples were found to react directly with ethylene oxide, either as a gas or as a solution. Attempts to form long polyether chains by direct reaction were unsuccessful. However, by the preparation of first polyether phosphates and then the reaction of these compounds with Zr(IV) species, polyether analogues of α-zirconium phosphate were prepared. These derivatives incorporate electrolytes and form novel colloidal dispersions.

Introduction

Zirconium bis(monohydrogen orthophosphate) hydrate, $Zr(HPO_4)_2\cdot H_2O$, is a crystalline, insoluble ion exchanger with a layered structure.[2] It has an interlayer spacing of 7.6 Å with zeolite-like cages between the layers. The free space leading into the cages is only large enough to allow a sphere of about 2.6 Å to pass unobstructed.[3] A second form of zirconium phosphate, with an interlayer spacing of 12.2 Å, is also known.[4] It has the composition $Zr(HPO_4)_2\cdot 2H_2O$, and while its structure is unknown, the layers are certainly different than those of the monohydrate. It will be referred to as γ-ZrP whereas the monohydrate is termed α-ZrP. Titration of α-ZrP with NaOH yields a half-exchanged phase, $ZrNaH(PO_4)_2\cdot 5H_2O$. On removal of the Na^+ with acid the original α-ZrP is not obtained. Rather, a higher hydrate with interlayer spacing of 10.4 Å, termed θ-ZrP, is formed.[3]

Several years ago, Yamanaka reported that γ-ZrP reacts with ethylene oxide to form derivatives of the type $Zr(HPO_4)_{2-x}(O_3POCH_2CH_2OH)_x\cdot H_2O$.[5] The interlayer spacing for the compound with $x = 2$ is 18.4 Å. Propylene oxide was also found to react similarly, but only half the phosphate groups were esterified.[6] In addition, these complexes were found to undergo ester interchange on refluxing with other organic phosphates and/or phosphoric acid.[7,8] Yamanaka was unable to obtain

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Table I. Uptake of Ethylene Oxide by α-Zirconium Phosphates of Different Crystallinities[b]

sample α-ZrP	SA, M^2/g	[EO], M/L	reacn time, h	uptake of EO, mol of EO/mol of ZrP	interlayer spacing, Å	TGA water content, mol	interlayer spacing (anhyd), Å
9:48	8	1	24	0.01	7.6		
4.5:48	26	1	48	0.34	7.6		
			96	0.66	13.4 (m) + 7.6 (s)[a]		
2.5:48	90	1	2	0.51	13.0 (w) + 7.6 (s)		
2.5:15	140	1	1	0.96	12.4	0.96	11.3
		1	2.5	1.38	13.4	0.78	13.0
		1	10	1.52	14.5	0.71	13.9
		1	24	1.65	14.7	0.94	13.9
		3	1	1.68	13.6	1.21	13.2
		3	2.5	1.72	13.9	0.55	13.8
		3	10	1.75	14.4	0.68	14.2
		3	24	1.78	14.7	1.21	14.6
		1	2.5[c]	1.96	15.5		
		1	24[c]	1.84	15.1		

[a] Ligand: s = strong, m = medium; w = weak. [b] All reactions at room temperature unless otherwise noted. [c] Temperature of reaction 60 °C.

similar derivatives of α-ZrP, and this apparently stemmed from the fact that the oxides could not diffuse between the α layers to reach the P–OH sites. If in fact this is the reason, then the surface phosphate groups, which are accessible to ethylene oxide, should still become esterified. Since we recently reported the preparation of α-zirconium phosphates possessing high surface areas,[9] a means of testing this hypothesis was at hand.

A second incentive for this study was to determine whether large polyether chains would form by subsequent polymerization of ethylene oxide on the anchored surface groups. Polyethers are known to incorporate electrolytes, thereby becoming ionic conductors.[10] If polyethers are anchored to the inorganic sheets, it might be possible to insolubilize them and thus use them as conducting polymers in the presence of water. For this purpose an indirect method of preparation was found to be satisfactory. Other potential uses in separations science readily suggest themselves for these compounds.

Experimental Section

Sample Preparation. α-Zirconium phosphates of different surface areas (and crystallinities) were prepared by refluxing a gel in H_3PO_4 of different concentrations for varied lengths of time.[9] The gel was prepared as described previously.[9,11] These samples will be referred to as α-ZrP(x:y), where x is the concentration of H_3PO_4 and y is the time of reflux in hours. The smaller these two numbers are, the greater is the surface area.[9] θ-ZrP was prepared in the usual way[3] from the half-exchanged phase $ZrNaH(PO_4)_2{\cdot}5H_2O$, which was itself prepared by titration of α-ZrP(10:100) with NaOH. θ-ZrP was stored in water as it readily dehydrates to α-ZrP on standing in air.

Reactions with Ethylene Oxide. Solutions of ethylene oxide (1–3 M) were prepared each time, just prior to use, by bubbling a known weight of the gas into a predetermined volume of distilled, deionized water. A weighed amount of zirconium phosphate was added such that the volume to solid ratio was constant at 100:1. The samples, in plastic bottles, were stirred magnetically, at room temperature unless otherwise specified, for different lengths of time. The mixtures were then filtered and washed with 300 mL of distilled, deionized water and air dried. In some instances, usually at the end of the reactions, gaseous ethylene oxide was further bubbled through the solution with shaking to increase the uptake of oxide. Samples of zirconium phosphate were also treated by passing gaseous ethylene oxide directly over the solid held in a platinum boat inside a glass tube.

Preparation of Ethylene Glycol Phosphoric Acids. The general preparation will be illustrated by the description for the tetrameric compound. 1,11-tetraethylene glycol (Aldrich), $C_8H_{18}O_5$ (**1**) (15.7 g, 0.080 mol), was dissolved in 50 mL of CCl_4 in a three-neck round-bottom flask. The flask was fitted with a separatory funnel, a reflux condenser, and a vacuum (water-line) connection. To the solution in the flask was added dropwise 3.7 mL (6.1 g, 0.040 mol) of $POCl_3$ (Mallinckrodt) in 60 mL of CCl_4 by means of the dropping funnel. During this addition, the whole was kept under gentle suction to remove HCl, while stirring ~~was accomplished~~ magnetically. After 1 h the mixture was cooled to ~6 °C with an ice bath followed by dropwise addition of 20 mL of water. The solvent was then evaporated to its original volume under reduced pressure and an excess of solid $Ba(OH)_2$ (Fisher) added. This neutralized any HCl that was not removed by suction and phosphoric acid that formed from hydrolysis of $POCl_3$. Solid dry ice was added to precipitate excess Ba^{2+}, and the mixed barium phosphate and carbonates were filtered off. The filtrate was then concentrated under reduced pressure to 50 mL and 400 mL of ethyl alcohol added. When the mixture was allowed to stand overnight in a refrigerator, additional $BaCO_3$, as well as $BaCl_2$, precipitated. This was filtered off and the solvent volume reduced to 100 mL under reduced pressure. When 300 mL of acetone was added (slowly), the solution became cloudy as the barium salt of the polyether phosphoric acid began to precipitate. The mixture was stirred vigorously to produce a precipitate, which was then allowed to settle. The clear supernatant was decanted and 50 mL of additional acetone added. This was repeated twice, and the solid was then recovered by filtration; yield 14.2 g (87%). Anal. Found: C, 23.22; H, 4.22; loss on ignition, 53.4%. Calcd for $BaO_3PO(CH_2CH_2O)_4H{\cdot}H_2O$: C, 22.50; H, 4.47; loss on ignition, 53.5%. The TGA curve clearly showed the loss of 1 mol of water below 100 °C.

Reaction of Tetraethylene Glycol 1-Phosphate with $ZrOCl_2$. The barium salt of tetraethylene glycol 1-phosphate (**2**) (16 g, 0.042 mol) was dissolved in 100 mL of water and enough sulfuric acid added to precipitate 90% of the Ba^{2+}. The $BaSO_4$ was filtered off and the filtrate passed through a column of Dowex 50-X8 in the acid form to remove the remainder of the Ba^{2+}. Then 2.53 g (0.0078 mol) of $ZrOCl_2{\cdot}8H_2O$ (Magnesium Elektron) in 25 mL of water was added with stirring. A white precipitate formed immediately, but the mixture was stirred for 15 h at room temperature to ensure complete reaction. The filtered solid was washed with water followed by 30 mL of acetone and air-dried; yield 4.5 g. Anal. Found: C, 30.33; H, 5.05. Calcd for $Zr[O_3PO(CH_2CH_2O)_4H]_2$: C, 30.18; H, 5.38.

Analysis and Characterization of the Samples. Each of the zirconium phosphate preparations was subjected to X-ray powder diffraction (Scintag PAD-II, Cu Kα radiation) and TGA analysis (Cahn TG 3600 heating rate of 4°/min under N_2). One sample was decomposed by treating with strong NaOH to solubilize the phosphate groups followed by dissolution of the residue in H_2SO_4. The solutions were analyzed by ICPA (inductively coupled plasma arc) and showed less than 100 ppm impurities and a 2:1 ratio of P to Zr. Samples that were reacted with ethylene oxide were also characterized by X-ray, TGA, and infrared spectral means (KBr disk, Perkin-Elmer 520B) and subjected to carbon and hydrogen analysis (at the Texas A&M Center for Trace Characterization).

Results

The initial series of experiments was carried out with four samples of α-ZrP of widely varying crystallinities and hence surface areas. These solids were shaken at room temperature with 1–3 M ethylene oxide solutions. The results are shown in Table I. The extent of reaction or moles of ethylene oxide bonded to the layers is shown in column 5. As expected, the most crystalline sample, 9:48, did not incorporate ethylene oxide between the layers as shown by the interlayer spacing of 7.6 Å, which is identical

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Table II. Reaction of Ethylene Oxide with θ-ZrP

θ-ZrP prepared from	[EO], M	reacn time, h	uptake of EO, mol of EO/mol of ZrP	interlayer spacing, Å	TGA water content, mol	interlayer spacing (anhyd), Å
α-ZrP(9:48)	1	16	2.49	15.5		
α-ZrP(10:100)	1	2	1.80	12.8	0.98	12.3
	1	16	2.45	16.1	1.07	15.0
	1	48	2.46	17.0	1.22	15.6
	3	2	2.44	16.7	1.18	15.2
	3	16	2.58	16.7	0.89	15.8
	3	48	2.60	17.3	0.73	

Table III. Reactions of Zirconium Phosphates with Gaseous EO and Miscellaneous Solution Reactions

expt no.	synth method	reacn time, h	uptake of EO,[a] mol of EO/mol of ZrP	interlayer spacing, Å
I-38	α-ZrP (2.5:15) + EO(g)	2	4.74	16.8
I-40	α-ZrP (2.5:48) + EO(g)	26	7.43 (6.9)	21.1
I-41	I-40 washed		3.10	16.8
I-39	α-ZrP (3.5:48) + EO(g)	2	0.78 (0.32)	7.6
I-97	α-ZrP (2.5:48) + water, EO bubbled in	3	2.88	16.2
(I-39H)	γ-ZrP + EO(g)	2	4.50	25.2
I-52	γ-ZrP + EO(g)	7	9.09 (8.74)	19.6
II-49A	γ-ZrP + EO(g) (washed)	1	2.30	18.8
II-49B	γ-ZrP + EO(g) (washed)	3		19.4
II-49C	γ-ZrP + EO(g) (washed)	5		20.8
II-49D	γ-ZrP + EO(g) (washed)	8		21.1
II-49E	γ-ZrP + EO(g) (washed)	12		21.3
II-49F	γ-ZrP + EO(g) (washed)	16	3.05	21.5
II-55	γ-ZrP + water, EO bubbled in	8	0.65	17.2 (1 H_2O) 16.0 (dry)
I-76	θ-ZrP + water, EO bubbled in	5	2.77	17.0 (dry) 26.8 (wet)

[a] Numbers in parentheses are values from elemental analysis; others are from TGA.

with that of α-ZrP.[13,14] However, a small amount (0.01 mol) of ethylene oxide did react, presumably with surface P–OH groups. If each surface phosphate group had been esterified, the total organic oxide content would have been 0.015 mol/mol of α-ZrP. This value is arrived at by recognizing that each phosphate group in α-ZrP occupies 24 Å^2 of layer space.[9]

In contrast, a poorly crystalline sample, 2.5:15, immediately incorporated ethylene oxide between the layers. The reaction was initially relatively rapid but slowed appreciably with time. Comparisons of the products obtained from 3 M ethylene oxide with those from 1 M ethylene oxide show that the former contain more organic oxide for the same values of interlayer spacing. We interpret this as meaning that a larger amount of polymerization occurred at the surface with the 3 M solution.

A zirconium phosphate of intermediate crystallinity, 4.5:48, which was stirred with a 1 M solution of ethylene oxide for 48 h, was found to contain 0.34 mol/mol of ZrP. No increase in interlayer spacing was observed. If all the ethylene oxide is assumed to be on the surface, this represents a ratio of 6.5 mol of organic oxide/mol of phosphate group. When this sample was retreated for a total of 96 h, the amount of ethylene oxide uptake almost doubled but now a portion of the solid had an increased interlayer distance of 13.4 Å.

The above results are readily explained when it is recognized that poorly crystalline samples of the exchanger such as 2.5:15 swell in water.[11] The increase in interlayer distances allows ethylene oxide to diffuse into the interior of the particles and react with all of the phosphate groups. In contrast, more crystalline samples do not swell and reaction therefore only takes place at the surface. However, when the polyether chain becomes long enough, stronger wetting of the surface layer may occur as will be shown subsequently. This could cause sufficient swelling in the surface layers to allow access of ethylene oxide to these swollen portions of the crystal.

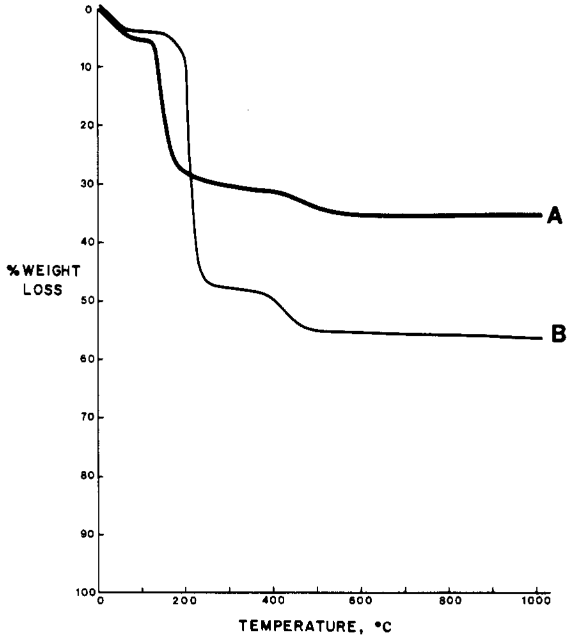

Figure 1. Thermogravimetric weight loss curves for (A) $Zr[O_3PO(CH_2CH_2O)_{1.22}H]_2 \cdot 1.18H_2O$ and (B) for $Zr[O_3PO(CH_2CH_2O)_4H]_2 \cdot 1.37H_2O$.

Reactions of θ-ZrP. The θ phase of zirconium phosphate can be prepared from α-ZrP[3,15] or by direct precipitation.[16,17] It is a more highly hydrated form of α-ZrP with an interlayer spacing of 10.4 Å. Thus, if our explanation for the reactivity of α-ZrP-(2.5:15) toward ethylene oxide is correct, then θ-ZrP should also behave similarly. Accordingly, θ-ZrP samples were prepared by treating highly crystalline sodium-exchanged α-ZrP samples with HCl. The resultant θ-ZrP was then allowed to react with ethylene

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Table IV. Infrared Spectra of Polyethylene Glycol and Polyether Phosphate Derivatives[a]

PEO (M_r 400)	BaO_3PO-$(CH_2CH_2O)_4H$	ZrP-EO	3, $n = 4$	assignt
3420 vs, b	3430 vs, b	3380 vs, b	3440 vs, b	OH str
		2950 m	2940 m	CH str
	2920 w-m	2920 m		CH str
2890 vs, b	2880 w-m	2880 m	2880 m	CH str
1625 s, b	1645 m	1640 m	1630 m	$\delta(H_2O)$
	1470 w-m			$\delta(CH_2)$
1447 s, b	1457 m	1460 m	1450 m	$\delta(CH_2)$
1345	1352	1355 w-m	1350 w	$W(CH_2)$, ν(C-C)
1290 ms	1300 w-m		1285 w (sh)	$t(CH_2)$
1245 s	1250 m	1245	1240	$t(CH_2)$
	1230 m			
1100 vs, b	1060 vs, b			ν(C-O-C)
				$\nu(PO_4)$
	995 m	950–1200 vs, b	950–1200 vs, b	ν(P-O-C)
				ν(C-O-C)
	960 m			
885 w				
830 w-m	830 w		825	
	800 w	799 m	800	
	600 w	600 m		
	540 w	550 ms		
	470 w			

[a] Intensity designations: vs = very strong; s = strong; m = medium; w-m = weak to medium; sh = shoulder; b = broad.

oxide in the same manner as described for α-ZrP. The results are collected in Table II. It is evident from the data that not only was the reaction more rapid but also a larger total amount of ethylene oxide was incorporated. This undoubtedly results from the fact that the interior P–OH groups are more readily accessible to the ethylene oxide.

Characterization of the Complexes. The amount of ethylene oxide taken up in each of the reactions was determined by means of thermogravimetric analysis of the products. The TG results were checked by carbon and hydrogen analysis of several of the samples. A typical weight loss curve is shown in Figure 1A. It may be interpreted on the basis of reactions 1–3.

$$Zr[O_3PO(CH_2CH_2O)_nH]_2{\cdot}XH_2O \xrightarrow{25-80\ ^\circ C} Zr[O_3PO(CH_2CH_2O)_nH]_2 + XH_2O \quad (1)$$

$$Zr[O_3PO(CH_2CH_2O)_nH]_2 \xrightarrow[O_2]{120-160\ ^\circ C} Zr(HPO_4)_2 + 4nCO_2 + 4nH_2O \quad (2)$$

$$Zr(HPO_4)_2 \xrightarrow{\sim 400\ ^\circ C} ZrP_2O_7 + H_2O \quad (3)$$

The first weight loss, which occurs from room temperature to just below 100 °C, results from volatilization of water hydrogen bonded to the polyether chains (eq 1) and amounts to about 1 mol/mol of complex (Tables I and II). The second weight loss begins at about 120 °C and is characterized by an initial steep slope in the TG curve signaling the loss of organic material (eq 2). However, some carbonization occurs and the carbon deposit burns off slowly. Thus the slope becomes less steep, but before all the carbon is lost, the final water loss resulting from phosphate condensation takes place (eq 3). Since the volatile organic matter was not identified, it is treated as being oxidized to CO_2 and H_2O. It remains then to determine the value of n from the observed weight loss. This is readily done by using the equation

$$\frac{2nE + 18.02}{2nE + 284.2} = F \quad (4)$$

where $E = 44.05$, the molecular weight of ethylene oxide, F is the fractional weight loss of the anhydrous sample, and 284.2 is the formula weight of $ZrP_2O_7 + H_2O$. The denominator is then the formula weight of the anhydrous zirconium phosphate polyethylene complex. In the TG pattern shown $F = 0.320$ and $n = 1.22$ or the total moles of ethylene oxide incorporated is 2.44. Analysis for carbon and hydrogen gave 2.53 mol. The difference in these values may be due to incomplete burnoff of carbon in the TG method as the final sample recovered after heating to 800 °C is grey to black.

Infrared Spectra. The infrared spectra of the polyethylene oxide complexes of α-ZrP, for which n exceeded 1, exhibited a broad band centered at 3380 cm^{-1} representing OH stretching vibrations of both water and the terminal hydroxyl groups of the polyether (Table IV). A second weaker band at 1640 cm^{-1} represents the ν_2 water band. Bands at 2880, 2920, and 2950 cm^{-1} as well as 1458 and 1355 cm^{-1} represent CH_2 vibrations. These bands are also present in the polyether glycols as a broad unresolved band centered at 2890 cm^{-1}. The region from 1260 to 900 cm^{-1} consisted of several broad overlapping bands that result from phosphate vibrations as well as those of polyethers, particularly the C–O–C stretch centered at 1100 cm^{-1}. A sharp band at 885 cm^{-1} is probably due to the C–C vibration.

Comparison of the above results with a spectrum of a sample for which n was 0.46 revealed some interesting differences in the high-wavenumber region. Two sharp bands were observed at 3600 and 3520 cm^{-1}, and a shoulder was also present at 3250 cm^{-1} on the main OH stretching band centered at 3400 cm^{-1}. These bands correspond to those observed in pure α-ZrP (3590, 3510, 3280, and 3150 cm^{-1}).[12,18] Examination of the X-ray powder pattern for this sample showed that α-ZrP is indeed present. In fact, we could correlate the presence of unreacted α-ZrP by means of X-ray diffraction with the IR absorption bands characteristic of α-ZrP in the OH stretching region. Thus at low uptakes of ethylene oxide the product appears to be a mixture of unreacted α-ZrP and a solid phase in which n may be close to 1.

Additional Methods of Synthesis. The preparations described in the preceding sections yielded products with low values of n. One of the objectives of this study was the preparation of long-chain polyether complexes of zirconium phosphate. Clearly some new methods of synthesis were required and those investigated included use of nonaqueous solvents and amine intercalates, bubbling of ethylene oxide directly into the aqueous α-ZrP slurry, direct reaction of gaseous ethylene oxide with solid α-ZrP, and the use of a polymerization catalyst. The results are shown in Table III. Gaseous ethylene oxide was found to react directly and exothermically with solid γ-ZrP and α-ZrP of low crystallinity. However, the change in interlayer spacing was not a good guide as to the amount of ethylene oxide that reacted. In the case of α-ZrP only the less crystalline solids were able to incorporate ethylene oxide between the layers but a good part of the reaction also took place at the surface. This is shown by experiment I-40, where TG analysis showed that the solid contained 7.43 mol of

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ethylene oxide/formula weight. When this solid was washed and air-dried, the ethylene oxide content was reduced to 3.10 mol (experiment I-41) with only a 4.3-Å decrease in the interlayer spacing.

γ-ZrP reacted very vigorously with gaseous ethylene oxide. In experiments I-39H and I-52 high uptakes of ethylene oxide were observed. However, the product with less organic matter exhibited the larger interlayer spacing. The dilemma was resolved with the next series of experiments (II-49A–F), in which γ-ZrP was allowed to react with gaseous ethylene oxide for different lengths of time but the products were washed in water to remove any excess organic matter and air-dried. In this case, all the unreacted ethylene oxide (or ethylene glycol) was removed by washing and the interlayer spacing was therefore a true measure of the amount of organic incorporated through bonding to the phosphate layers. The results are in good agreement with those of Yamanaka.[5] Thus, the sample (I-52) with a 19.6-Å interlayer spacing must have incorporated ~2.5 mol (n = 1.25) of ethylene oxide and the remaining organic material must reside on the surface of the crystals. This was proved by washing the gummy solids (II-49A–F), which removed the color and stickiness and on drying yielded a fine white, free-flowing powder of comparable interlayer spacings. However, when it was allowed to stand in moist air, the sample gained weight with expansion of its interlayer spacing by intercalating water. This we will see is a general phenomenon. The larger the polyether chains, the greater the swelling of the solid on exposure to moisture.

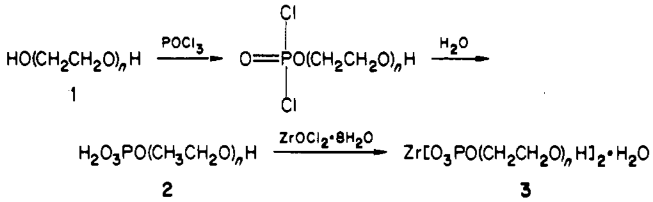
Another synthetic technique that was tried was to disperse the solid sample in water and then bubble gaseous ethylene oxide directly into the slurry. This technique was effective with poorly crystalline α-ZrP(2.5:48) (Table III, experiment I-97) and with the expanded layer θ form (I-76) but not with γ-ZrP. Even when ethylene oxide was passed through the slurry for 8 h, less than 1 mol was taken up by γ-ZrP.

In many cases, the products of the above reaction when wet had a much larger interlayer spacing because of the uptake not only water but also ethylene glycol. This was shown by the fact that the water washings from experiment I-40 gave a negative test for an oxirane ring but a positive test for vicinal –OH groups.

An interesting result was obtained when butylamine intercalates of α-ZrP(10:100) were allowed to react with gaseous ethylene oxide. The completely saturated amine intercalate, with an 18.6-Å interlayer spacing,[19] did not react. However, an intercalate with only 2 mequiv/g of amine (30% of capacity) gave a mixture of the 100% intercalate and a solid containing bound ethylene oxide (d_{002} = 13.4 Å).

The use of nonaqueous solvents such as methanol and benzene in place of water in the above synthetic procedures yielded products with about the same values of n as obtained in aqueous media.

Preparation of Long-Chain Polyether Derivatives. The addition of $ZrOCl_2$ to an excess of a polyether phosphate was found to result in the preparation of a polyether-derivatized α-zirconium phosphate. The sequence of reactions described in the experimental section may be represented schematically as



$$\underset{\mathbf{1}}{HO(CH_2CH_2O)_nH} \xrightarrow{POCl_3} O{=}\overset{Cl}{\underset{Cl}{P}}O(CH_2CH_2O)_nH \xrightarrow{H_2O}$$

$$\underset{\mathbf{2}}{H_2O_3PO(CH_3CH_2O)_nH} \xrightarrow{ZrOCl_2\cdot 8H_2O} \underset{\mathbf{3}}{Zr[O_3PO(CH_2CH_2O)_nH]_2\cdot H_2O}$$

The TG curve for **3** for which n = 4 is given in Figure 1B. The sample had been air-dried and therefore retained 1 mol of water. The water loss (3.82%) took place below 80 °C and was followed by loss of the polyether chains beginning at ~160 °C. A final weight loss, beginning at 400 °C, results from the condensation reaction shown in eq 3. The magnitude of this weight loss was always larger than expected because the polyether decomposition is not complete at the lower temperatures. Rather, a carbon deposit accumulated during the decomposition of the polyether chains and this carbon burns off slowly under the nitrogen atmosphere. This slow burnoff of carbon was also responsible for the lower than expected total weight loss (57.7% observed vs. 59.4% required for n = 4).

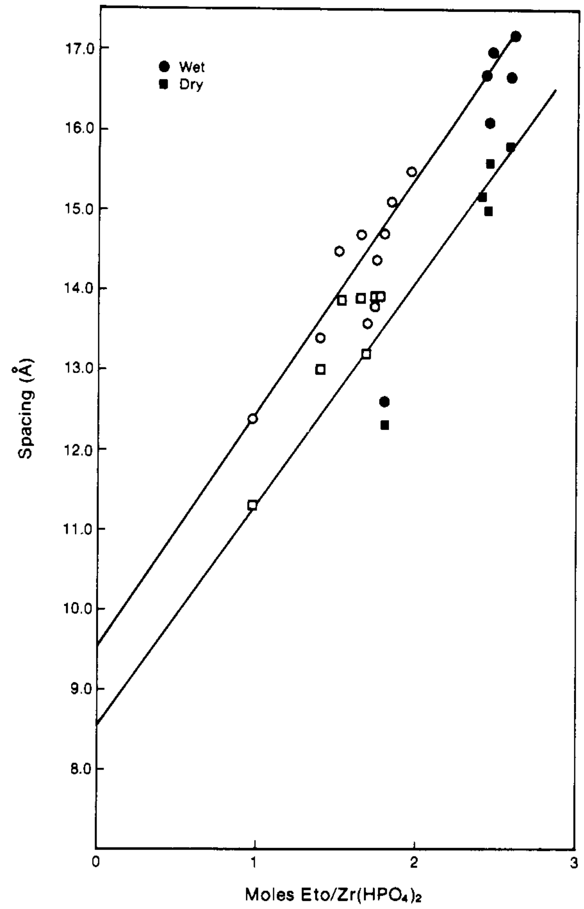


Figure 2. Plot of interlayer spacing of α-zirconium phosphate as a function of the number of moles of ethylene oxide incorporated. Open symbols are for α-ZrP(2.5:15) and filled symbols for α-ZrP(10:100); circles represent samples containing 1 mol of water, and squares are for anhydrous samples.

Infrared spectra for $BaO_3PO(CH_2CH_2O)_4H$ (**3**) and a derivative prepared by the direct reaction of ethylene oxide with α-ZrP (ZrP-EO) are presented in Table IV. A spectrum for polyethylene glycol of molecular weight 400 is included for comparison purposes. The close similarity of the infrared bands of the three derivatives with each other and with those of the polyethylene glycol further substantiates the nature of the derivatives. It should be noted that the polyether C–O–C stretch occurs at 1100 cm^{-1} but this band is masked by the presence of the phosphate vibrations in the three derivatives.

A second polyether complex with a chain length averge of n = 9 was prepared and found to have an interlayer distance of 39.3 Å. This complex became colloidally dispersed when agitated in water. It readily sorbed electrolytes such as NaCNS, $CuCl_2$, $PdCl_2$, and $[Ru(bpy)_3]Cl_2$. Detailed descriptions of the longer chain polyether complexes and their chemical behavior will be presented in a subsequent paper.

Discussion

This study has shown that both α-ZrP and γ-ZrP react with ethylene oxide in a similar fashion. The interlayer spacing in γ-ZrP is 12.2 Å.[4] This is sufficiently large to allow relatively unobstructed diffusion of ethylene oxide into the interior with consequent esterification of all the monohydrogen phosphate groups. In α-ZrP the highly crystalline solids have a much smaller interlayer spacing (7.6 Å)[13] and the crystals do not swell in water. The passageways between the layers have a free diamter of only

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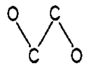
(19) Clearfield, A.; Tindwa, R. M. *J. Inorg. Nucl. Chem.* **1979**, *41*, 871.

2.6 Å[3,14] so diffusion into the interior is effectively blocked. However, with solids of low crystallinity the interlayer spacing may be larger as the state of hydration is greater.[11,20] Furthermore, the forces holding the layers together are weaker and thus less energy is required to expand the layers. This combination of circumstances allows ethylene oxide to diffuse into the interior, resulting in extensive reaction.

The ion-exchange reactions of crystalline α-ZrP are known to occur at the surface of the crystal and proceed by a diffusion mechanism.[21] The ions form a new phase at the periphery of the crystal and diffuse with advancing phase boundary. Thus, the exchanged phase coexists in the same crystal or particle with the unexchanged phase. One would expect that the esterification proceeds simiarly. That is, the surface phosphate groups tend to create a barrier toward diffusion to the interior. However, the resulting P–OCH_2CH_2OH groups are hydrophilic so that some additional swelling might be expected. The swelling allows further diffusion of ethylene oxide inward with concomitant reaction at the interior sites. This mechanism explains why mixtures of unreacted α-ZrP and the esterified phase occur together. Since diffusion is slow and proceeds from the surface inward, portions of the interior may remain totally unesterified even when the uptake approaches 2 mol.

Yamanaka has explained the interlayer distances observed in ethylene oxide esterified γ-ZrP on the basis of fully extended chains, i.e., a distance of 3.5 Å for the oxygen–oxygen trans–trans



length. A plot of interlayer distance as a function of ethylene oxide content for α-ZrP is shown in Figure 2. The slope of the line for the anhydrous products is 2.79 Å and for the hydrated (average 1 mol of H_2O) is 2.95 Å. Thus the chains are not fully extended. This may result from the fact that the distance between chains in α-ZrP, 5.3 Å, is probably larger than in γ-ZrP, since it is known from density considerations that the metal atoms are more densely packed in the latter compound.[22]

The direct interaction of ethylene oxide with α-ZrP, θ-ZrP, and γ-ZrP did not yield products with chain lengths greater than 2. This is inferred from the low values of n and the interlayer spacings. Presumably the large amount of energy required to expand the layers precludes extensive polymerization from occurring. Thus, we were led to the indirect route of preparing polyether phosphates from which the α-layered polyether complexes precipitate on contact with soluble Zr(IV) salts. These derivatives become more hydrophilic as the chain length of the polyether increases. This is shown by the greater degree of swelling on contact with water culminating in the colloidal dispersion of the complex when $n = 9$. However, the colloidal particles could be recovered by centrifugation or filtration through fine Millipore filters, showing their colloidal nature.

The ready uptake of electrolytes and coordination complexes by the zirconium polyether derivatives presages some exciting applications in electrochemistry, heterogenization of soluble catalysts, and novel separation procedures.

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Registry No. 1, 112-60-7; $POCl_3$, 10025-87-3; $BaO_3PO(CH_2CH_2O)_4H$, 96194-46-6; $ZrOCl_2$, 7699-43-6; $Zr[O_3PO(CH_2CH_2O)_4H]_2$, 96194-47-7.

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Synthesis and Properties of *tert*-Butyl-Substituted Vanadylphthalocyanine Dyes

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Soluble vanadylphthalocyanine dyes of various degree of *tert*-butyl substitution, $(t\text{-Bu})_n$VOPc, have been synthesized by reacting varying amounts of 4-*tert*-butylphthalonitrile and phthalonitrile with vanadium trichloride. The number of *tert*-butyl substituents on the VOPc ring is calculated from the elemental analysis results, which are in good agreement with the ^{1}H NMR data and are compatible with the mass spectrometric results. The solid-state properties of $(t\text{-Bu})_n$VOPc were studied by absorption spectroscopy and the X-ray powder diffraction technique, and results show that, at $n = 4.0$, the dye molecules form a non-IR-absorbing, amorphous VOPc phase I in the solid state and that, at $n = 1.4$, the crystalline, IR-absorbing VOPc phase II is formed. These results are discussed in terms of a steric effect on the packing of $(t\text{-Bu})_n$VOPc molecules into the phase II of VOPc in the solid state.

Introduction

Vanadylphthalocyanine (VOPc), like the parent phthalocyanine and many of its metal derivatives, possesses photoconductive and semiconductive properties. It has been shown that VOPc is a photosensitive pigment useful in photoelectrophoretic[1] and xerographic[2,3] imagings and more recently ablative optical recording.[4] The polymorphic behavior of VOPc has been studied by Griffiths, Walker, and Goldstein.[5] These authors show that in the solid state VOPc may exist in three different morphological forms, namely phases I–III. Among the three phases, phase II is a thermodynamically stable, crystalline material and exhibits strong near-IR absorption ($\lambda_{max} \sim 840$ nm). This near-IR absorptivity makes VOPc a very attractive photoreceptor candidate for diode laser scanned xerographic applications.[3] As a pigment, VOPc has limited solubility in organic solvents. Established purification procedure for VOPc, which involves dissolution of VOPc in concentrated sulfuric acid and reprecipitation of VOPc by discharging the resulting sulfuric acid solution into ice water, is very tedious and labor intensive.[6]

It was felt that this difficult purification process could be avoided by modification of VOPc with various solubilizing groups. The resulting VOPc dye, being highly soluble in organic solvents, could thus be purified by conventional solution recrystallization. Among various substituent groups, *tert*-butyl,[7–9] trimethylsilyl,[9] and sulfamide[10] groups seem to give the highest solubilizing effect

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