Mechanism of the Formation of Organic Derivatives of γ-Zirconium Phosphate by Topotactic Reactions with Phosphonic Acids in Water and Water−Acetone Media

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The rates of the topotactic reactions between γ-zirconium phosphate and phenylphosphonic acid in water and water−acetone mixtures at various temperatures were investigated. The slow rates of the process in aqueous medium or in water−acetone mixtures at temperatures lower than 50 °C were attributed to a slow interdiffusion of $O_2P(OH)_2^-$ and $O_2P(OH)(C_6H_5)^-$ groups in the interlayer region of γ-ZrP. Similar to ion-exchange processes, the replacement begins in the external part of the interlayer region and progresses toward the central region with the formation of an advancing phase boundary. In water−acetone mixtures at temperatures higher than 60 °C an exfoliation of γ-ZrP was found. Thus, the initial process is very fast since the substitution can take place directly on the surface of the exfoliated γ-lamellae. However, after a certain degree of substitution, a flocculation of the colloidal dispersion, which slows down the rate of the further topotactic substitution, was observed. Some considerations on the topotactic substitution occurring on the surface of the exfoliated lamellae and on the mechanism of the diffusion of the exchanging species in the interlayer region are also reported.

Introduction

The preparation of organic derivatives of γ-zirconium phosphate by topotactic reaction with phosphonic acids in 1:1 water−acetone medium at 80 °C was first reported by Yamanaka many years before the elucidation of the γ-layer structure of metal(IV) phosphates.[1] At that time γ-zirconium phosphate was erroneously formulated as $Zr(HPO_4)_2{\cdot}2H_2O$, and its structure was believed to be similar to that of α-$Zr(HPO_4)_2{\cdot}H_2O$.[2] Thus, although many γ-organic derivatives were obtained by this method,[3] no correct interpretation of the mechanism of the topotactic reaction was possible and no explanations of the role of acetone and temperature were attempted.

The structure of γ-metal(IV) phosphates (M^{IV} = Zr, Ti) has been recently elucidated.[4] Today, we also know that they must be formulated as $M^{IV}PO_4{\cdot}H_2PO_4{\cdot}2H_2O$ (hereafter written $M^{IV}PO_4{\cdot}O_2P(OH)_2{\cdot}2H_2O$, to show more clearly the two oxygen atoms linked to M^{IV} and the other two oxygen atoms of the acid OH groups). The chemistry of γ-metal phosphates was investigated again and reinterpreted on the basis of new structural knowledge. Many new phosphinate, phosphonate, and even diphosphonate derivatives with a microporous pillared structure have therefore been prepared[5] by topotactic reactions similar to that originally used by Yamanaka. However, in spite of the structural advances and preparative successes, still very little is known about the mechanism of the topotactic reactions. It seemed therefore of interest to investigate in detail the rate of the topotactic reactions in water and water−acetone mixtures at different temperatures.

The reaction chosen[6] was the replacement of $O_2P(OH)_2^-$ anions of γ-zirconium phosphate with phenylphosphonate anions $O_2P(OH)(C_6H_5)^-$.

Experimental Section

Materials. Phenylphosphonic acid (>98%) was a Fluka AG product. Zirconyl chloride octahydrate was a Merck proanalysis product. All the other chemicals were C. Erba RPE grade. γ-Zirconium phosphate (hereafter γ-ZrP) was prepared according to the procedure described in ref 7. The interlayer distance, obtained from the X-ray powder diffraction pattern, was 1.22 nm. The specific surface area, determined by BET, was 10 $m^2\ g^{-1}$.

Instrumental Details and Methods. The relative proportions of phosphonates to phosphates in the solids were obtained by quantitative ^{31}P liquid NMR analysis, with a Bruker AC 200 spectrometer, as described in ref 6.

The amount of dihydrogen phosphate groups released by γ-ZrP to the solutions was analyzed by ion chromatography with a DIONEX series 2000 1/sp, AS4A column and $NaHCO_3$ 1.7×10^{-3} M/Na_2CO_3 1.8×10^{-3} M solution as eluent. The uptake of the phosphonate groups by γ-ZrP was assumed to be equal to the dihydrogen phosphate released (see eq 1). The percentages of the topotactic replacement were obtained as an average of ^{31}P liquid NMR and ion chromatography analysis.

XRD patterns of the samples were recorded by the step scanning procedure (step size 0.03°) with the help of a computerized Philips PW1710 diffractometer using Ni-filtered Cu Kα radiation.

Procedures for the Topotactic Reaction. (A) Water Solution. Weighed amounts of γ-ZrP (0.25 g) were contacted, under shaking, with 50 mL of a 8×10^{-3} M solution of phenylphosphonic acid. At fixed intervals (ranging from 5 min to 40 days), the solids were separated by centrifugation (3 min).

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(B) Water−Acetone Mixture. At different temperatures, a weighed amount of γ-ZrP (0.25 g) was dispersed in 35 mL of a 1:1 water−acetone mixture with shaking for about 10 min, and then 15 mL of a 2.6×10^{-2} M solution of phenylphosphonic acid, previously heated at the corresponding temperature, was added. At fixed reaction times, the samples were rapidly cooled to room temperature in an ice−NaCl bath (1 min) and centrifuged.

Results and Discussions

The topotactic reaction of the formation of monophosphonate derivatives of γ-ZrP can be written as

$$\gamma\text{-ZrPO}_4\cdot\text{O}_2\text{P(OH)}_2\cdot 2\text{H}_2\text{O} + \text{O}_2\text{PR}'\text{R}^- \rightleftarrows \gamma\text{-ZrPO}_4\cdot\text{O}_2\text{PR}'\text{R} + \text{O}_2\text{P(OH)}_2^- \quad (1)$$

where R is an organic radical, whereas R′ can be either an organic radical or an OH group.

As will be discussed in more detail later, this topotactic reaction can be regarded as a ligand-exchange reaction. Ligand exchange, like ion exchange, is essentially a stoichiometric process, and the equilibrium of the topotactic reaction can therefore be described in terms of selectivity coefficients (also called separation factors), defined in the same way as for ion-exchange processes.[8] Therefore, the selectivity coefficient of γ-ZrP for the phenylphosphonic acid can be written $S_c = (\overline{\text{Ph}}/\overline{\text{P}})(\text{P}/\text{Ph})$, where Ph and P and $\overline{\text{Ph}}$ and $\overline{\text{P}}$ are the molar fractions of $O_2P(OH)C_6H_5$ and $O_2P(OH)_2$ groups in solution and in γ-ZrP, respectively.

At 80 °C, the selectivity coefficient of the above reaction, carried out on preswelled γ-ZrP, in order to reduce the equilibration times, has previously been estimated[9] to be equal to about 2. From this value, it is possible to calculate that, under the experimental conditions used here, the reaction can reach an equilibrium value in which about 38.2% of the original $O_2P(OH)_2$ is substituted by $O_2POHC_6H_5$.

If the equilibrium (1) is shifted toward right (e.g., by renewing the solutions) the formation of an organic derivative should be expected. However, steric hindrance between adjacent organic groups may prevent the formation of the fully exchanged derivatives. It has been previously found in the preparation of the phenylphosphonate derivative[6] that the maximum possible topotactic substitution was not greater than about 66%.

Preliminary experiments on the rate of the topotactic substitution (hereafter rts), initially carried out in water and in 1:1 water−acetone at temperatures of 25 and 80 °C, showed that high values were obtained only with 1:1 water−acetone mixtures at 80 °C, confirming that Yamanaka, in his pioneering works,[1] had already chosen good experimental conditions for the preparation of the first γ-organic derivatives. Under these conditions, about 15% of the topotactic substitution was obtained in less than 15 min. This very rapid rts cannot be explained by a simple mechanism of interdiffusion of phenylphosphonate and dihydrogen phosphate anions since the diffusion rate of large ligands in the interlayer region of γ-ZrP is expected to be very slow. On the other hand, the initial high rts cannot be accounted for by the replacement of dihydrogen phosphate groups present on the external surface of the original γ-ZrP microcrystals, since the estimated percentage of this substitution is not more than 1.5%.

The problem was finally understood when, from parallel research on the formation of intercalated acetone phases in γ-ZrP, it was discovered that γ-ZrP can undergo a process of exfoliation in water−acetone mixtures with the formation of a colloidal dispersion. The exfoliation process was investigated in detail and the results reported elsewhere.[10] Here it is sufficient to recall that the greater part of the exfoliation takes place only at temperatures higher than 60 °C and for acetone contents in the mixture ranging from 35 to 80% (in volume).

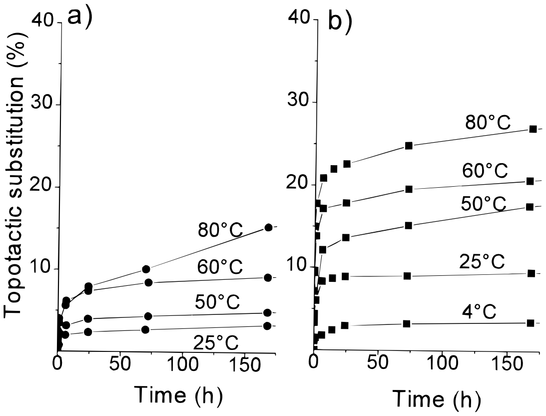

Figure 1. Initial rate of the topotactic reaction between γ-ZrP and phenylphosphonic acid solution at different temperatures (a) in water and (b) in a 1:1 water−acetone mixture. Conditions: 0.25 g of γ-ZrP/50 mL of phenylphosphonic acid, 8×10^{-3} M.

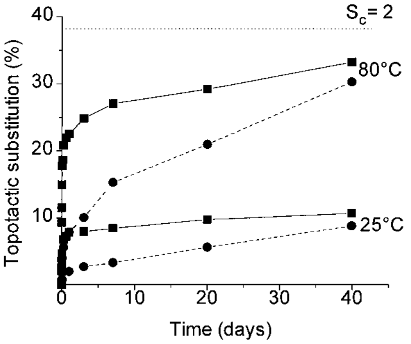

Figure 2. Rate of the topotactic reaction measured over a period of 40 days in water (dashed lines) and a 1:1 water−acetone mixture (solid lines), at 25 and 80 °C, respectively. Conditions: as in Figure 1.

It seemed therefore useful to examine and discuss separately the mechanism of the topotactic substitution in the aqueous medium, where exfoliation of γ-ZrP was never found in the temperature range examined, and in the water−acetone medium at temperatures >60 °C and <50 °C, in order to see the effect of the exfoliation on rts.

Formation of γ-Organic Derivatives in Aqueous Medium. The rate of the topotactic reaction, at different temperatures, is shown in Figure 1a, while Figure 2 (dashed curves) shows the rate of the reaction at 25 and 80 °C over a period of 40 days. Since γ-ZrP is not exfoliated in aqueous medium, the process of formation of the γ-organic derivatives can only proceed through an interdiffusion of ligands in the interlayer region. Thus, after a small uptake of the phosphonate groups on the external surface of the crystals, a small amount of organic derivative is expected to be formed in the external part of the interlayer region with the formation of a phase boundary. Then, as found in ion-exchange processes occurring in layered materials,[11] the reaction is expected to proceed through an advancing phase boundary, as schematically shown in the left part of Figure 3. The XRD patterns of the samples at an intermediate degree of substitution indeed showed that the

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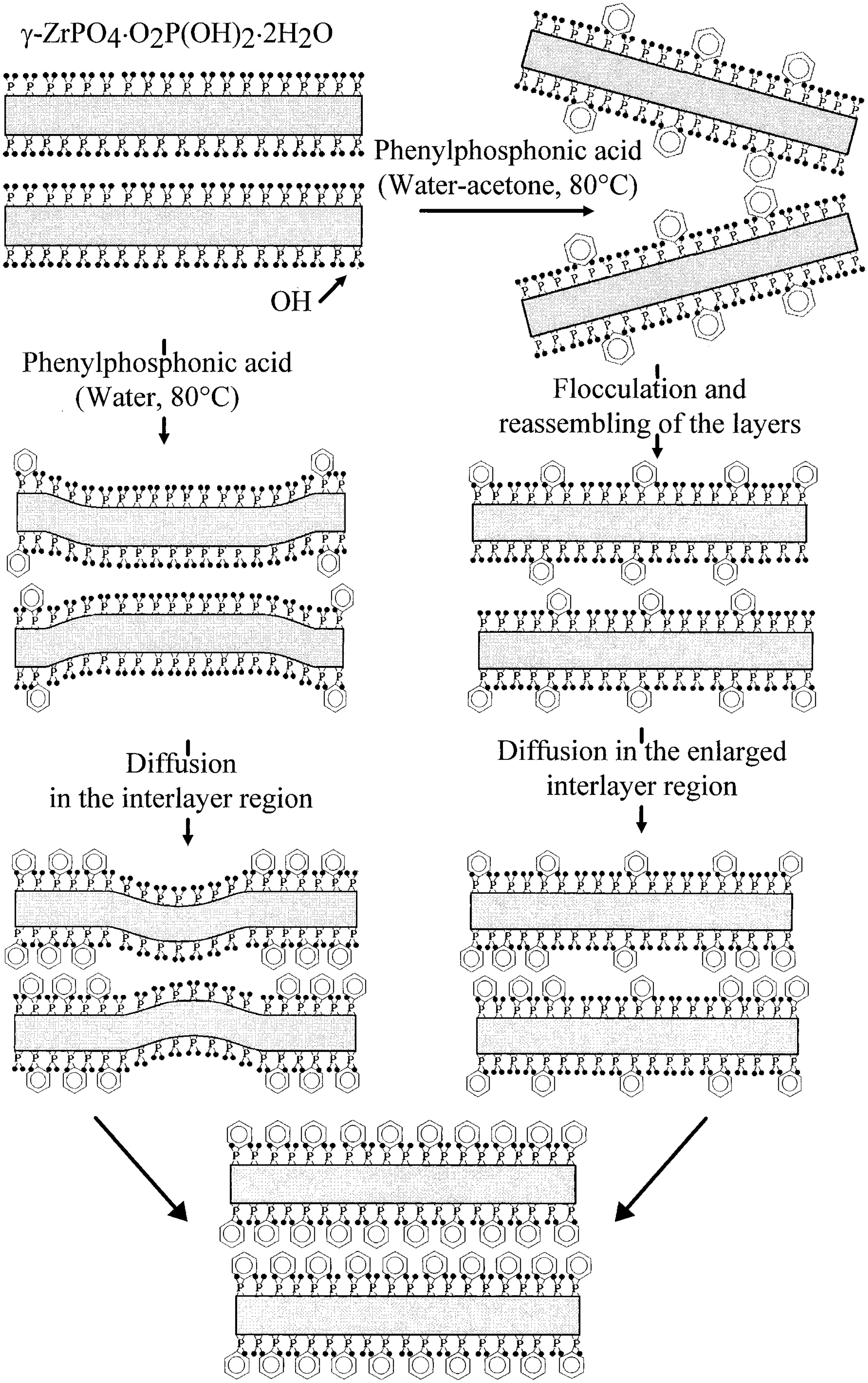


Figure 3. Schematic drawing of the topotactic reaction mechanism (a) in microcrystals of γ-ZrP (e.g., in water) and (b) in exfoliated lamellae of γ-ZrP (e.g., in a 1:1 water−acetone mixture at 80 °C).

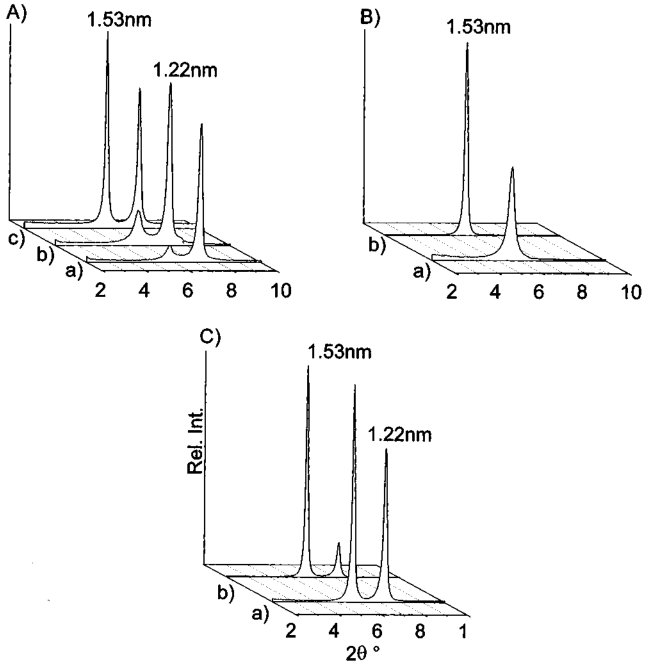


Figure 4. X-ray diffraction patterns of wet samples, at different exchange percentages, obtained from topotactic reaction between γ-ZrP and phenylphosphonic acid solutions. (A) Water at 80 °C: (a) 7.5%; (b) 15%; (c) 25%. (B) 1:1 water–acetone mixture at 80 °C: (a) 7.5%; (b) 15%. (C) 1:1 water–acetone mixture at 40 °C: (a) 7.5%; (b) 12.5%.

original γ-ZrP phase is progressively converted into the organic derivative with a discontinuous change of the interlayer distance from 1.22 to 1.53 nm (Figure 4A).

Owing to the large species involved in the topotactic reactions, the phase boundary is expected to move very slowly toward the central part of the microcrystals, and this explains the slow gradual substitution process, especially at temperatures lower than 50 °C. It was, however, found that the process can proceed at an appreciable rate at higher temperatures. From an extrapolation of the curves of Figure 2 it can be estimated that the equilibrium (represented as a dotted line for $S_c = 2$) is only reached in a very long time at 25 °C (more than 200 days) whereas at 80 °C is attained in a shorter time (about 50 days). Thus, organic derivatives can be also prepared in aqueous medium, at 80 °C, in an acceptable time. The effect of the temperature on the topotactic reaction in aqueous medium will be discussed later.

Formation of γ-Organic Derivatives in 1:1 Water–Acetone at Temperatures Higher Than 60 °C. As recalled before, an exfoliation of γ-ZrP crystals takes place in 1:1 water–acetone medium at temperatures ≥60 °C. The substitution reaction can therefore occur directly on the surface of the exfoliated lamellae, without interdiffusion of the ligands in the interlayer region. This explains the high initial rate of the topotactic reaction (see Figures 1b and 2). As more and more organic groups are attached to the exfoliated inorganic lamellae, the hydrophobic interactions become stronger and stronger until a flocculation of the partially converted γ-zirconium phosphate phosphonate, $ZrPO_4(O_2P(OH)_2)_{1-x}(O_2PR)_x \cdot nH_2O$, occurs. The value of x depends on the nature of the organic radical, the concentration of the phosphonic acid, and the time of reaction.

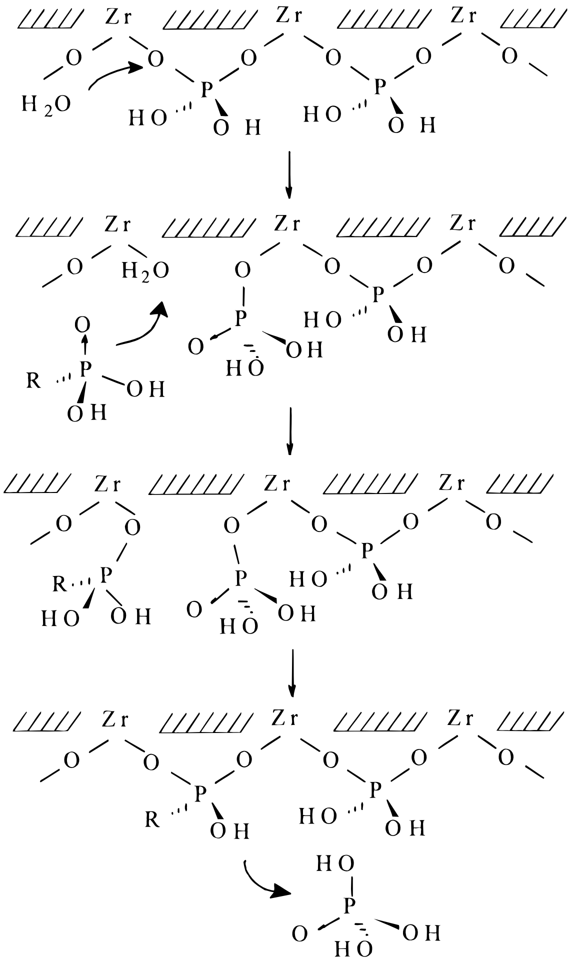
The XRD patterns of the samples obtained after the flocculation showed that the reflection at 1.22 nm, characteristic of the original γ-ZrP phase, disappears even for very low conversions and a single phase with an interlayer distance of 1.53 nm, characteristic of the fully exchanged phase, was found at conversions higher than 7% (see Figure 4B). This behavior is in agreement with the expectation that the phosphate groups are distributed throughout the interlayer region. In any case, after the flocculation, the further substitution must occur through an interdiffusion in the interlayer region with a mechanism similar to that previously discussed in aqueous media. Accordingly, although this substitution now takes place in a phase exhibiting a larger interlayer distance than the original γ-ZrP, the rts decreases appreciably after the flocculation. For example, at 80 °C the flocculation occurs after 15 min at about 20% of topotactic substitution (see Figure 1b).

A schematic view of the topotactic reaction in 1:1 water–acetone mixtures at temperatures higher than 60 °C is shown in the right part of Figure 3. Note that, in this case, the advancing phase boundary is not formed. However, irregular distribution of the phosphonate groups, with higher concentration in the external part of the interlayer region, must be expected for all of the phases in which the full conversion has not yet been obtained. It can be finally noted that the extrapolated time for the establishment of the equilibrium is longer in water–acetone media than in water. However, at 80 °C, 50% of the equilibrium in water is reached in about 16 days, while in water–acetone the equilibrium is reached in only about 3 h. Thus, the exfoliation of γ-ZrP crystals has a great influence on the initial rts. These data are therefore very important for the choice of experimental conditions used in the preparation of the γ-organic derivatives.

Formation of γ-Organic Derivatives in 1:1 Water–Acetone at Temperatures Lower than 50 °C. As previously reported,[10] exfoliation does not occur to a great extent under these conditions. Accordingly, rates appreciably lower than those at 80 °C were found at 50 °C (see Figures 1b and 2). The XRD patterns of derivatives at a low degree of conversion showed the coexistence of two immiscible phases. Two patterns of samples with 7.5 and 12.5% substitution prepared at 40 °C are shown in Figure 4C. Thus, the formation of the γ-organic derivatives is expected to occur with a mechanism similar to that previously discussed in aqueous media through a slow interdiffusion of the exchanging species in the interlayer region of γ-ZrP (i.e., with formation of an advancing phase boundary).

Some Considerations on the Mechanism of the Topotactic Reaction. (A) Processes Occurring on the Surface of γ-Exfoliated Lamellae. As discussed before, the topotactic reaction of formation of γ-organic derivatives with monophosphonic acids can be regarded as an exchange process of monovalent anionic ligands. It must, however, be considered that in γ-ZrP the original $O_2P(OH)_2^-$ ligands are coordinated to zirconium atoms through two oxygens; therefore, the process can be more precisely regarded as an exchange between bidentate (monovalent) anionic ligands. It is thus to be expected that the process must occur in at least two steps. In the first step, one of the oxygens of the $O_2P(OH)_2^-$ ligand is detached from the zirconium atom, thus allowing the anchoring of one of the oxygens of the $O_2PR'R^-$ ligand to this free coordination site. The reaction is then completed in the second step, in which the second oxygen of the leaving $O_2P(OH)_2^-$ is also replaced by the entering $O_2PR'R^-$ ligand. It is likely that intermediate processes, e.g., a first hydrolytic substitution of one of the oxygens of $O_2P(OH)_2$ by water or OH^- groups, followed by the replacement with one of the oxygens of the $O_2PR'R^-$ ligand, also take place. As an example, a mechanism in which hydrolytic substitutions are involved is schematically depicted in Scheme 1. In any case, independent of the detailed mechanism of the topotactic reaction, an experimental value of the time necessary to reach 50% of the equilibrium value ($t_{1/2}$) can be determined if the flocculation of the exfoliated lamellae

Scheme 1



is avoided. In this case, the slow diffusion process has no influence since concentration differences in the bulk solution can be leveled out by agitation and, hence, the necessary transfer of the phosphates and phosphonates in both the γ-ZrP and the solution occurs only by convection. To avoid the flocculation of the exfoliated lamellae, the reaction was carried out in the presence of small amounts of phosphonic acid (50 mL of 1.57 $\times$ 10^{-3} M/0.25 g of γ-ZrP). Under these conditions, about 10% of the total substitution was to be expected at the equilibrium if $S_c = 2$ is assumed. Figure 5 shows that the degree of substitution indeed tends with time to reach the equilibrium calculated (dotted line in Figure 5). A $t_{1/2}$ value of about 8 min can therefore be evaluated. It must, however, be considered that the true $t_{1/2}$ must be much lower than this value since the times reported in Figure 5 include the cooling and centrifugation times (about 3 min) necessary for the flocculation and separation of the exfoliated lamellae (see Experimental Section). We are unable to quantify the rts during the cooling and separation of the samples. Nevertheless, since the rate of substitution during the time necessary to separate the derivative from the solution is expected to be appreciably lower than the rate occurring at 80 °C on the exfoliated lamellae, the true $t_{1/2}$ value must also be much lower than 8 min. Due to the uncertainty of the rts during the cooling and separation of the samples, more precise determination of the $t_{1/2}$ values cannot be obtained. For the same reason, evaluations of the rate constant and of the order of the reaction were not attempted. Nevertheless, in spite of the lack of precise information, the data reported here indicate unequivocally that the substitution of the $O_2P(OH)_2^-$ groups is very fast. The long times required for the preparation of derivatives with high degrees of conversion are therefore essentially due to the slow diffusion of the interexchanging species in the interlayer region of γ-ZrP after its flocculation. This conclusion has important implications for the choice of the reaction times in the preparation of the organic γ-derivatives at various degrees of substitution. Single phases of partially substituted derivatives with a homogeneous distribution of organic groups in the interlayer region are expected to be formed only when very short reaction times (10−15 min) are used. For longer times, the partial or total flocculation of the exfoliated lamellae can occur, giving products with a higher concentration of organic groups in the external part of the interlayer region.

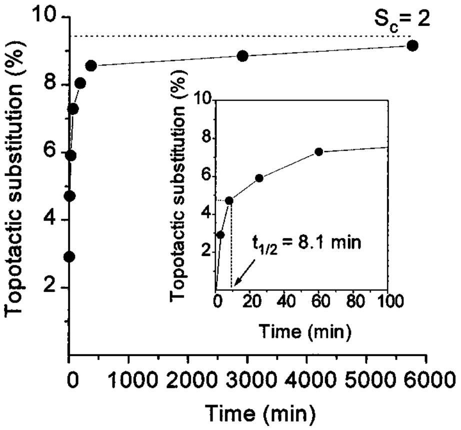
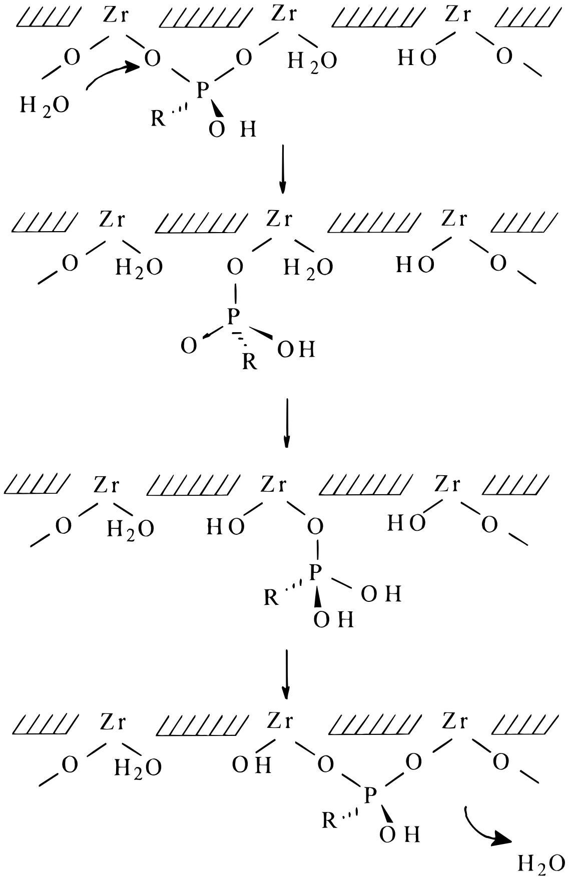


Figure 5. Rate of the topotactic reaction in exfoliated lamellae of γ-ZrP. Conditions: 1:1 water−acetone mixture at 80 °C, 0.25 g of γ-ZrP/50 mL of phenylphosphonic acid, 1.57 $\times$ 10^{-3} M.

Scheme 2



(B) Processes Occurring in the Interlayer Region. Since organic γ-derivatives have also been obtained in aqueous medium with nonexfoliated γ-ZrP, a certain interdiffusion of phosphate and phosphonate groups in the interlayer region must be admitted. Models based on a partial hydrolysis, followed by rearrangement and coordination of one oxygen of these groups to an adjacent partially hydrolyzed zirconium, can be derived to explain these slow interdiffusion processes. One of these models is schematically illustrated in Scheme 2. Further research will, however, be necessary to clarify the exact mechanism of the interdiffusion of entering and leaving species in the interlayer region.

Conclusions

The results reported have definitively clarified that the main reason why the rate of the topotactic formation of γ-organic derivatives is faster in water−acetone mixtures than in water is the formation of colloidal dispersions of γ-ZrP lamellae. Thus, not only the standard conditions (i.e., 1:1 water−acetone mixture at 80 °C) but also all temperature ranges and acetone concentrations at which a good exfoliation of γ-ZrP is obtained (i.e., temperatures higher than 60 °C and acetone from 35 to 80% (in volume)) can be used to prepare organic derivatives of γ-ZrP.

It was also established that the use of colloidal dispersions of γ-ZrP is a very convenient method only for the fast preparation of partially converted organic derivatives. Note, however, that the exfoliation and reassembling of the γ-ZrP layers in water−acetone mixtures greatly decreases the order and the number of the layers of the original microcrystals with consequent broadening of the peaks of the obtained derivatives. Thus, in spite of the longer time of the equilibrium, it could be convenient to carry out the topotactic reaction in water if products with a better degree of crystallinity are wished.

Finally, it is noteworthy that the topotactic preparation of the γ-organic derivatives from exfoliated γ-ZrP is a rare example (maybe the first) in which a crystalline compound is first transformed into a colloidal dispersion and then, after chemical modifications obtained by fast topotactic reactions, again recomposed.

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