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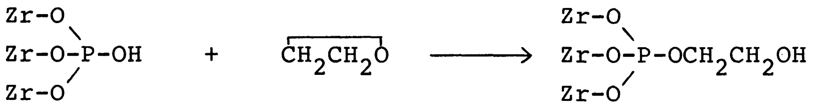
EXCHANGE REACTION BETWEEN $HPO_4{}^{2-}$ AND $C_6H_5OPO_3{}^{2-}$ IN A HETEROGENEOUS SYSTEM WITH γ-ZIRCONIUM PHOSPHATE, $Zr(HPO_4)_2 \cdot 2H_2O$

Shoji YAMANAKA and Makoto HATTORI
Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Hiroshima 730

The monohydrogen orthophosphate ions on the interlayer surfaces of a cation exchanger γ-zirconium phosphate, $Zr(HPO_4)_2 \cdot 2H_2O$, are exchanged with monophenyl orthophosphate ions of the external solution, and a new type of compound $Zr(C_6H_5OPO_3)(HPO_4) \cdot 2H_2O$ is formed. The exchange is reversible. The compound reverts to the initial γ-zirconium phosphate in orthophosphoric acid solutions.

Zirconium bis(monohydrogen orthophosphate) dihydrate, $Zr(HPO_4)_2 \cdot 2H_2O$, hereafter called γ-zirconium phosphate or γ-ZrP, is an insoluble inorganic ion-exchanger with a layer structure[1]. Various kinds of polar organic molecules can be introduced to the interlayer spaces with accompanying changes in basal spacing[2,3]. When ethylene oxide is taken up in the interlayer spaces of γ-ZrP from aqueous solutions, it reacts with the monohydrogen orthophosphate groups on the interlayer surfaces of γ-ZrP, and forms phosphoric ester links[4] :

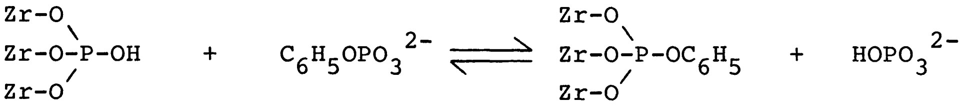


$$\begin{array}{l}\mathrm{Zr{-}O}\\ \mathrm{Zr{-}O{-}P{-}OH}\\ \mathrm{Zr{-}O}\end{array} + \overline{\mathrm{CH_2CH_2O}} \longrightarrow \begin{array}{l}\mathrm{Zr{-}O}\\ \mathrm{Zr{-}O{-}P{-}OCH_2CH_2OH}\\ \mathrm{Zr{-}O}\end{array} \qquad (1)$$

The reaction is quantitative and an organic derivative of the inorganic layers, $Zr(O_3POCH_2CH_2OH)_2 \cdot H_2O$ (refered to as ZrP·2EO), is obtained. Propylene oxide also reacts with γ-ZrP in a similar way[5].

ZrP·2EO can persist in acidic solutions without the presence of phosphate ions. However, in H_3PO_4 solution, it reverts to the initial γ-ZrP by exchanging the phosphoric ester ions ($HOCH_2CH_2OPO_3{}^{2-}$) with $HPO_4{}^{2-}$ ions of the external solution[6].

In the present study, an attempt has been made to exchange $HPO_4{}^{2-}$ ions on the interlayer surfaces of γ-ZrP with phosphoric ester ions by using monophenyl orthophosphoric acid ($C_6H_5OPO_3H_2$) as a phosphoric ester, and it has been found that the following exchange occurs reversibly:



$$\begin{array}{l}\mathrm{Zr{-}O}\\ \mathrm{Zr{-}O{-}P{-}OH}\\ \mathrm{Zr{-}O}\end{array} + C_6H_5OPO_3{}^{2-} \rightleftharpoons \begin{array}{l}\mathrm{Zr{-}O}\\ \mathrm{Zr{-}O{-}P{-}OC_6H_5}\\ \mathrm{Zr{-}O}\end{array} + HOPO_3{}^{2-} \qquad (2)$$

γ-Zirconium phosphate (1 g) prepared according to the method described elsewhere[1] was dispersed into 50 ml of 1 M $C_6H_5OPO_3H_2$ solution in a mixture of equal volumes of acetone and water, and heated under reflux for 10 hr. Then, the dispersed solid was separated by using Teflon filter, washed with acetone and dried in the air.

X-ray powder diffraction analysis was carried out on the dried sample. The basal reflections due to γ-ZrP disappeared within an hour and the basal spacing was enlarged to 16.43 Å from 12.27 Å of the initial spacing of γ-ZrP. Several reflections corresponding to the higher orders of the enlarged spacing were observed.

The initial γ-ZrP behaves as a cation exchanger. The interlayer hydrogen ions are exchanged with sodium ions in NaOH solutions. The sodium ion-exchanged form reversibly changes into the initial γ-ZrP on washing with HCl solution. On the contrary, γ-ZrP treated with $C_6H_5OPO_3H_2$ was easily hydrolyzed into a gel in 1 N NaOH even at room temperature. The gel separated by filtration followed by washing with water was zirconium hydroxide gel and converted to ZrO_2 on heating. The filtrate was analyzed by cellulose thin-layer chromatography, and two spots for $C_6H_5OPO_3^{2-}$ and PO_4^{3-} were observed at R_f = 0.61 and 0.35, respectively. The solvent used for the development was prepared by mixing 25 ml of ethyl alcohol, 7.5 ml of concentrated ammonia solution, 15 ml of water, and 100 mg of trichloroacetic acid. The spots were visualized by the procedure described previously[4)]. The reaction product of γ-ZrP with $C_6H_5OPO_3H_2$ solution could persist in 1 N HCl at 95°C for one day without any change in the spacing.

Electron microscope examination showed that the size of the initial γ-ZrP platelets was unchanged during the refluxing in $C_6H_5OPO_3H_2$ solution. In addition, the electron diffraction patterns obtained on the refluxed platelets having a basal spacing 16.43 Å with the plates perpendicular to the electron beam essentially coincided with that of the initial γ-ZrP shown in a previous study[1)].

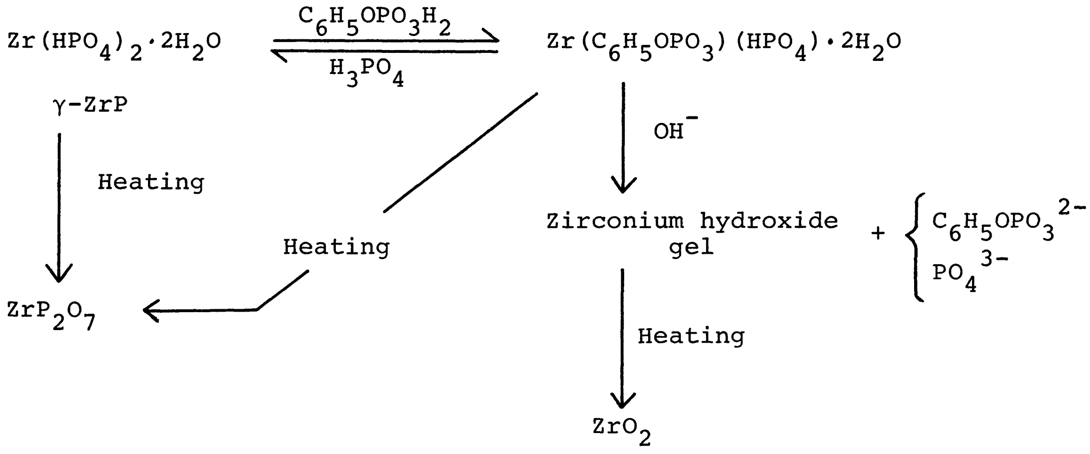
Evidently, the above results lead to a conclusion that the exchange occurs between HPO_4^{2-} ions of γ-ZrP and $C_6H_5OPO_3^{2-}$ ions of the external solution, and the layer framework of γ-ZrP is unchanged by the exchange.

Differential thermogravimetric analysis (TG-DTA) was performed on the reaction product up to 1000°C for a heating rate of 10°C/min. The loss in weight was observed stepwise. The first weight loss (W_1) accompanied by a broad endothermic peak around 80°C was attributed to adsorbed water. The water removed on heating was readsorbed immediately when the sample was allowed to stand in the air. The second weight loss (W_2) began at 292°C with intense exothermic peaks and finally the sample converted to ZrP_2O_7. Thus, the weight loss observed subsequent to the dehydration of adsorbed water was assigned to the decomposition and oxidation of the interlayer phenyl groups and the dehydration accompanied by the formation of ZrP_2O_7. The weight losses (W_1 and W_2) observed are shown in Table 1, together with the data of

Table 1. Summary analytical results for γ-ZrP treated with monophenyl orthophosphoric acid

	ZrO_2	P_2O_5	W_1 RT ~ 200°	W_2 200 ~ 1000°
Found (%)	31.08	35.39	8.76	24.20
Calculated (%) for $Zr(C_6H_5OPO_3)(HPO_4)\cdot 2H_2O$	31.18	35.92	9.11	23.79

Scheme I.



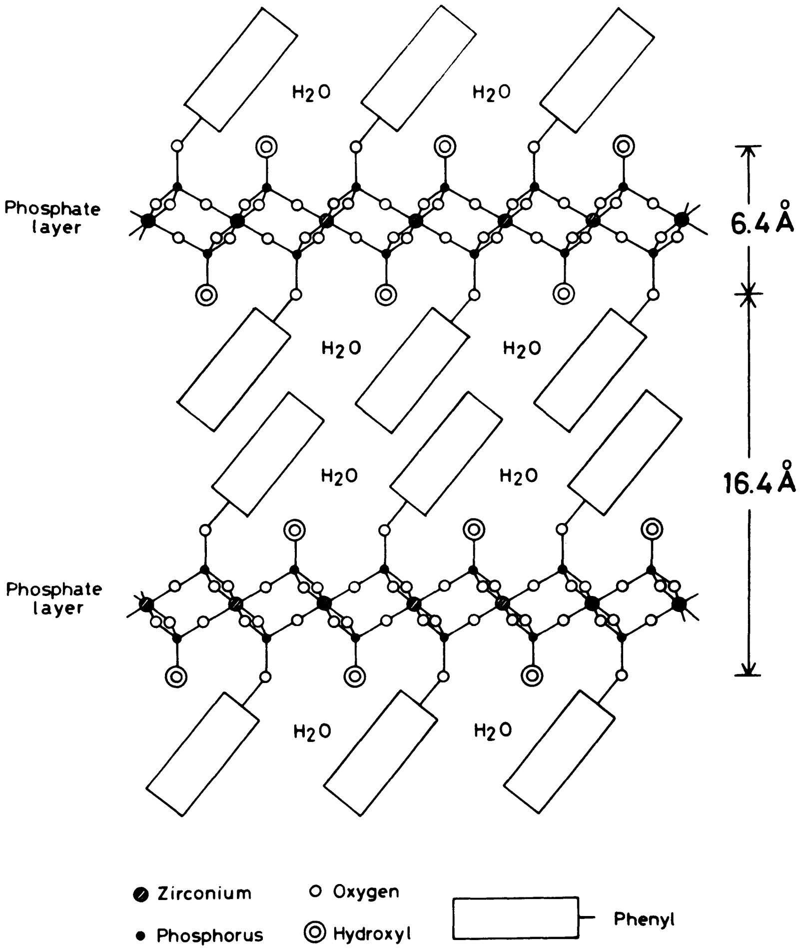


Fig. 1. Structural model for $Zr(C_6H_5OPO_3)(HPO_4) \cdot 2H_2O$ with a basal spacing 16.4 Å

the chemical analyses of ZrO_2 and P_2O_5. The analyses show that the reaction product obtained is $Zr(C_6H_5OPO_3)(HPO_4)\cdot 2H_2O$, indicating that half of HPO_4^{2-} ions of γ-ZrP are exchanged with $C_6H_5OPO_3^{2-}$ ions.

The monophenyl orthophosphate ions in $Zr(C_6H_5OPO_3)(HPO_4)\cdot 2H_2O$ were reversibly exchanged with HPO_4^{2-} ions by heating in 1 M H_3PO_4 at 70°C for several hours. The X-ray powder pattern of the sample heated in the solution coincided with that of the initial γ-ZrP, $Zr(HPO_4)_2\cdot 2H_2O$. The related reactions in this study are summarized in Scheme I.

A possible structural model for $Zr(C_6H_5OPO_3)(HPO_4)\cdot 2H_2O$ is proposed in Fig. 1. Although the definite structure of γ-ZrP is yet unknown, it seems to be reasonable to estimate the thickness of each phosphate layer (oxygen to oxygen distance) to be about 6.4 Å [1,5,7]. The observed basal spacing of 16.43 Å can be explained in terms of the phenyl groups linked to the phosphate layers with the molecular planes inclined to the layers. Since half of HPO_4^{2-} ions in γ-ZrP remain unexchanged, it seems likely that cavities are formed around the unexchanged sites, where water molecules can be held.

γ-Zirconium phosphate is known as a cation exchanger. The hydrogen ions in the interlayer spaces can be exchanged with various kinds of cations. It is interesting to note that the cation exchanger can also act as an anion exchanger between HPO_4^{2-} ions and $C_6H_5OPO_3^{2-}$ ions. We are now investigating the similar exchange reactions of HPO_4^{2-} with various kinds of phosphoric esters. The results will be published elsewhere in the near future.

References

1. S. Yamanaka and M. Tanaka, J. Inorg. Nucl. Chem. 41, 45 (1979).
2. S. Yamanaka and M. Koizumi, Clays Clay mineral. 23, 477 (1975).
3. S. Yamanaka, Y. Horibe, and M. Tanaka, J. Inorg. Nucl. Chem. 38, 323 (1976).
4. S. Yamanaka, Inorg. Chem. 15, 2811 (1976).
5. S. Yamanaka, M. Tsujimoto, and M. Tanaka, J. Inorg. Nucl. Chem. 41, 605 (1979).
6. S. Yamanaka, H. Maeda, and M. Tanaka, J. Inorg. Nucl. Chem. (in press).
7. A. Clearfield, R. H. Blessing, and J. A. Stynes, J. Inorg. Nucl. Chem. 30, 2249 (1968).

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