

## **THERMAL DECOMPOSITION OF ORGANIC DERIVATIVES OF CRYSTALLINE ZIRCONIUM PHOSPHATE**

### **III. Thermal decomposition of diethylene glycol, benzyl alcohol and benzylamine intercalates of zirconium phosphate**

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The diethylene glycol, benzyl alcohol and benzylamine derivatives of  $\alpha$ - and  $\gamma$ -zirconium phosphates were prepared and their thermal behaviour was investigated by means of differential thermal analysis. In all cases, the derivatives of  $\alpha$ -zirconium phosphate were more stable than those of  $\gamma$ -zirconium phosphate.

The structures of organic derivatives of  $\alpha$ - and  $\gamma$ -zirconium phosphates are similar, the only difference being the location of  $\equiv\text{P-OH}$  groups replaced by  $\equiv\text{P-OR}$  or  $\equiv\text{P-R}$  groups [1]. These materials may be regarded as organic-inorganic ion-exchangers, especially if they contain ionogenic groups such as  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$  or  $\text{N}(\text{CH}_3)\text{Cl}$  in the organic radical. However, the behaviour of such materials has received relatively little attention in recent years [2].

Data connected with the thermal decomposition of such materials are presented in this paper.

#### **Experimental**

The organic derivatives were prepared as follows:

5.0 g of crystalline material ( $\alpha$  or  $\gamma$  form) was equilibrated with 100 ml of a saturated solution of the organic molecule for 4 days at room temperature ( $25 \pm 1^\circ$ ). The precipitate formed was then dried in an oven at  $40^\circ$  to constant weight, and stored in a desiccator. The prepared samples were identified

by analytical, X-ray powder diffraction and IR spectrophotometric methods, as described earlier [3].

The thermal decomposition of the materials was investigated in the same way as reported previously [4]. Diethylene glycol (DEG), benzyl alcohol and benzylamine were used as organic molecules.

## Results and discussion

The prepared organic derivatives were shown by X-ray diffraction measurements to be crystalline, having a layered structure with different interlayer distances (Table 1).

In general, the investigated materials exhibited similar thermal behaviour, but certain differences were observed.

Table 1 Analytical data

Samples	Org/inorg ratio, mmole	Interlayer dist. ( <i>d</i> ), nm	Total weight loss, %
$\alpha$ -zirconium-phosphate ( $\alpha$ -ZrP)	–	0.76	13.37
$\gamma$ -zirconium-phosphate ( $\gamma$ -ZrP)	–	1.22	32.74
D.E.G. – $\alpha$ -ZrP	1 : 1.45	0.96	33.41
D.E.G. – $\gamma$ -ZrP	1 : 1.4	1.17	28.84
Benzylalcohol – $\alpha$ -ZrP	1 : 1	2.10	41.31
Benzylalcohol – $\gamma$ -ZrP	1 : 1	2.27	57.26
Benzylamine – $\alpha$ -ZrP	1 : 2	1.90	43.11
Benzylamine – $\gamma$ -ZrP	1 : 2	2.30	22.13

### 1. Diethylene glycol (DEG) derivatives:

a) Figure 1 presents the thermal curves of the DEG derivative of  $\alpha$ -zirconium phosphate. There are endothermic peaks with weight loss at 93°, 250°, 405° and 580°, and an exothermic peak without weight loss at about 750°.

The first endothermic process is connected with the loss of crystal water, the second with the decomposition of DEG, and the third and fourth with the loss of organic molecule and structural water, respectively.

The decomposition of  $\text{HPO}_4^{2-}$  groups immediately follows the loss of organic molecules and generally occurs at a higher temperature than for  $\alpha$ -zirconium phosphate.

b) Figure 2 shows the thermal curves of the DEG derivative of  $\gamma$ -zirconium phosphate. The same processes were found as for the  $\alpha$ -zirconium phosphate derivative, except that the first endothermic process had a two-step character. The data in Table 1 suggest the following thermal decompositions:

a)

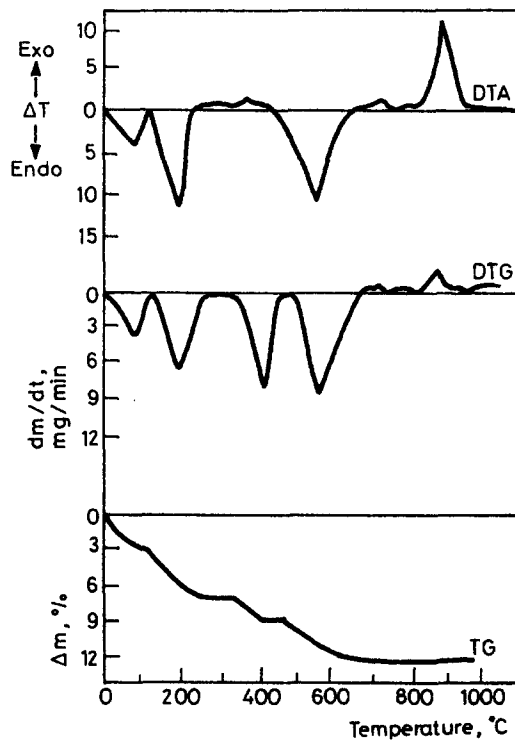
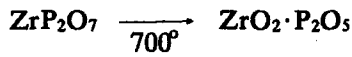
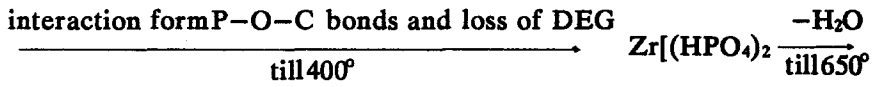
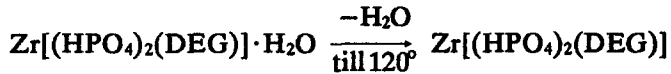


Fig. 1 TG, DTG and DTA curves of diethylenglycol intercalated of  $\alpha$ -ZrP

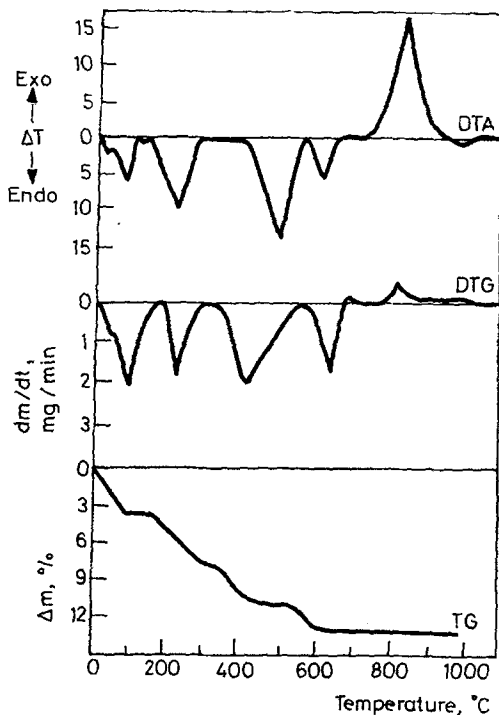
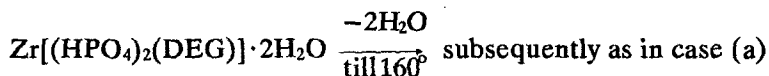


Fig. 2 TG, DTG and DTA curves of diethylenglycol intercalated of  $\gamma$ -ZrP

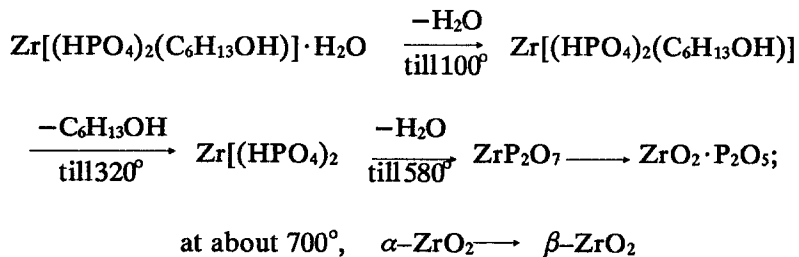
b)



## 2. Benzyl alcohol derivatives

a) The curves of the  $\alpha$ -zirconium derivative (Fig. 3) reveal endothermic peaks with weight loss at  $80^\circ$ ,  $280^\circ$  and  $520^\circ$ , followed by an exothermic peak without weight loss at about  $740^\circ$ .

The first process is the loss of crystal water, the second the decomposition of benzyl alcohol, and the third the loss of structural water. The exothermic process can be ascribed to a crystalline change in the zirconium dioxide. The thermal decomposition of the material may be described as follows:



b) (Fig. 4) The thermal decomposition of the  $\gamma$ -zirconium phosphate derivative showed a similar character, with the following differences:

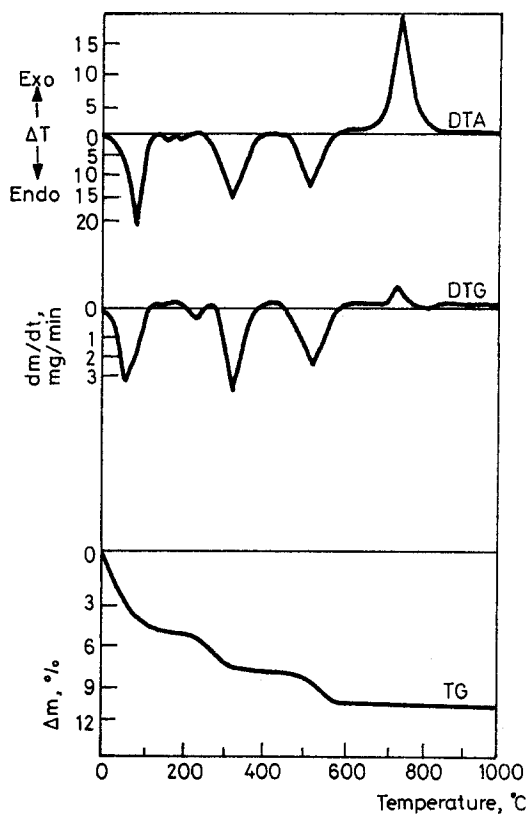
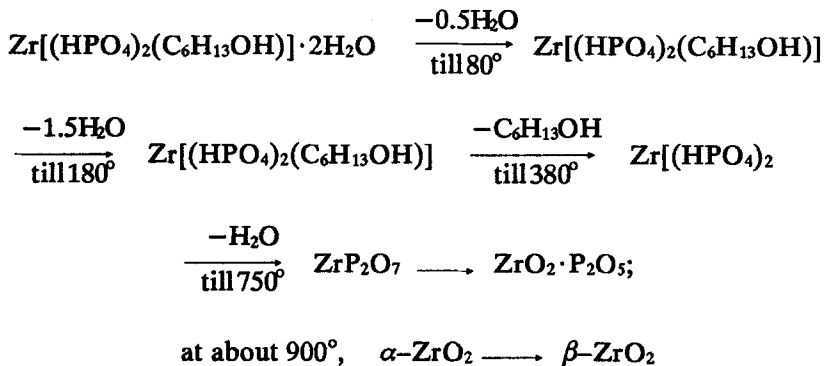


Fig. 3 TG, DTG and DTA curves of benzylalcohol intercalated of  $\alpha\text{-ZrP}$



### 3. Benzylamine derivatives

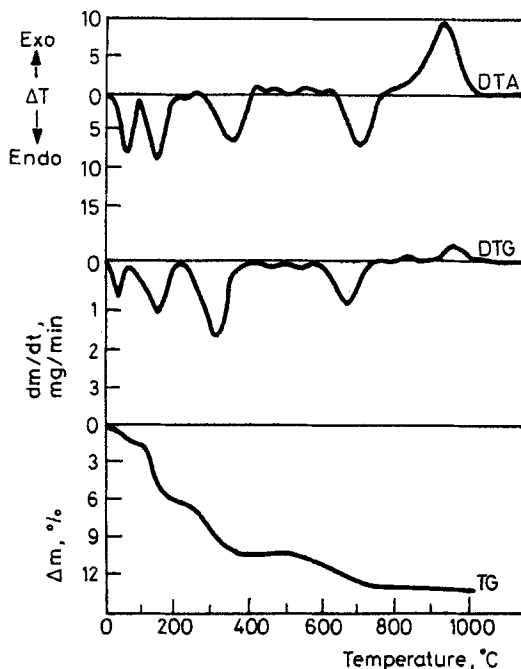
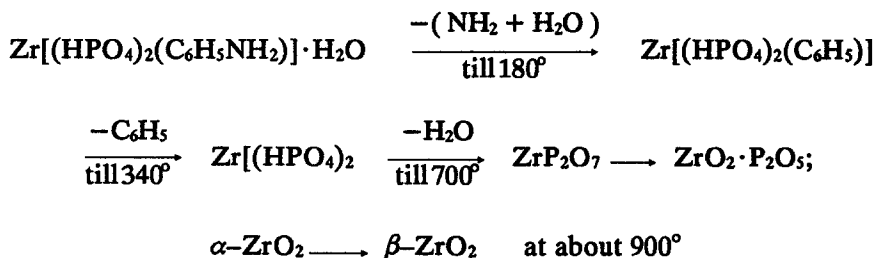


Fig. 4 TG, DTG and DTA curves of benzylalcohol intercalated of  $\gamma$ -ZrP

a) The curves for the  $\alpha$ -zirconium phosphate derivative (Fig. 5) show endothermic peaks with weight loss at  $50^\circ$ ,  $120^\circ$ ,  $280^\circ$  and  $640^\circ$ , and an exothermic peak without weight loss at about  $900^\circ$ .

The first and second processes are the loss of  $\text{NH}_2$  groups and crystal-water, respectively. This is followed by scission of the ring, with total loss of

the organic molecule. Next, at a little higher temperature, as usual, the  $\text{HPO}_4^{2-}$  groups decomposed, with the loss of structural water. Finally, at about  $900^\circ$  the crystal form of zirconium dioxide changed. The thermal decomposition of the material may be proposed as follows:



b) The curves for the  $\gamma$ -zirconium phosphate derivative (Fig. 6) reveal similar processes as found for the  $\alpha$ -zirconium phosphate derivative, with the following differences: endothermic peaks are observed at  $50^\circ$ ,  $110^\circ$ ,  $270^\circ$  and  $510^\circ$ , and an exothermic one at  $690^\circ$ .

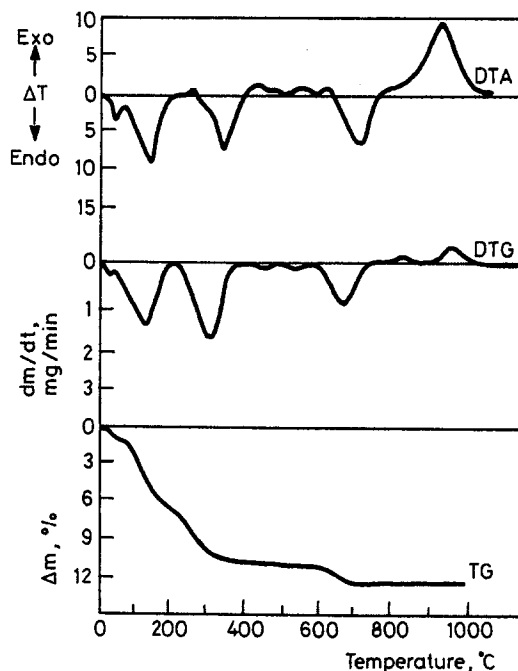
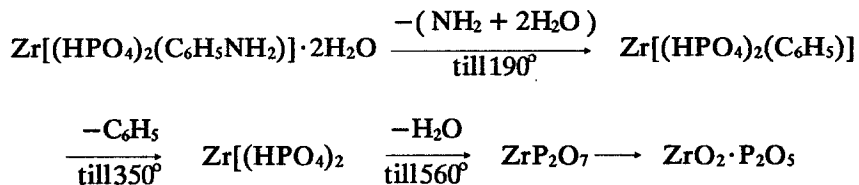


Fig. 5 TG, DTG and DTA curves of benzylamine intercalated of  $\alpha$ -ZrP

The tabulated data suggest the following thermal decomposition of the material:



The above results indicate that all the investigated materials in general decompose in a similar way.

The following differences were found:

a) In the case of DEG, a difference was observed between the loss of

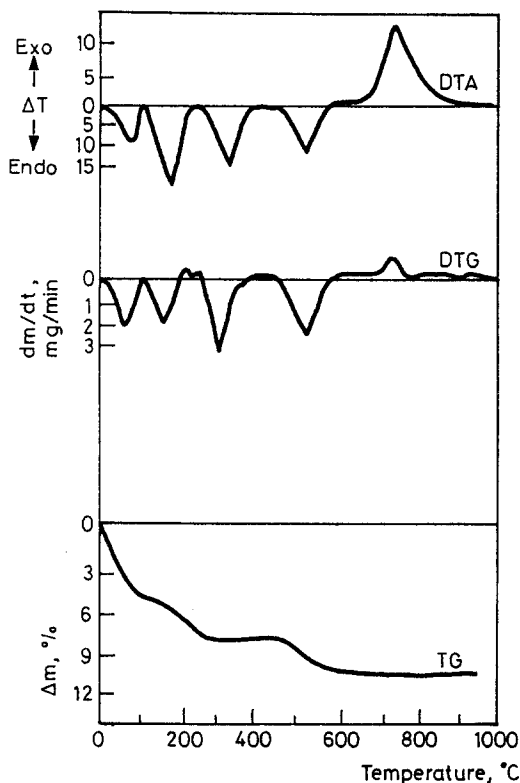


Fig. 6 TG, DTG and DTA curves of benzylamine intercalated of  $\gamma$ -ZrP

crystal water from the  $\alpha$ - (one mole up to  $120^\circ$ ) and  $\gamma$ -zirconium phosphate (2 moles up to  $160^\circ$ ) derivatives.



b) In the case of benzyl alcohol, the  $\alpha$ -zirconium phosphate derivative lost its crystal water content in one step up to 100°, while the  $\gamma$ -form lost it in two, unequal steps. The organic molecule was decomposed up to 320° and 380°, respectively, and as a result the structural water was also lost at higher temperature (580° and 750°, respectively).

c) In the case of benzylamine, the  $\alpha$ -zirconium phosphate derivative lost its crystal water, together with the NH<sub>2</sub> group, up to 180°. After scission of the ring, the organic molecule was lost. This process was completed at 340°, following which the structural water was lost up to 700°. Decomposition of the HPO<sub>4</sub><sup>2-</sup> groups led to reordering of the molecule, yielding zirconium pyrophosphate, which immediately decomposed to ZrO<sub>2</sub>·P<sub>2</sub>O<sub>5</sub>. Finally, the crystalline form of ZrO<sub>2</sub> changed ( $\alpha \rightarrow \beta$ ), which is known in the literature [5].

In the case of the  $\gamma$ -zirconium phosphate derivative, the HPO<sub>4</sub><sup>2-</sup> groups decomposed faster, this process being completed at a lower temperature (560°).

To summarize, the thermal decompositions of the investigated samples were similar, consisting of the following stages:

- loss of crystal water and NH<sub>2</sub> groups,
- esterification, or ring scission, followed by loss of the organic molecule,
- decomposition of HPO<sub>4</sub><sup>2-</sup> groups and loss of structural water,
- formation of oxides,
- change of crystalline form of ZrO<sub>2</sub>.

The temperatures of these processes reveal that  $\alpha$ -zirconium phosphate derivatives are thermally more stable than those of  $\gamma$ -zirconium phosphate.

## References

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**Zusammenfassung** — Es wurden Diethylenglykol-, Benzylalkohol- und Benzylamin-Derivate von  $\alpha$ - und  $\gamma$ -Zirkoniumphosphaten hergestellt und ihr Thermisches Verhalten mittels DTA untersucht. In allen Fällen waren die Derivate der  $\alpha$ -Zirkoniumphosphate stabiler als die der  $\gamma$ -Zirkoniumphosphate.