Journal of Thermal Analysis, Vol. 37 (1991) 549-556

THERMAL DECOMPOSITION OF ORGANIC DERIVATIVES OF CRYSTALLINE ZIRCONIUM PHOSPHATE

I. Thermal decomposition of *n*-alkanol derivatives of γ-zirconium phosphate

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(Received September 3, 1990)

Organic derivatives of γ-zirconium phosphate were investigated. The *n*– alkanol derivatives lost their crystal and structural water in several steps. The thermal stability of the molecules increased with increasing number of carbon atoms in the alkyl chain. The investigated materials are less stable than α-zirconium phosphate derivatives.

The behaviour of organic derivatives of crystalline α-zirconium phosphate, obtained by direct contact of an alcohol solution and zirconium phosphate at room temperature has been investigated in recent years [1].

The organic derivatives of γ-zirconium phosphate have not received the same degree of attention, though their thermal decomposition may likewise provide information about their behaviour.

This paper reports data on the *n*-alkanol derivatives.

Experimental

γ-Zirconium phosphate was prepared as described by Clearfield [2]. The *n*-alkanol derivatives were made as follows: to 2.0 g of γ-zirconium phosphate 100 ml of protonated *n*-alkanol was added dropwise and the mixture was then equilibrated for 4 days at room temperature (25 ±2°). The precipitate formed was identified by X-ray powder diffraction and IR

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spectrophotometric methods. For protonation, the *n*-alkanols were contacted for half an hour with 0.1 mol/cm^3 conc. perchloric acid ($HClO_4$) solution before use.

The X-ray and IR spectrophotometric determinations were performed under the conditions described earlier [3].

Differential thermal analyses [4] were carried out with a MOM-C derivatograph: heating rate: 10 deg/min, temp. range: 25-900°, sample weight: 50-100 mg, reference: Al_2O_3, atmosphere: air. The results were evaluated by computer program [5].

The results are shown in Figs 1-5.

Results and discussion

The synthetized samples were shown by X-ray diffraction measurements to be crystalline, having a layered structure with different interlayer distances. The interlayer distance increased with increasing number of carbon atoms in the alkyl chain (0.25 nm/C_n) [6].

The thermal decompositions of the materials were generally similar in character.

a) *Methanol intercalate.* Figure 1 reveals endothermic peaks with weight loss at 90°, 120° and 540° and an exothermic peak without weight loss at 760°.

Table 1 Analytical data

Sample	Org/inorg ratio, mmole	Interlayer distance *d*, in nm	Total weight loss, %
γ – zirconium phosphate (γ – ZrP)	–	1.22	32.74
methanol/ γ – ZrP	1 : 1	1.28	61.13
ethanol/ γ – ZrP	1 : 1	1.52	54.80
propanol/ γ – ZrP	1 : 1	1.78	44.74
butanol/ γ – ZrP	1 : 1	2.02	44.74
pentanol/ γ – ZrP	1 : 1	2.29	43.08

The first peak relates to methanol loss, the second to crystal water loss, and the third to the loss of structural water i.e. the destruction of HPO_4^{2-} groups, followed by total reorganization of the molecule. The exothermic peak characterizes the change in the crystalline form of ZrO_2 [7].The analytical and IR spectrophotometric results concerning the composition and total mass loss data (Table 1) suggest the following decomposition process:

$$Zr[(HPO_4)_2(CH_3OH)]\cdot 2H_2O \xrightarrow[\sim 50^{\circ}]{-CH_3OH} Zr(HPO_4)_2\cdot 2H_2O \xrightarrow[\text{till}\,190^{\circ}]{-2H_2O}$$

$$Zr(HPO_4)_2 \xrightarrow[\text{till}\,590^{\circ}]{-H_2O} ZrP_2O_7 \xrightarrow[\sim 700^{\circ}]{} ZrO_2\cdot P_2O_5\ ;$$

$$\underset{\text{(cubic)}}{\alpha - ZrO_2} \xrightarrow[\sim 900^{\circ}]{} \underset{\text{(monoclinic)}}{\beta - ZrO_2}$$

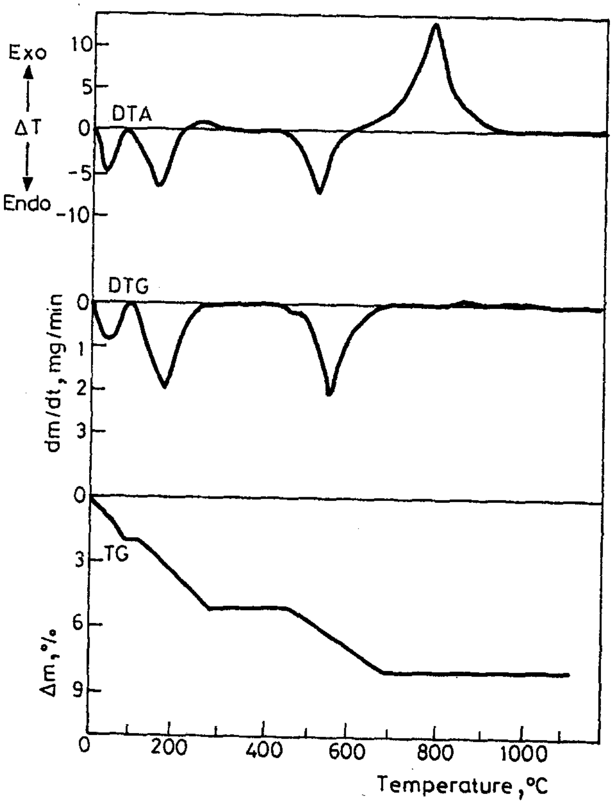

Fig. 1 Thermoanalytical curves of methanol intercalated γ-zirconium phosphate

b) *Ethanol intercalate.* Figure 2 demonstrates endothermic peaks with weight loss at 90°, 110° and 470° and an exothermic peak without weight loss at 780°. The first processes involves the loss of ethanol, the second the loss of crystal water, and the third the loss of structural water.

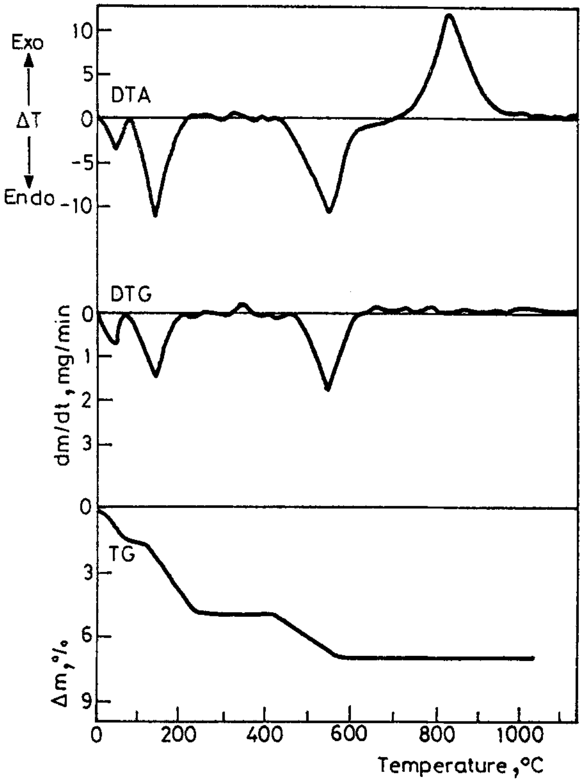

Fig. 2 Thermoanalytical curves of ethanol intercalated γ-zirzonium phosphate

The data in Table 1 point to the following thermal decomposition:

$$Zr[(HPO_4)_2(C_2H_5OH)]\cdot 2H_2O \xrightarrow[\text{till } 90^0]{-\text{EtOH}} Zr(HPO_4)_2\cdot 2H_2O \xrightarrow[\text{till } 160^0]{-2H_2O}$$

$$Zr(HPO_4)_2 \xrightarrow[\text{till } 590^0]{-H_2O} ZrP_2O_7 \xrightarrow[\sim 780^0]{} ZrO_2\cdot P_2O_7$$

c)*Propanol intercalate.* Endothermic peaks with weight loss are observed at 32°, 130°, 250° and 550°, and exothermic peaks without weight loss at 720° and 1000° (Fig. 3).

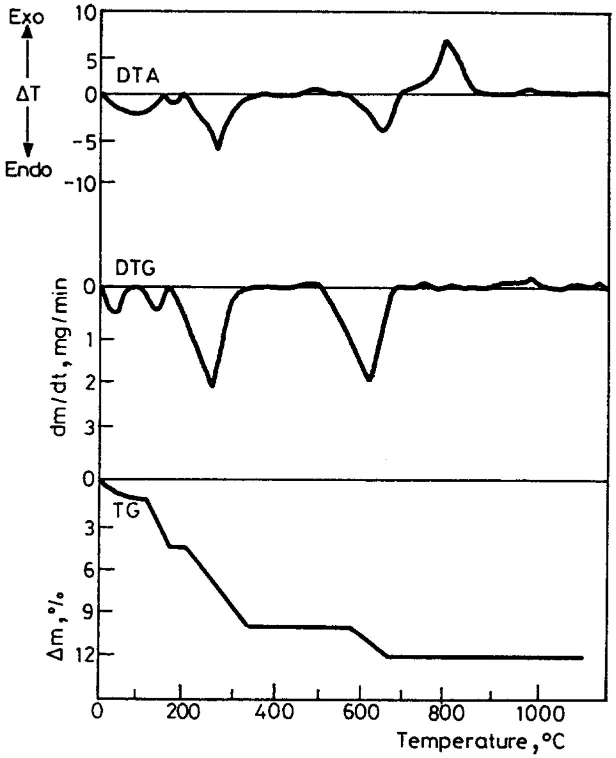

Fig. 3 Thermoanalytical curves of propanol intercalated γ – zirconium phosphate

The first peak relates to the loss of water adsorbed on the surface, the second to the loss of propanol, and the third to the loss of crystal water. The HPO_4^{2-} groups decomposed at about 500°, as shown by the peak at 550°. The exothermic processes are connected with the conversion to pyrophosphate and the crystalline change in the ZrO_2, respectively. The following scheme of thermal decomposition may be proposed:

$$Zr[(HPO_4)_2(C_3H_7OH)]\cdot 2H_2O \xrightarrow[\text{till } 50^{\circ}]{-H_2O} Zr[(HPO_4)_2(C_3H_7OH)]\cdot 2H_2O$$

$$\xrightarrow[\text{till }170^{0}]{-C_3H_7OH} Zr(HPO_4)_2\cdot 2H_2O \xrightarrow[\text{till }250^{0}]{-2H_2O} Zr(HPO_4)_2 \xrightarrow[\text{till }690^{0}]{-H_2O} ZrP_2O_7$$

$$\xrightarrow[\sim 750^{0}]{} ZrO_2\cdot P_2O_5$$

d) *Butanol intercalate.* Figure 4 exhibits endothermic peaks with weight loss at 50°, 160° and 505°; and an exothermic peak without weight loss at about 710°. The first and second endothermic processes relate to the loss of butanol and crystal water, and the third to the loss of structural water.

As a difference from the previously mentioned alkanols, in this case the propanol and crystal water are lost practically together. The thermal decomposition may be described as follows:

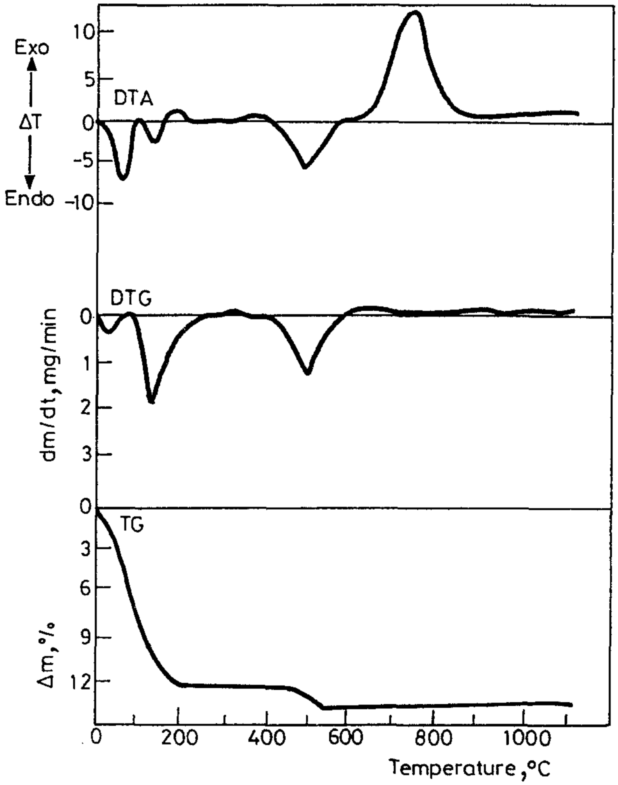

Fig. 4 Thermoanalytical curves of butanol intercalated γ-zirconium phosphate

$$\mathrm{Zr[(HPO_4)_2(C_4H_9OH)]\cdot 2H_2O} \xrightarrow[\text{till } 205^\circ]{\substack{-\mathrm{C_4H_9OH} \\ -2\mathrm{H_2O}}} \mathrm{Zr(HPO_4)_2} \xrightarrow[\text{till } 560^\circ]{-\mathrm{H_2O}}$$

$$\mathrm{ZrP_2O_7} \xrightarrow[\sim 700^\circ]{} \mathrm{ZrO_2\cdot P_2O_7}$$

e) *Pentanol intercalate.* Figure 5 reveals endothermic peaks with weight loss at 50°, 180° and 500°, and an exothermic peak without weight loss at 730°. The first two processes are the loss of crystal water and pentanol, in parallel. The third process is the loss of structural water, while the exothermic process is connected with the reorganization of the oxides.

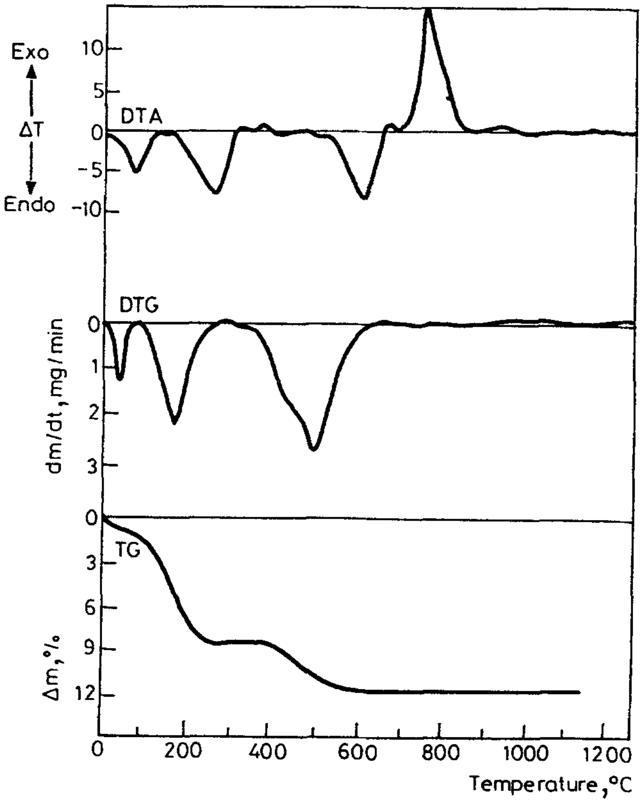

Fig. 5 Thermoanalytical curves of pentanol intercalated γ-zirconium phosphate

The following decomposition may be suggested:

$$Zr[(HPO_4)_2(C_5H_{11}OH)]\cdot 2H_2O \xrightarrow[\text{till } 180^\circ]{\substack{-C_5H_{11}OH \\ -2H_2O}} Zr(HPO_4)_2 \xrightarrow[\text{till } 500^\circ]{-H_2O} ZrP_2O_7$$

$$\xrightarrow[\sim 730^\circ]{} ZrO_2\cdot P_2O_7\,;$$

$$\alpha - ZrO_2 \xrightarrow[\sim 900^\circ]{} \beta - ZrO_2$$

The above data permit the following conclusions:

- the alkanols are lost first;
- this is followed by crystal water loss, which occurs at a slightly higher temperature than for the pure phosphate;
- the alkanols higher than propanol are lost together with the crystal water; in these cases the processes occur in a protracted way, continuing up to higher temperature;
- the change in the crystalline form of zirconium dioxide proceeds as described in the literature.

The above results correlation with those on α-zirconium phosphate n – alkanol derivatives. The α-crystalline derivatives are more stable (the processes take place at higher temperature) than the γ-crystalline derivatives.

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Zusammenfassung — Es wurden organische Derivate von γ-Zirkoniumphosphat untersucht. Die n-Alkanolderivate geben ihr Kristall- und Strukturwasser in mehreren Schritten ab. Die thermische Stabilität der Moleküle wächst mit steigender Kohlenstoffatomanzahl in der Alkylkette. Die untersuchten Substanzen zeigen eine geringere Stabilität als die-Zirkoniumphosphatderivate.