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THERMAL DECOMPOSITION OF ORGANIC DERIVATIVES OF CRYSTALLINE ZIRCONIUM PHOSPHATE
II. Thermal decomposition of *n*-alkylamine derivatives of γ-zirconium phosphate

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The thermal decompositions of *n*-alkylamine (ethylamine, propylamine, butylamine and pentylamine) derivates of γ-zirconium phosphate were investigated. The samples exhibited similar mechanisms of decomposition.

Zirconium phosphate, containing acidic groups, has a strong tendency to intercalate strong Brönsted bases such as *n*-alkylamines, which are readily intercalated within the interlayer region of both α- and γ-zirconium phosphates, even from dilute solution [1]. The behaviour of *n*-alkylamine derivatives of α-zirconium phosphate has been investigated in recent years [2], but the *n*-alkylamine derivatives of γ-zirconium phospahte have not been investigated so far and their thermal behaviour is unknown.

Experimental

The *n*-alkylamine derivates of γ-zirconium phosphate (γ-ZrP) were prepared as follows: in each case, 5.0 g of γ-ZrP was mixed with 33 ml of distilled water. To this mixture, 66 ml of *n*-alkylamine solution was added in 10 ml portions under continuous stirring. After a short time, a white gelatinous precipitate formed. Subsequently, 19 ml of conc. HCl solution was added. During this process, the gel was transformed into a liquid phase, and in one hour a normal precipitate was formed. After separation, the precipitate was washed until chloride-free and dried in an oven at 40° to

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constant weight. Ethylamine, propylamine, butylamine and pentylamine were used in the experiments.

The *n*-alkylamine derivatives were identified by analytical, X-ray powder diffraction and IR spectrophotometric methods under the conditions described earlier [3], while the thermal behaviour of the samples was investigated by means of differential thermal analysis as reported previously [4]. The IR spectra are shown in Fig. l, and the thermalcurves of the samples in Figs 2-4.

Fig. 1 IR spectra of *n*-alkylamine intercalates of γ-zirconium phosphate
1 - ethylamine, 2 - propylamine, 3 - butylamine, 4 - pentylamine

Results and discussion

The prepared samples were shown by X-ray diffraction measurements to be crystalline, having a layered structure with an interlayer distance of 1.57 nm, 1.77 nm and 1.97 nm respectively. It was found that the interlayer distance increased with increase of the number of carbon atoms (C_n) in the alkyl chain (0.2 nm/C_n) [5]. The samples exhibited similar thermal behaviour in general, but differences were observed between them.

a) *Ethylamine derivative.* Figure 2 shows endothermic peaks with weight loss at 30°, 180°, 500° and 700°, and an exothermic process without weight loss at 800°. On the basis of the analytical and IR spectrophotometric results concerning the composition and also the total mass loss data (Table 1), the thermal decomposition of the ethylamine derivate of γ-zirconium phosphate may be described as follows:

$$Zr[(HPO_4)_2(C_2H_5NH_2)]\cdot 2H_2O \xrightarrow[\text{till } 180^\circ]{-2H_2O} Zr[(HPO_4)_2(C_2H_5NH_2)]$$

$$\xrightarrow[500^\circ]{-C_2H_5NH_2} Zr(HPO_4)_2 \xrightarrow[\text{till } 700^\circ]{-H_2O} ZrP_2O_7 \xrightarrow[800^\circ]{} ZrO_2\cdot P_2O_5$$

Table 1 Analytical data

Sample	Org/inorg ratio, mmole	Interlayer dist. *d*, nm	Total weight loss, %
γ-zirconium phosphate (γ-ZrP)	–	1.22	32.74
ethylamine / γ-ZrP	1 : 2	1.57	31.18
propylamine / γ-ZrP	1 : 2	1.77	42.88
butylamine / γ-ZrP	1 : 2	1.97	43.11
pentylamine / γ-ZrP	1 : 2	2.18	43.01

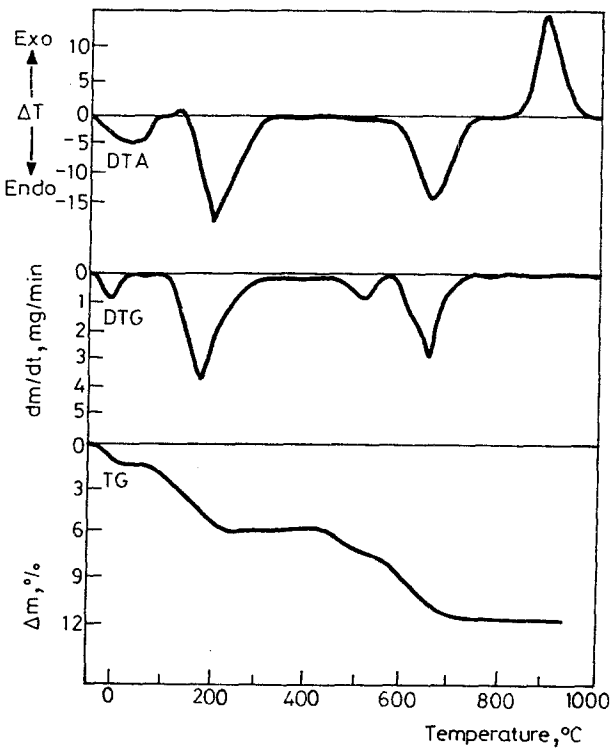

Fig. 2 Thermoanalytical curves of ethylamine intercalate of γ-zirconium phosphate

b) *Propylamine intercalate.* Figure 3 reveals endothermic peaks with weight loss at 35°, 110°, 250° and 630°, and an exothermic peak without weight loss at 780°. The thermal decomposition of the propylamine intercalate of γ-zirconium phosphate may be proposed as follows:

$$Zr[(HPO_4)_2(C_3H_7NH_2)]\cdot 2H_2O \xrightarrow[\text{till } 110^\circ]{-2H_2O} Zr[(HPO_4)_2(C_3H_7NH_2)]$$

$$\xrightarrow[250^\circ]{-C_3H_7NH_2} Zr(HPO_4)_2 \xrightarrow[\text{till } 630^\circ]{-H_2O} ZrP_2O_7 \xrightarrow[\text{till } 780^\circ]{} ZrO_2\cdot P_2O_5$$

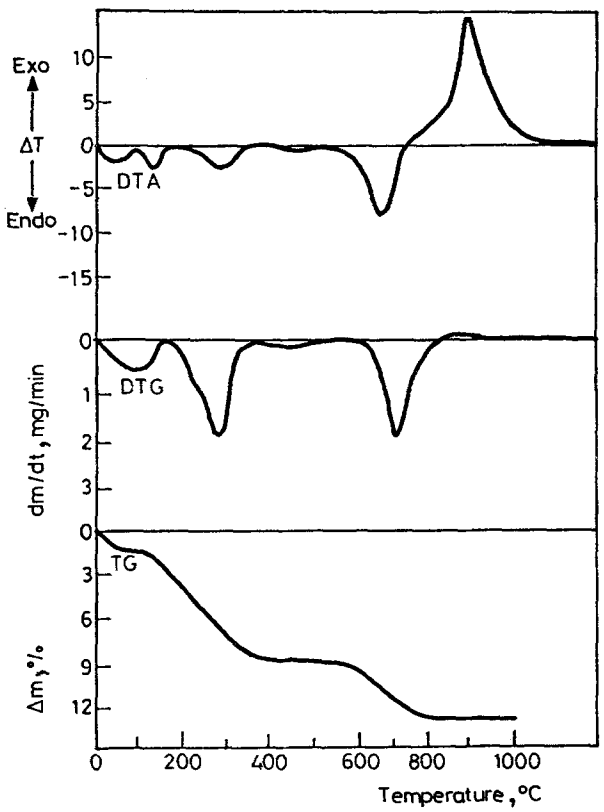

Fig. 3 Thermoanalytical curves of propylamine intercalate of γ – zirconium phosphate

c) *Butylamine intercalate.* Figure 4 reveals endothermic peaks with weight loss at 90°, 160° and 520°, and an exothermic peak without weight loss at 850°.

The following mode of thermal decomposition of the butylamine intercalate of γ-zirconium phosphate may be proposed:

$$Zr[(HPO_4)_2(C_4H_9NH_2)]\cdot 2H_2O \xrightarrow[\text{till } 90^\circ]{-2H_2O} Zr[(HPO_4)_2(C_4H_9NH_2)]$$

$$\xrightarrow[\text{till } 260^\circ]{-C_4H_9NH_2} Zr(HPO_4)_2 \xrightarrow[\text{till } 600^\circ]{-H_2O} ZrP_2O_7 \xrightarrow[\text{till } 900^\circ]{} ZrO_2\cdot P_2O_5$$

d) *Pentylamine intercalate.* Endothermic peaks with weight loss are to be seen at 90°, 140° and 505°, and an exothermic peak without weight loss at 900° (Fig. 5). The thermal decomposition of the pentylamine intercalate of γ-zirconium phosphate may be described as follows:

$$Zr[(HPO_4)_2(C_5H_{11}NH_2)]\cdot 2H_2O \xrightarrow[\text{till } 160^\circ]{-2H_2O} Zr[(HPO_4)_2(C_5H_{11}NH_2)]$$

$$\xrightarrow[\text{till } 300^\circ]{-C_5H_{11}NH_2} Zr(HPO_4)_2 \xrightarrow[\text{till } 560^\circ]{-H_2O} ZrP_2O_7 \xrightarrow[\sim 700^\circ]{} ZrO_2\cdot P_2O_5$$

In general, the thermal decomposition of the *n*-alkylamine intercalates of γ-zirconium phosphate consists of the following stages:

-loss of the crystal water,

-loss of the organic molecule,

-loss of the structural water originating from the decomposition of HPO_4^{2-} groups,

-reorganization of the oxides (at about 700°), and

-change of the crystal form of ZrO_2.

In the case of ethylamine (and probably also methylamine), the thermal decomposition is more difficult than for higher *n*-alkylamines. Part of the crystal water ($\approx$1 mole) is lost at a low temperature, while the remainder is lost together with the decomposed organic molecules up to 280°.

Further losses occur in the temperature interval 450-550°, while the decomposition of HPO_4^{2-} groups and the loss of structural water is com-

pleted at about 700°, much higher than for the initial crystalline γ-zirconium phosphate.

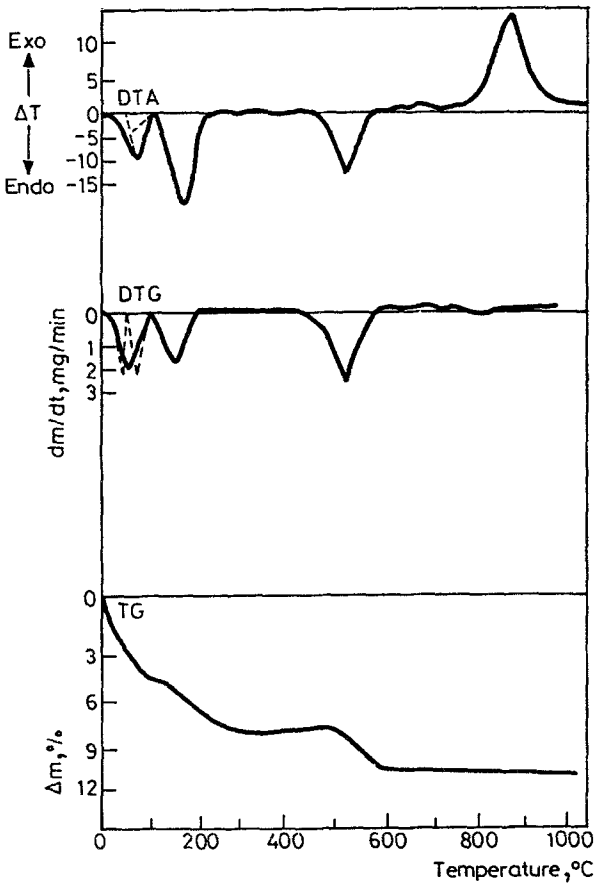

Fig. 4 Thermoanalytical curves of butylamine intercalate of γ – zirconium phosphate

The thermoanalytical curves of the derivatives of propylamine and higher amines were found to be similar. The crystal water was lost at a relatively low temperature, followed immediately by the loss of organic molecules, while the process of decomposition of HPO_4^{2-} groups and the reordering of all molecule proceed at a relatively high temperature (~700°).

The results indicated that the intercalated organic molecule facilitated the loss of crystal water. On the other hand, this water acts as a stabilizer, for after or partially during its loss the organic molecule immediately decomposes and is evolved.

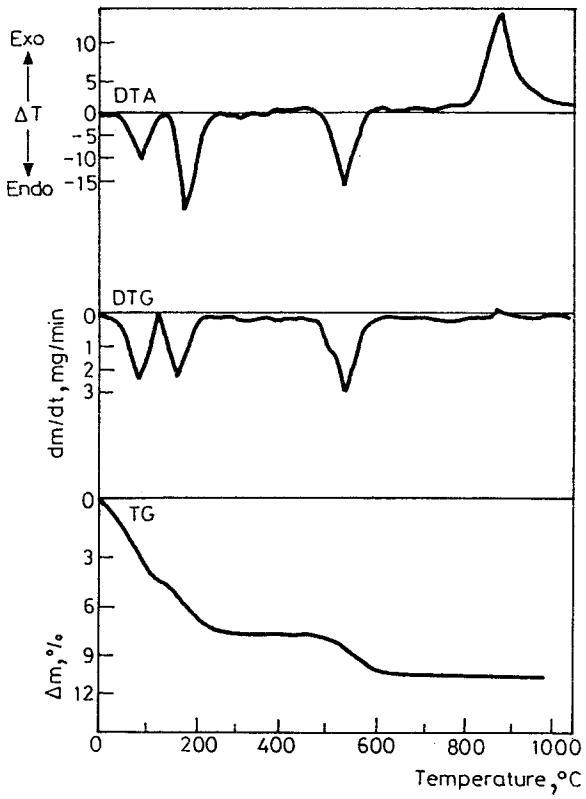

Fig. 5 Thermoanalytical curves of pentylamine intercalate of γ – zirconium phosphate

Further, the decomposition of the organic molecule present in the interlayer region retards the decomposition of the HPO_4^{2-} groups of the crystalline material, as a result of which the reordering of all these molecules takes place at higher temperature.

References

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Zusammenfassung — Es wurde die thermische Zersetzung von *n*-Alkylamin- (Ethylamin-, Propylamin-, Butylamin- und Pentylamin-) Derivaten von γ-Zirkoniumphosphat untersucht. Die Proben weisen einen ähnlichen Zersetzungsmechanismus auf.