THERMAL BEHAVIOUR OF ZINC PHENOXYACETATE

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The thermal behaviour of solid zinc phenoxyacetate was investigated by DSC and TG techniques. The results obtained showed that this compound is a dihydrate and that the water molecules are differently bonded. The compound melts and then decomposes in two steps, with the formation of $ZnCO_3$ and ZnO, respectively. The thermodynamic parameters associated with the thermal processes were evaluated.

The commercial and industrial importance of phenoxyalkanoic acids is known, and they have therefore been widely studied, particularly in recent years [1–3]. Some metal salts of these acids are also important compounds because of their antimicrobial activity [4].

During a study of the formation equilibria in solutions of the complexes of phenoxyacetic acid with bivalent metals, we also prepared the corresponding solid salts. There are few papers in the literature on these compounds in solution, and very few relating to the solid state [5–8]; it has been reported that they are dehydrates in the solid state and that they release both water molecules at 120° (or at 105°), but no information is available on the thermodynamic parameters associated with the dehydration and decomposition processes. Some structures of different salts have been suggested [9].

We intend to study the thermal behaviour of these compounds, in order to obtain the thermodynamic parameters associated with the thermal processes and to correlate the obtained results with the structures.

In this paper we report studies on zinc phenoxyacetate.

Experimental

Materials: Zinc phenoxyacetate was obtained by mixing aqueous solutions of phenoxyacetic acid (Fluka), KOH (C. Erba RP) and zinc sulfate (C. Erba RP) in stoichiometric ratios. The solid product obtained was crystallized from water and successively filtered and dried by pump at room temperature.

TG and DTG measurements: TG and DTG measurements were performed with a Mettler TA 3000 thermoanalyser, using alumina open crucibles, in a dynamic nitrogen atmosphere (3.6 l h^{-1}). The sample weights were about 15–30 mg.

The activation energies and the apparent reaction orders were evaluated by a literature method [10].

DSC measurements: The DSC measurements were performed with a Mettler 20 DSC instrument, in a dynamic nitrogen atmosphere (5 l h^{-1}). The samples were put in aluminium covered pans, an empty, covered pan being used as reference. The enthalpy values associated with the thermal processes were evaluated by using the ΔH of melting of indium $(6.79 \text{ cal g}^{-1})$ as calibration standard, and are reported in $k/J \text{ mol}^{-1}$.

Results

The DSC, TG and DTG curves of phenoxyacetic acid were preliminarily recorded, in order to compare its thermal behaviour with that of zinc phenoxyacetate.
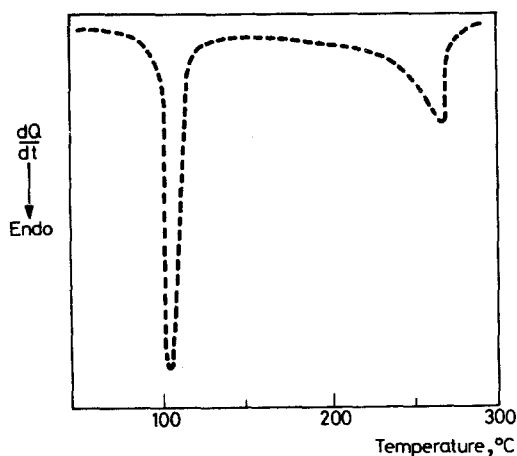

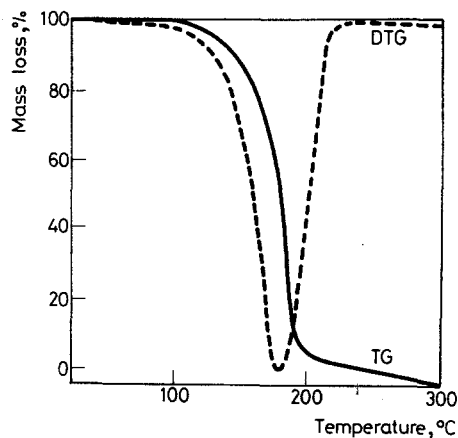**Fig. 1** DSC curve of phenoxyacetic acid

Fig. 2 TG and DTG curves of phenoxyacetic acid

The DSC curve (Fig. 1) showed that phenoxyacetic acid melts at $100.3°$ ($\Delta H_m = 27.45$ kJ mol^{-1}) and decomposes exothermally above $210°$. The TG and DTG curves (Fig. 2) displayed a weight loss (98.2%) in a single step in the temperature range $102–205°$. Since the TG measurements were performed in open vessels, the observed weight loss can be due to the complete vaporization of the investigated compound before its decomposition.

Zinc phenoxyacetate was next investigated. This compound, obtained as reported in the Experimental, was dried in vacuo (10^{-3} mm Hg) at room temperature, and was then analysed. Elemental analysis showed that the product was an anhydrous compound (C: exp. 51.7%, theor. 52.27%; H: exp. 3.74%, theor. 3.83%; Zn: exp. 17.58%, theor. 17.71%), differently from what was reported in the literature. DSC and TG measurements were also performed: they agreed with each other and with the elemental analysis results. Corresponding DSC and TG curves are reported in Figs 3 and 4.

The zinc phenoxyacetate was also dried at $60°$, but no difference was observed in comparison with the product dried in vacuo.

These results mean that it is impossible to dry this compound in vacuo or at a temperature higher than room temperature without removal of the crystallization water molecules, if present.

In order to obtain further information, we performed TG, DTG and DSC measurements on the compound prepared as reported in the Experimental and left it in a dryer for several days at room temperature. A very low heating rate (0.3 deg min^{-1}) was used in both kinds of measurements.

The TG and DTG curves showed four steps, in the temperature intervals $50.6–74.4°$, $74.4–82.1°$, $225–380°$ and $380–480°$, respectively (Fig. 5).
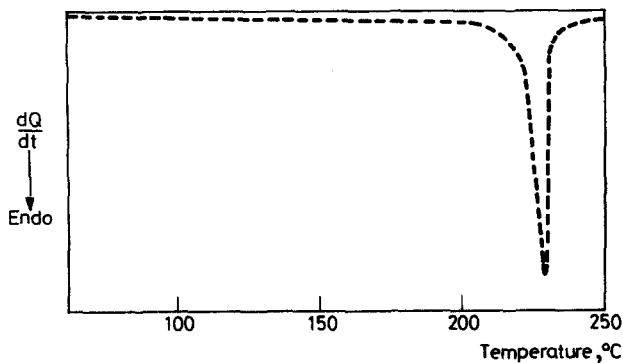
Fig. 3 DSC curve of zinc phenoxyacetate dried in vacuo (10^{-3} mm Hg) at room temperature
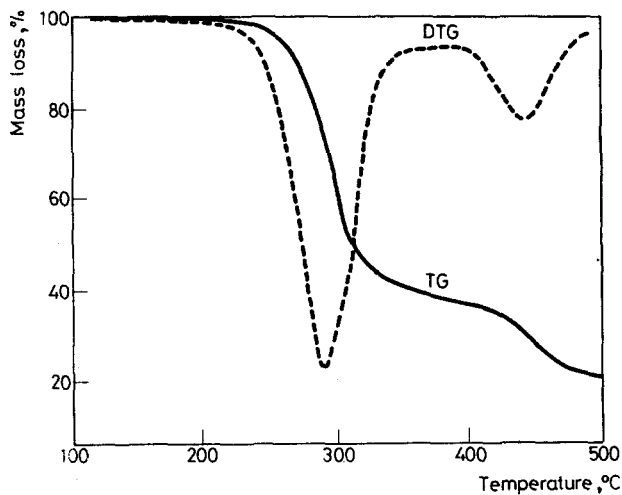

Fig. 4 TG and DTG curves of zinc phenoxyacetate dried in vacuo (10^{-3} mm Hg) at room temperature
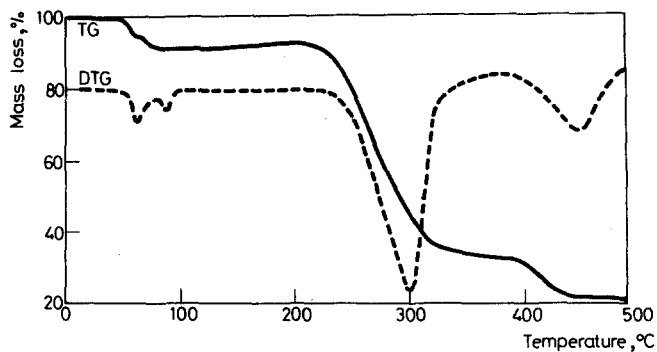

Fig. 5 TG and DTG curves of zinc phenoxyacetate left in a dryer at room temperature for several days

The weight losses in the first two steps are due to dehydration and correspond to the loss of 1.5 and 0.5 water molecules.

The two steps observed at higher temperatures can be attributed to the decomposition of the anhydrous compound. The results indicate that zinc carbonate is first obtained (in the temperature range 225–380°), which successively decomposes to form zinc oxide in the temperature range 380–480°. Table 1 gives the results on the dihydrate; no difference was observed between the products dried in vacuo or in the oven, apart from the dehydration processes. The thermodynamic parameters associated with the decomposition processes were not evaluated because the two steps were partially superimposed.

Table 1 Temperatures, experimental and theoretical weight losses, and corresponding activation energies and reaction orders of the thermal processes of zinc phenoxyacetate dihydrate. The theoretical weight losses were calculated via the formula reported in the conclusion

T, °C	Exp. weight loss, %	Theor. weight loss, %	E_a, kJ mol^{-1}	n
50.6–74.4	6.95	6.70	226.3	1.5
74.4–82.1	1.97	2.08	452.9	0.85
225–380	61.53	60.21	n.e.	n.e.
380–480	10.02	10.96	n.e.	n.e.

DSC measurements too were performed on the product dried at room temperature in a dryer. The DSC curve (Fig. 6) showed three endothermic effects: the first two in the temperature ranges 54.5–77.0° and 77.0–87.1° were not well
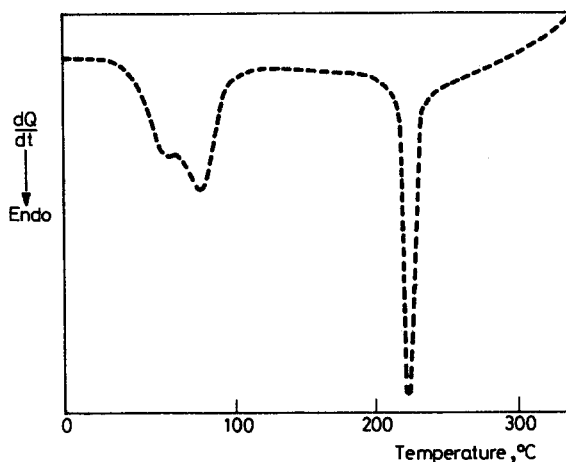
Fig. 6 DSC curve of zinc phenoxyacetate left in a dryer at room temperature for several days

resolvable, so that the total enthalpy effect associated was evaluated ($\Delta H_T = 111.48$ kJ mol^{-1}), but it was impossible to estimate the enthalpy values associated with each step. At higher temperatures (222–230°), another endothermic effect was observed, followed from decomposition.

The first two thermal effects correspond to the dehydration steps observed in the TG measurements, the small differences in temperature being due to the different experimental conditions.

The endothermic effect observed in the temperature range 222–230° can not be associated with the first decomposition step observed by TG, but is due to the melting of the anhydrous salt ($\Delta H_m = 42.72$ kJ mol^{-1}). The melting process was confirmed with a Kofler apparatus. No difference was observed between the DSC curve of the dihydrate and that of the anhydrous compound, apart from the thermal effects due to dehydration.

The elemental analysis agreed with these results.

Conclusions

All the measurements accord with one another and demonstrate that zinc phenoxyacetate is a dihydrate in the solid state. The dehydration temperature is lower than that reported in the literature (120°), indicating that the water molecules are bonded weakly. This explains the impossibility of drying this compound in vacuo or at a temperature higher than room temperature without removal of the crystallization water molecules.
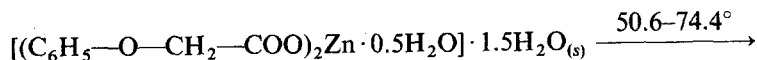
The presence of two dehydration steps clearly shows that the water molecules are bonded differently; quantitative investigation of the TG measurements suggests that the following formula can be attributed to solid zinc phenoxyacetate dihydrate:

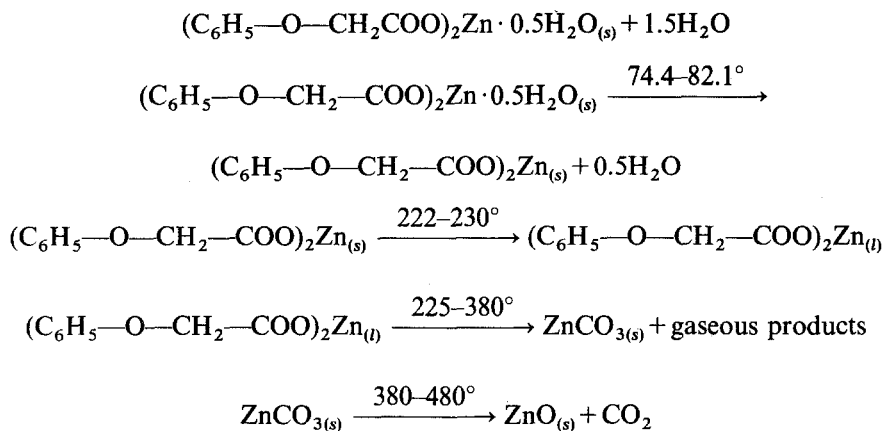$$[(C_6H_5\text{—}O\text{—}CH_2\text{—}COO)_2Zn \cdot 0.5H_2O] \cdot 1.5H_2O$$

in which 0.5 water molecules are located in the inner, and 1.5 in the outer coordination sphere. This agrees with the activation energies associated with the two dehydration steps. These results suggest that the structure of solid zinc phenoxyacetate is different from that reported in the literature. One water molecule probably forms a bridge between two zinc phenoxyacetate molecules, excluding the presence of bridging acetate groups.

The compound melts in the temperature range 222–230° and then decomposes exothermally with the formation of zinc carbonate first, follows by zinc oxide together with gaseous products.

The thermal processes can be illustrated by the following scheme:

$$[(C_6H_5\text{—}O\text{—}CH_2\text{—}COO)_2Zn \cdot 0.5H_2O] \cdot 1.5H_2O_{(s)} \xrightarrow{\quad 50.6\text{–}74.4° \quad}$$

$$(C_6H_5-O-CH_2COO)_2Zn \cdot 0.5H_2O_{(s)} + 1.5H_2O$$

$$(C_6H_5-O-CH_2-COO)_2Zn \cdot 0.5H_2O_{(s)} \xrightarrow{74.4-82.1°}$$

$$(C_6H_5-O-CH_2-COO)_2Zn_{(s)} + 0.5H_2O$$

$$(C_6H_5-O-CH_2-COO)_2Zn_{(s)} \xrightarrow{222-230°} (C_6H_5-O-CH_2-COO)_2Zn_{(l)}$$

$$(C_6H_5-O-CH_2-COO)_2Zn_{(l)} \xrightarrow{225-380°} ZnCO_{3(s)} + \text{gaseous products}$$

$$ZnCO_{3(s)} \xrightarrow{380-480°} ZnO_{(s)} + CO_2$$

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Zusammenfassung — Mittels DSC und TG wurde das thermische Verhalten von festem Zink-phenoxyazetat untersucht. Die Ergebnisse zeigen, daß diese Verbindung ein Dihydrat ist, in dem die beiden Wassermoleküle unterschiedlich gebunden sind. Die Verbindung schmilzt und zersetzt sich anschließend unter der Bildung von ZnCO₃ und ZnO in zwei Schritten. Die thermodynamischen Parameter der thermischen Prozesse wurden bestimmt.

Резюме — Методом ТГ и ДСК изучено термическое поведение твердого феноксиацетата цинка. Полученные результаты показали, что данное соединение является дигидратом с различным характером координации молекул воды. Соединение сначала плавится, а затем разлагается в две стадии с образованием соответственно, карбоната цинка и оксида цинка. Определены термодинамические параметры этих термических процессов.