

THERMAL BEHAVIOUR OF SOLID COMPLEXES OF PHENOXYALKANOIC ACIDS AND DIVALENT METALS

IV. Study on cadmium and mercury(II) phenoxyacetates

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(Received March 1, 1995)

Abstract

Solid cadmium and mercury(II) phenoxyacetates were prepared and investigated by DSC and TG techniques. The cadmium salt decomposed in two steps with the loss of 1.5 water molecules at first and the successive formation of CdCO_3 as final product. $\Delta_{\text{deh}}H^\circ$ associated with the loss of one water molecule was compared with the corresponding values obtained for other phenoxyacetates previously studied and the obtained results were discussed. Anhydrous mercury(II) phenoxyacetate gave, on heating, HgCO_3 which successively decomposed with the formation of gaseous products and a little amount of solid residue.

Keywords: cadmium phenoxyacetate, complexes, DSC, mercury(II) phenoxyacetate, TG

Introduction

The chemistry of phenoxyalkanoic acids have been largely investigated because some of these compounds are used as herbicides [1]. The formation in solution of their complexes with transition metals was also widely studied because they can be formed in processes occurring in soil or in plants [2–5], but very few papers have been published on these compounds in the solid state [6–10].

In several previous papers [11–13] we studied the thermal behaviour of some solid phenoxyacetates of divalent transition metals and we reported kinetic parameters associated with their dehydration and decomposition. We also observed that our results partially disagreed with some results reported in literature.

On continuing our investigation in this field, we report in this work our studies on the thermal behaviour of solid cadmium and mercury(II) phenoxyacetates.

Experimental

Materials

Very high purity Indium (NIST-SRM 758) was used for the heat calibration of calorimeter. Phenoxyacetic acid (FLUKA), cadmium sulphate, mercury(II) sulphate and KOH (C.ERBA) were used without further purification.

The cadmium and mercury(II) salts of phenoxyacetic acid were obtained by mixing aqueous solutions of phenoxyacetic acid, potassium hydroxide and cadmium or mercury(II) sulphate in stoichiometric ratios. The solid products obtained were filtered, crystallized from water several times and then dried by pump at room temperature.

The metal percentages in the obtained compounds were checked by AA spectrophotometry.

DSC measurements

Calorimetric runs were carried out with a Mettler Mod. 20 differential scanning calorimeter coupled with Mettler TC 10A processor, in a dynamic nitrogen atmosphere (51 h^{-1}) at the heating rate of $4 \text{ deg}\cdot\text{min}^{-1}$. For measurements the samples were put in aluminium sealed crucibles, another empty sealed aluminium crucible being used as reference.

Both heat flow and temperature calibrations were made according to the operating instructions of equipment, by using the two calibration programs of TC 10A processor [14].

The heat flow calibration was based on the heat of fusion of an exactly weighed quantity (about 6 mg) of pure indium (NIST).

The value of $3.267 \text{ kJ}\cdot\text{mol}^{-1}$, suggested by supplier, was used as enthalpy of fusion of indium. This value well agrees with the value selected in the last IUPAC compilation on reference materials for enthalpy measurements [15].

The calibration of the temperature of calorimeter was based on the temperatures of fusion of indium, lead and zinc. The sealed aluminium crucible supplied by Mettler, which contained these three metals in separate compartments, was used. The temperatures of fusion which supplier incorporated in the calibration program of processor were 429.75, 600.55 and 692.65 K for indium, lead and zinc respectively. These values are in very good agreement with those recommended in a recent paper concerning various temperature calibration materials [16].

Several runs with fresh indium samples were carried out to check if the equipment displayed correct values of temperature and heat of fusion. In every case obtained values were within 0.02 and 0.2 percent respectively with the temperature and enthalpy standards.

TG and DTG measurements

TG and DTG measurements were performed by a Mettler TA 3000 thermoanalyser coupled with the same TC 10A processor used for calorimetric experiments.

The temperature calibration of thermobalance was made by using the three metal samples (alumel, nickel and trafoperm) supplied by Mettler and according to the operating instructions of equipment [14].

Weighed quantities of the investigated compounds were put in open alumina crucibles and then heated in a dynamic nitrogen atmosphere ($3.6 \text{ l}\cdot\text{h}^{-1}$).

The activation energies were evaluated by both a literature method [17] and the suitable 'kinetic' built-in program of processor, but no difference was observed between the two procedures.

Results

Calorimetric and thermogravimetric measurements were performed on both Cd and Hg(II) phenoxyacetates, and the results obtained were compared with those of other phenoxyacetates previously investigated.

DSC measurements

The DSC curves, recorded at $4 \text{ deg}\cdot\text{min}^{-1}$, showed different behaviour for the two compounds examined.

For cadmium phenoxyacetate a sharp endothermic peak was observed in the temperature range $89.5\text{--}122.0^\circ\text{C}$, followed by a very irregular endo-exothermic one at higher temperature ($165\text{--}500^\circ\text{C}$). We attributed the first to the dehydration of salt and the second to the decomposition of the dehydrated compound obtained. The enthalpy and activation energy values associated with the dehy-

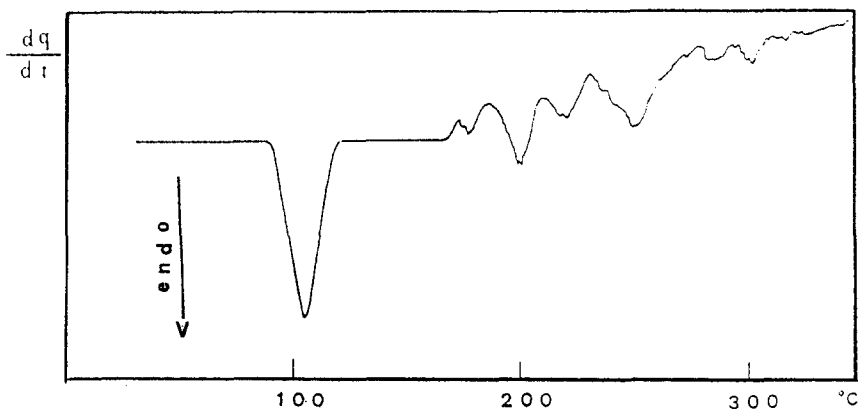


Fig. 1 DSC curve of cadmium phenoxyacetate

dration process were evaluated and were reported in Table 1. The DSC curve was reported in Fig. 1.

The DSC curve of Hg(II) phenoxyacetate (Fig. 2) showed only an irregular endo-exothermal peak from 138.1°C, which we attributed to decomposition. This result suggested that this compound is anhydrous in the solid state.

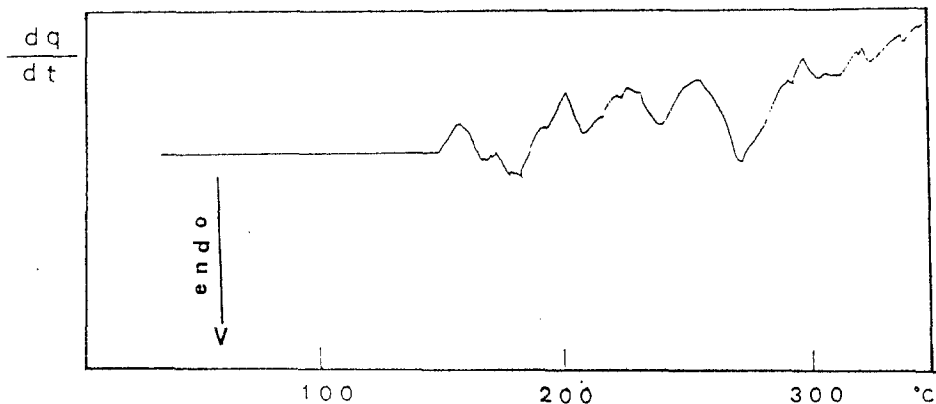


Fig. 2 DSC curve of mercury(II) phenoxyacetate

TG and DTG measurements

The TG and DTG curves of cadmium phenoxyacetate (Fig. 3), recorded at 4 deg·min⁻¹, showed a single step at lower temperature (84.8–110.2°C) due to dehydration of compound. The weight loss evidenced the presence of 1.5 water

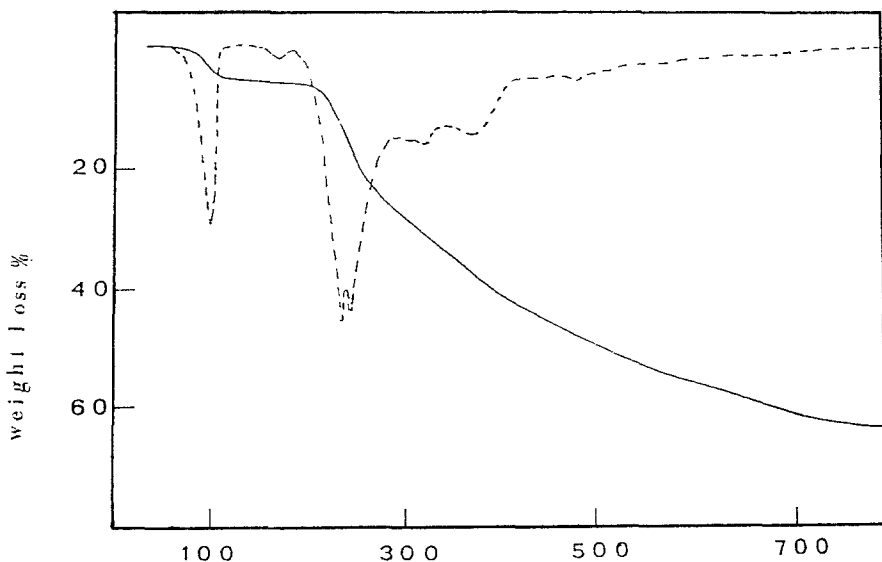


Fig. 3 TG and DTG curves of cadmium phenoxyacetate

Table 1 Temperatures, ΔH values, weight losses and activation energies associated with the thermal processes

Compounds	DSC measurements				TG measurements			
	$T /$ $^{\circ}\text{C}$	process	$\Delta H /$ $\text{kJ}\cdot\text{mol}^{-1}$	$E_a /$ $\text{kJ}\cdot\text{mol}^{-1}$	$T /$ $^{\circ}\text{C}$	process	weight loss %	$E_a /$ $\text{kJ}\cdot\text{mol}^{-1}$
$(\text{C}_6\text{H}_5\text{-O-CH}_2\text{-COO})_2\text{Cd}$	89.5–122.0	Dehydr.	93.4	164.5	84.8–110.2	Dehydr.	6.05	154.1
$1.5\text{H}_2\text{O}$	165.0–500.0	Decomp.	n.e.	n.e.	170.0–800.0	Decomp.	55.86	n.e.
$(\text{C}_6\text{H}_5\text{-O-CH}_2\text{-COO})_2\text{Hg}$	138.1–500.0	Decomp.	n.e.	n.e.	145.0–233.0	1st step of decomp.	46.52	190.8
					233.0–290.2	2nd step of decomp.	46.27	95.43

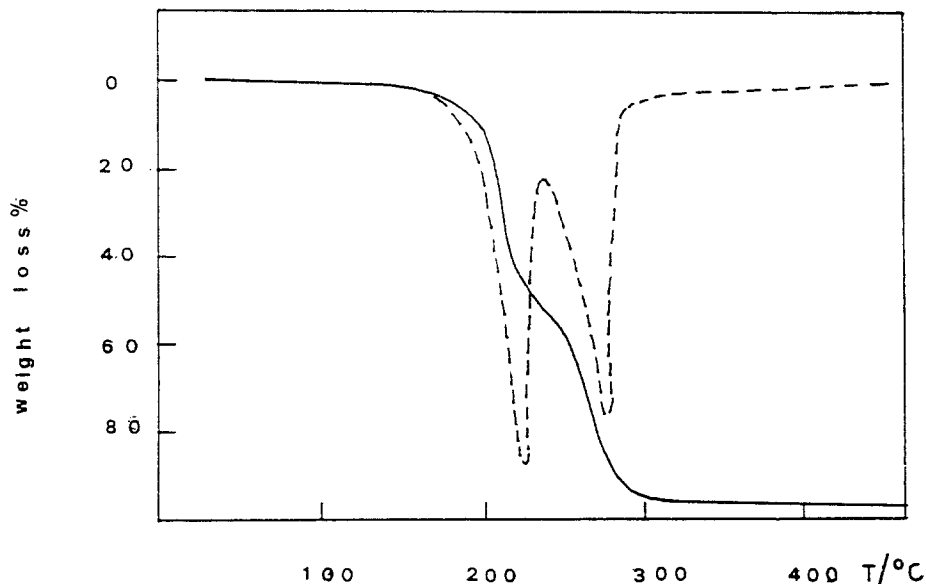


Fig. 4 TG and DTG curves of mercury(II) phenoxyacetate

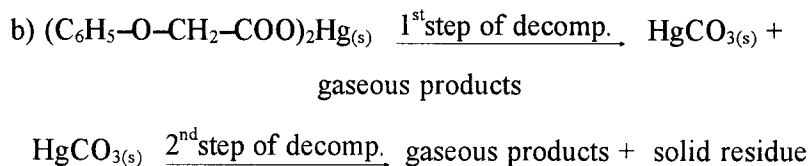
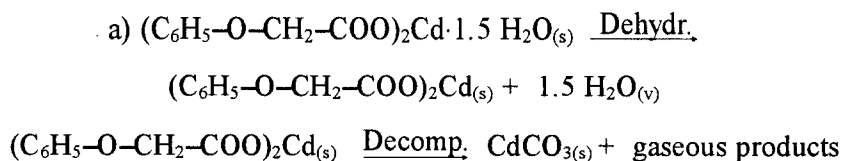
molecules for each molecule of Cd phenoxyacetate, differently from all other phenoxyacetates previously investigated and from it was reported in literature [10]. No difference was observed performing TG measurements at $0.3 \text{ deg}\cdot\text{min}^{-1}$. At higher temperatures (from about 170 up to 800°C) a continuous irregular decomposition process was observed.

The total weight loss indicated the formation of CdCO_3 as solid residue, but no information could be obtained about intermediate steps. The results were reported in Table 1.

Different behaviour was observed for Hg(II) phenoxyacetate (Fig. 4). The absence of thermal process in the temperature range near 100°C confirmed that this is an anhydrous compound. At higher temperatures two sharp consecutive thermal processes, in the temperature intervals $145.0\text{--}233.0$ and $233.0\text{--}290.2^\circ\text{C}$ were observed. The results, reported in Table 1, agreed with the formation of HgCO_3 (thermal process at $145.0\text{--}233.0^\circ\text{C}$) which successively decomposed with the formation of gaseous products and of a little amount (about 7.2 %) of solid residue.

Dicussion

Thermogravimetric measurements were in good agreement with DSC ones for both compounds studied, a part little differences in the temperatures of thermal processes, due to different experimental conditions. Experimental data indicated that the following thermal processes occurred:



The dehydration ΔH value of cadmium salt was measured (Table 1) and compared with the dehydration enthalpies of hydrate Zn, Cu(II), Co(II) and Ni(II) phenoxyacetates previously determined [11–13]. Since the number of hydration water molecules is not the same for all compounds compared, we evaluated for each compound the enthalpy contribution associated with the loss of one water molecule ($\Delta_{\text{deh}}H^*$), which could be considered a measure of metal–water bond strength. The $\Delta_{\text{deh}}H^*$ values so obtained decreased according to this order: Co>Ni>Cu>Cd>Zn (Table 2) but no regularity was observed as a function of the radius of metal ion.

This behaviour suggested that metal–water bond was not a simple ion–dipole interaction, and that the crystalline field appreciably contributed to the energy of bond. This contribution is not constant also because of the different co-ordination numbers of the metal ions in the complexes considered. By contrast the $\Delta_{\text{deh}}H^*$ values quite linearly decreased on increasing the atomic number of metal, but only for the metals (Co, Ni, Cu, Zn) of same transition series, while the value found for cadmium salt fell outside of the linearity (Fig. 5).

The dehydration activation energy of cadmium phenoxyacetate was also determined by both TG and DSC measurements, and the results obtained were in quite good agreement with each other (Table 1).

The value determined by TG technique was compared with the dehydration activation energies analogously previously obtained for other phenoxyacetates of transition metals [11–13] and the trend observed (Zn>Cd>Co>Ni) was quite opposite of that found for the $\Delta_{\text{deh}}H^*$ values (the dehydration activation energy of diaquo-bis-copper(II) phenoxyacetate could not be determined).

Also the decomposition processes of dehydrated Cd salt and anhydrous Hg salt were examined, but their behaviours were different from that of other phenoxyacetates previously studied, that decomposed with formation of MO ($M = \text{Co, Ni, Cu, Zn}$) as final product.

The dehydrated cadmium phenoxyacetate decomposed with formation of CdCO_3 by several irregular unresolvable steps. The irregularity of thermo-

Table 2 Enthalpy values associated with the loss of all water molecules ($\Delta_{\text{det}}H$ and with the loss of one water molecule only $\Delta_{\text{det}}H^*$) and activation energies for some phenoxyacetates of transition metals. Z is atomic number of metals

Compound	Z	$\Delta_{\text{det}}H / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{det}}H^* / \text{kJ} \cdot \text{mol}^{-1}$	$E_a / \text{kJ} \cdot \text{mol}^{-1}$
$(\text{C}_6\text{H}_5\text{--O--CH}_2\text{--COO})_2\text{Co} \cdot 2\text{H}_2\text{O}$	27	325.9	162.9	106.4
$(\text{C}_6\text{H}_5\text{--O--CH}_2\text{--COO})_2\text{Ni} \cdot 4\text{H}_2\text{O}$	28	495.1	123.8	101.7
$(\text{C}_6\text{H}_5\text{--O--CH}_2\text{--COO})_2\text{Cu} \cdot \text{H}_2\text{O}$	29	77.9	77.9	n.e.
$(\text{C}_6\text{H}_5\text{--O--CH}_2\text{--COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$	30	111.5	55.7	679.2
$(\text{C}_6\text{H}_5\text{--O--CH}_2\text{--COO})_2\text{Cd} \cdot 1.5\text{H}_2\text{O}$	48	93.4	62.3	154.1

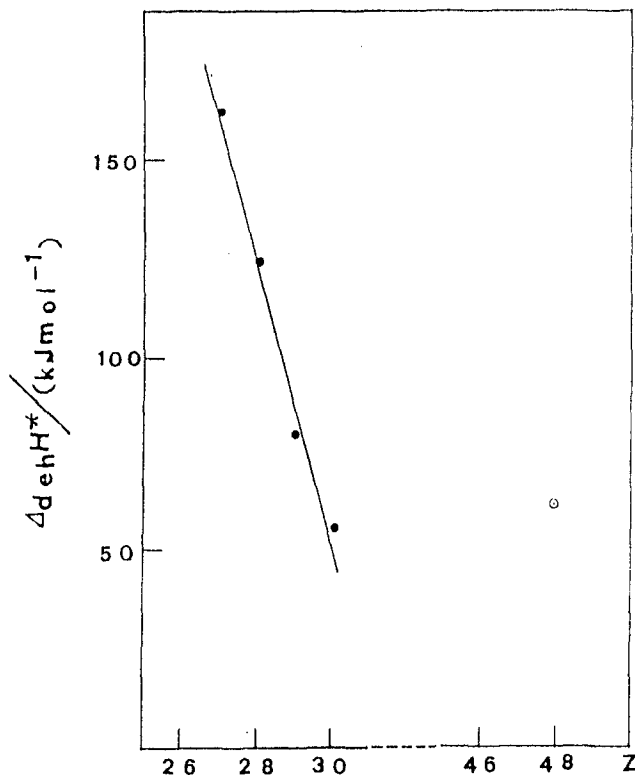


Fig. 5 Linear dependence of $\Delta_{deh}H^*$ on Z . The line was drawn using the solid symbols values only

gravimetric curve did not allow the evaluation of the activation energy associated with process.

Differently, anhydrous Hg phenoxyacetate decomposed with formation of $HgCO_3$ at first and gaseous products successively. The solid residue did not correspond to a mercury compound and was probably formed by organic not stoichiometric compounds. The activation energies associated with the steps of the decomposition process were evaluated, but no comparison was possible with other phenoxyacetates, as such as for cadmium phenoxyacetate, because of the different final stadium of process.

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Authors thank the Italian M.U.R.S.T. for financial support.

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