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THERMAL BEHAVIOUR OF SOLID COMPLEXES OF PHENOXYALKANOIC ACIDS AND DIVALENT METALS

II. Study on copper(II) phenoxyacetates

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Two solid copper(II) phenoxyacetates (anhydrous and dihydrate) were prepared and investigated by DSC and TG techniques. The results obtained indicated that the water molecules of the dihydrate compounds were weakly and differently bonded; also, both anhydrous and dihydrate compound decomposed with formation of CuO as final product, but by different steps. Some thermodynamic parameters associated with the observed thermal processes were evaluated and the results obtained were discussed and interpreted.

Phenoxyalkanoic acids are very important compounds because some of them are used as herbicides, so that their metabolism, mode of action and use and the physicochemical aspects of their formulation have been investigated [1]. Also, their physical properties, kinetic and thermodynamic parameters and spectroscopic behaviour have been reported [2].

The salts of phenoxyalkanoic acids with some bivalent transition metals have great theoretical importance because they are formed when the acids react with the metals present in the soil or in the plants; some of these salts, for example copper(II) phenoxyacetate, are important also because of their antimicrobial activity [3].

The formation equilibria in solution of some salts of phenoxyalkanoic acids have been investigated [4, 5], but very few authors studied these salts in the solid state [6-9]; in particular, it was reported that the salts of phenoxyacetic acid and bivalent transition metals are dihydrate in the solid state and that their water molecules are both released at 120^o (or at 105^o), but no thermodynamic parameters associated with the dehydration and decomposition processes were evaluated [10].

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In a previous paper we studied the thermal behaviour of zinc phenoxyacetate, and we observed some differences in comparison with data reported in literature [11].

In this work we investigated the thermal behaviour of the copper(II) salts of phenoxyacetic acid.

Experimental

Materials

Stoichiometric quantities of phenoxyacetic acid (FLUKA), KOH (C. ERBA RP) and anhydrous copper(II) sulfate (C. ERBA RP) were disolved in water to form copper(II) phenoxyacetate.

Two different solid products were obtained: a green compound was formed when the solution was heated in order to speed up the precipitation of the solid salt; on the contrary, a blue solid compound precipitated if the solution was slowly evaporated at room temperature. Both compounds were analysed and investigated.

TG and DTG measurements

We performed TG and DTG measurements by a Mettler TA 3000 thermoanalyser. Weighed quantities of the investigated compounds (15-30 mg) were put in open alumina crucibles and successively heated in a dynamic nitrogen atmosphere (3.6 l h^{-1}).

The activation energies were evaluated by literature method [12].

DSC measurements

The DSC measurements were performed using a Mettler 20 DSC, in a dynamic nitrogen atmosphere (5 l h^{-1}). The samples were put in covered aluminium pans and an empty covered pan was used as reference. The enthalpy values associated with the thermal processes were evaluated using the ΔH melting of indium (6.79 cal g^{-1}) as calibration standard.

Results

The elemental analysis of the two products obtained (see experimental section) was preliminarily performed. The results showed that the green compound was anhydrous copper(II) phenoxyacetates (C: exp 52.70%, theor. 52.51%; H: exp 3.80%, theor. 3.86%; Cu: exp 17.31%, theor. 17.38%) and the blue compounds was diaquobis - copper(II) phenoxyacetate (C: exp 47.4%, theor. 47.80%: H: exp 4.62%, theor. 4.52%; Cu: exp 15.93%, theor. 15.82%). The DSC, TG and DTG measurements of both compounds were performed; the results obtained were compared with those of phenoxyacetic acid previously reported [11].

DSC measurements

The DSC curve of anhydrous copper(II) phenoxyacetate showed an endothermic peak in the temperature range 256.5-272° ($T_{\max}$ = 265.8°) due to

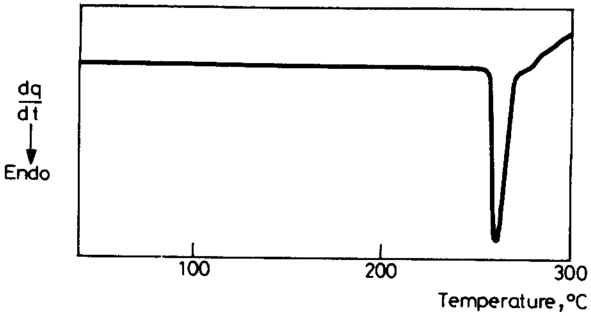

Fig. 1 The DSC curve of anhydrous copper (II) phenoxyacetate

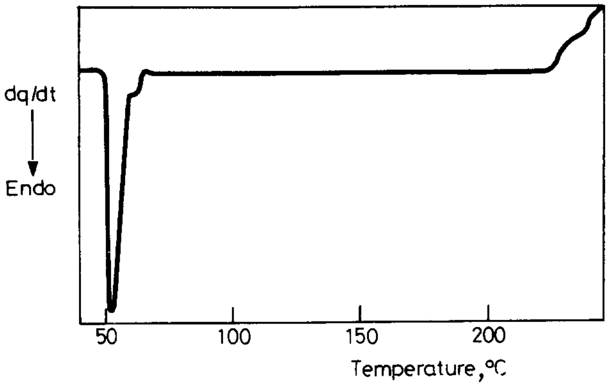

Fig. 2 The DSC curve of diaquobis-copper (II) phenoxyacetate

melting, immediately followed by an exothermic process due to decomposition (Fig. 1).

The DSC curve of diaquobis-copper(II) phenoxyacetate showed a double endothermic peak in the temperature range 53.8-61.5° that could be resolved only using very slow heating rates (0.2° min^{-1}). No other peak was observed at higher temperatures, because the compound decomposed exothermally without melting (Fig. 2).

The corresponding temperatures and enthalpic effects were evaluated and were reported in Table 1.

TG and DTG measurements.

The TG and DTG curves of the anhydrous copper(II) phenoxyacetate showed that it decomposed in a single step in the temperature range 245-365° (Fig 3).

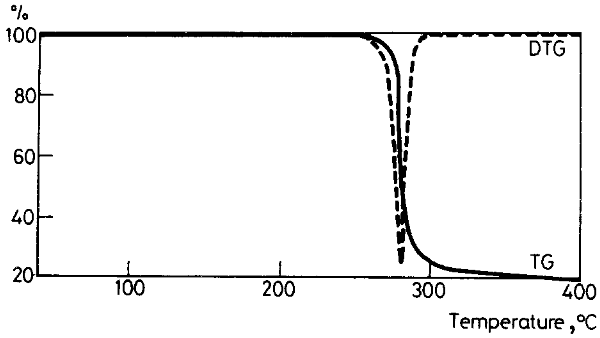

Fig. 3 The TG and DTG curves of anhydrous copper (II) phenoxyacetate

The analogous curves of diaquobis-copper(II) phenoxyacetate were also recorded and they exhibited several processes (Fig. 4): the two consecutive thermal processes observed in the temperature range 47.9-62.9° could be resolved only using very slow heating rates (0.2° deg.min^{-1}). At higher temperatures two other consecutive decomposition steps were observed in the temperature ranges 220-287 and 287-420°.

The temperatures and weight losses are summarized in Table 1.

Table 1 T (°C), ΔH (kJ mol^{-1}), weight losses (%) and activation energies (kJ mol^{-1}) of the thermal processes

	DSC measurements			TG measurements			
	T	ΔH	Process	T	weight loss, %	E_a	Process
$(C_6H_5\text{-}O\text{-}CH_2\text{-}COO)_2Cu$	265.8	68.90	melt.				
	275.0	-	decomp.	245-365	78.35	703.5	decomp.
$(C_6H_5\text{-}O\text{-}CH_2\text{-}COO)_2Cu.H_2O$	53.8-59.0	65.52	1st step of dehydr.	47.9-55.2	7.88	48.0	1st step of dehydr.
	59.0-61.5	12.38	2nd step of dehydr.	55.2-62.9	0.96	n.e.	2nd step of dehydr.
				220-287	60.15	192.2	1st step of decomp.
	220.0		decomp.				
				287-420	11.12	n.e.	2nd step of decomp.

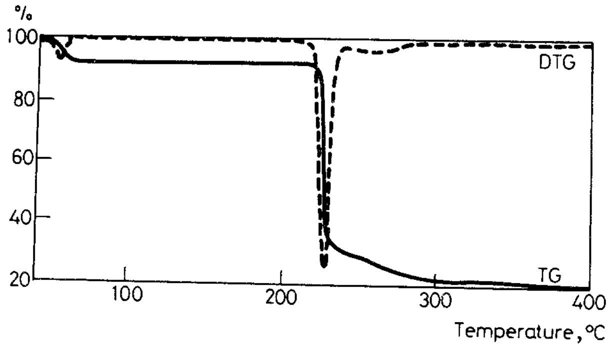

Fig. 4 The TG and DTG curves of diaquobis-copper (II) phenoxyacetate

Discussion

The comparison of the DSC curves of the two investigated compounds suggested that the thermal effects observed in the temperature range 50.1-58.5^0 were due to the dehydration of diaquobis-copper(II) phenoxyacetate.

It was confirmed by TG and DTG measurements, which showed, for the dihydrate compound, in analogous temperature range, a weight loss corresponding to two water molecules, the small temperature difference between DSC and TG measurements being explained by the different experimental conditions. The temperature of the dehydration process was much lower than that (105^0) reported in literature [10], and suggested that the water molecules were bonded weakly. This finding seemed to us to be in agreement with the impossibility to obtain the dihydrate compound from heated solutions.

The use of very slow heating rates in both DSC and TG measurements allowed to observe that the dehydration process occurred in two steps.

These results seemed to be in agreement with the crystal structure of diaquobis-copper(II) phenoxyacetate, in which hydrogen bonds of different lenghts, due to water molecules, were observed [7], the shorter one (2.7-2.8Å) holding together the molecules in chains and linking the chains to form sheets, the longer ones (3.0-3.1Å) being bifurcated hydrogen bonds and linking the sheets to each other.

The comparison between the DSC and TG measurements allowed to evaluate the enthalpic effect associated with each step (Table 1), but it was impossible to evaluate the activation energies associated with the second step.

We attributed the first step to the loss of water molecules forming the shorter hydrogen bonds and the second step to the loss of water molecules forming the longer bifurcated hydrogen bonds.

At higher temperatures both compounds decomposed with formation of CuO as final product, but different behaviours were observed: the anhydrous copper(II) phenoxyacetate melted and then decomposed in a single step; by contrast, the dehydrated diaquobis-copper(II) phenoxyacetate decomposed without melting in a double step, with formation of $CuCO_3$ at first and CuO as final product.

These different behaviours could be explained, in our opinion, by considering that the dehydration process of diaquobis-copper(II) phenoxyacetate gave an anhydrous compound having the same crystal structure as that of the dihydrate compound, in which nevertheless the absence of the two water molecules made the structure less stable.

This hypothesis was supported by the initial decomposition temperatures and with the activation energies observed.

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References

1 K. A. Hassall, The chemistry of pesticides, Mc Millan, London 1982.

2 S. S. Quee Hee and R. G. Sutherland, The phenoxyalkanoic herbicides, vol. I, CRC Press Inc, Boca Raton Florida (USA).

3 M. Blahova, B. Lucanska, V. Seressova, J. Sokolik, O. Svajlenova, A. Valent and M. Zemlicka, Farm. Obz, 55 (1986) 299.

4 L. Abate, R. Maggiore, C. Rigano and C. De Stefano, Thermochim. Acta, 149 (1986) 199.

5 L. Abate, R. Maggiore, C. Rigano and C. De Stefano, Thermochim. Acta, 162 (1990) 449.

6 J. G. Forrest, K. C. Prout and F. J. C. Rossotti, Chem. Comm., (1966) 658.

7 K. C. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust and F. J. C. Rossotti, J. Chem. Soc. A, (1968) 2791.

8 K. C. Prout, C. Walker and F. J. C. Rossotti, J. Chem. Soc. A, (1971) 556.

9 J. R. Carruthers, K. C. Prout and F. J. C. Rossotti, Acta Cryst., 331 (1975) 2044.

10 C. Natarajan and R. Rengasamy, Indian J. Chem., 18 A (1979) 356.

11 L. Abate, A. Chisari, R. Maggiore and G. Siracusa, J. Thermal Anal., 35 (1989) 2501.

12 E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.

Zusammenfassung — Es wurden zwei feste Kupfer(II)-phenoxyacetate (wasserfrei und Dihydrat) hergestellt und mittels DSC- und TG-Techniken untersucht. Die erhaltenen Ergebnisse zeigen, daß die Wassermoleküle des Dihydrates schwach und unterschiedlich gebunden sind. Sowohl die wasserfreie Verbindung als auch das Dihydrat zersetzen sich unter Bildung von CuO als Endprodukt, jedoch über unterschiedliche Schritte. Bezüglich des untersuchten thermischen Prozesses wurden einige thermodynamische Größen ermittelt und die erhaltenen Ergebnisse ausgewertet und interpretiert.