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Cu(II) PHENOBARBITURATES AND *N*-METHYL PHENOBARBITURATES. THERMAL DECOMPOSITION PROCESSES

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ABSTRACT

The thermal behaviour of complexes of phenobarbiturate and *N*-methylphenobarbiturate with Cu(II) was studied by thermogravimetry (TG) and differential thermal analysis (DTA). The complexes decompose in two steps: dehydration and decomposition of the anhydrous complex to metal oxides and carbonates. The activation energies of dehydration processes were determined and we can conclude that the water molecules interact weakly with the metallic ion.

INTRODUCTION

Studies on metal complexes of phenobarbitone and *N*-methyl phenobarbitone are currently being carried out in our laboratory. Although the synthesis and characterization of these complexes has been reported [1,2], their thermal behaviour has not been described in the literature. In this paper, the TG and DTA study of these compounds are reported.

EXPERIMENTAL

Methods

Thermal analyses were made with a Setaram thermobalance at heating rates of $10\,^{\circ}C\ min^{-1}$ and $4\,^{\circ}C\ min^{-1}$ under a dynamic oxygen atmosphere. Calcined Al_2O_3 was used as reference. Infrared spectra were obtained using KBr pellets on a Pye–Unicam SP 2000 spectrophotometer. The kinetic analysis of the dehydration processes was performed by means of the TG data obtained at variable temperatures.

Samples

The complexes $NaCuL_2(OH) \cdot 1.5H_2O$, $KCuP_2(OH) \cdot H_2O$, Na_2CuL_4 and $K_2CuP_4 \cdot 8H_2O$ were prepared as previously described [2].

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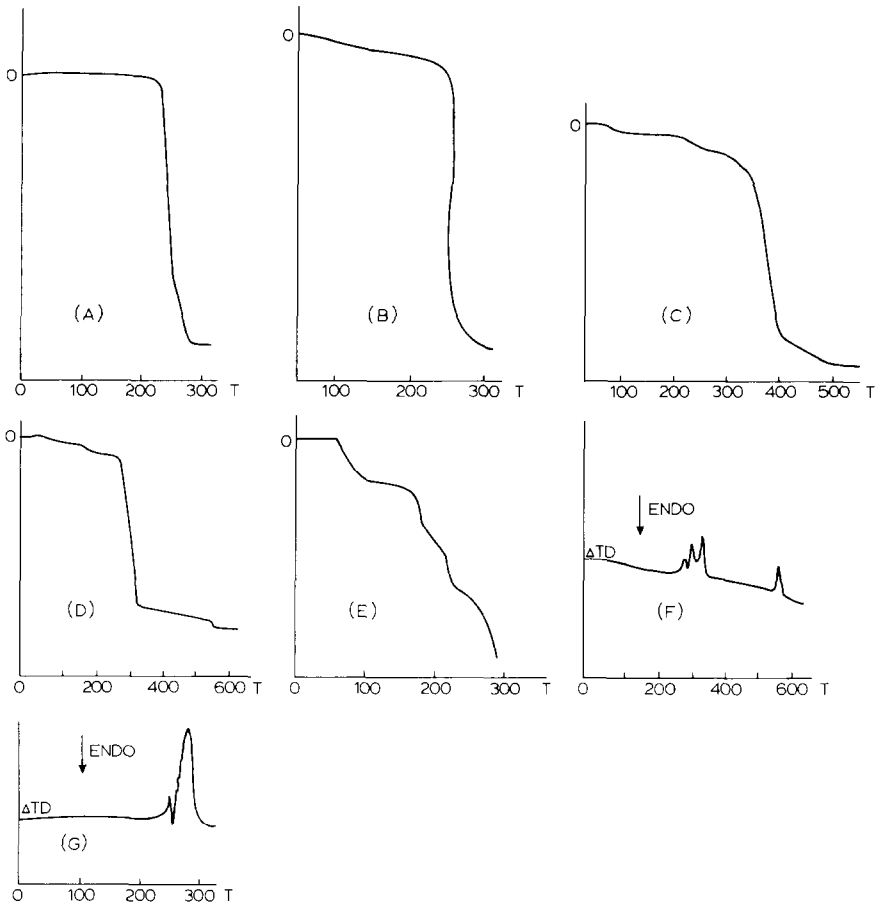

Fig. 1. TG curves of (A) Na_2CuL_4, (B) $NaCuL_2(OH)\cdot 1.5H_2O$, (C) $KCuP_2(OH)\cdot H_2O$, (D) $K_2CuP_4\cdot 8H_2O$. TG curve of (E) $K_2CuP_4\cdot 8H_2O$, and DTA curves of (F) $K_2CuP_4\cdot 8H_2O$, (G) Na_2CuL_4.

TABLE 1

Temperatures and weight losses of complexes studied

Compound	Temp. range of dehydration (°C)	Weight loss (%)		Temp. range of first-step decomposition (°C)	Weight loss (%)	
		Calc.	Obs.		Calc.	Obs.
Na_2CuL_4	–	–	–	210–315	76.8	75.5
$K_2CuP_4\cdot 8H_2O$	80–222	11.5	12.1	220–315	72.3	68.5
$NaCuL_2(OH)\cdot 1.5H_2O$	80–230	5.0	4.7	230–300	63.6	63.9
$KCuP_2(OH)\cdot H_2O$	80–220	4.3	4.9	250–400	67.1	67.2

RESULTS AND DISCUSSION

TG and DTA curves for the complexes are given in Fig. 1. The analytical data calculated from the curves in Fig. 1 are summarized in Table 1.

The thermal decomposition of the hydrated compounds takes place in two steps: (a) dehydration, (b) pyrolytic decomposition. The Na_2CuL_4 complex shows only the second stage.

Dehydration

The TG curve of $NaCuL_2(OH) \cdot 1.5H_2O$ shows several dehydration steps which overlap until 230 °C, which corresponds to a weight loss of 1.5 molecules of water and 0.5 OH groups.

The TG curve of $KCuP_2(OH) \cdot H_2O$ shows that the loss of water molecules takes place in two clearly defined steps, the first finishing at 80 °C with a weight loss indicating the elimination of one molecule of water. The observed weight loss for the second step at 220 °C corresponds to the loss of an OH group.

The TG curve of $K_2CuP_4 \cdot 8H_2O$ indicates a dehydration process involving several steps; however, the different weight losses are not defined in the TG curve. For a heating rate of 4 °C min^{-1} the TG curve (Fig. 1E) reflects well the several steps, at 80, 178 and 222 °C with a weight loss corresponding to two, three and three molecules of water, respectively (3.1, 4.5 and 4.5% calculated).

The DTA curve shows a broad endothermic peak indicating a complex dehydration process.

Non-isothermal kinetic analyses of these processes were carried out using Coats and Redfern methods [3,4] (Table 2). In all cases dehydration takes place by means of a nucleation mechanism, which corresponds to the F_1 model (Sharp notation [5]).

The existence of three different types of water molecules for $K_2CuP_4 \cdot 8H_2O$ and $NaCuL_2(OH) \cdot 1.5H_2O$ can be explained either by the different binding sites of each molecule of water in the initial structure or by the consecutive structural changes that can take place during the heating process. However, for $NaCuL_2(OH) \cdot 1.5H_2O$ and $KCuP_2(OH) \cdot H_2O$ we ob-

TABLE 2

Activation energies of the dehydration of the complexes

Compound	Activation energy (kcal mol^{-1})		
	1st step	2nd step	3rd step
$K_2CuP_4 \cdot 8H_2O$	8.92	16.02	27.14
$NaCuL_2(OH) \cdot 1.5H_2O$	11.70	11.40	32.43
$KCuP_2(OH) \cdot H_2O$	12.73	19.41	

served activation energies corresponding to the condensation process of OH groups.

Pyrolytic decomposition

The TG curve of $NaCuL_2(OH) \cdot 1.5H_2O$ shows a one-step weight loss at 230–300 °C which corresponds to the formation of a mixture of Na_2CO_3 and CuO, as shown by IR spectroscopy.

The TG curve of $KCuP_2(OH) \cdot H_2O$ shows a three-step weight loss (at 250–340, 340–400 and 400–530 °C) which corresponds to the formation of a mixture of K_2CO_3 and CuO, as shown by IR spectroscopy.

The TG curve of Na_2CuL_4 shows a two-step weight loss of 75.5% which overlaps, as seen in the curve at 210–315 °C. The final product is a mixture of Na_2CO_3 and CuO as in the other barbiturate complexes. The DTA curve shows two exothermic peaks, at 250 and 290 °C, corresponding to pyrolytic decomposition.

The TG curve of $K_2CuP_4 \cdot 8H_2O$ shows a one-step weight loss in the 220–315 °C temperature range. The residue is a mixture of K_2CO_3 and CuO, as revealed by the IR spectrum. The DTA curve shows three exothermic peaks, at 250, 290 and 320 °C, which correspond to pyrolytic decomposition, indicating a complex process.

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