Thermochimica Acta, 54 (1982) 233–236
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

THERMAL DECOMPOSITION OF TRIS-MORPHOLINE COMPLEXES OF COPPER(II) CARBOXYLATES

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(Received 5 October 1981)

This is a continuation of our work on the thermal decomposition of adducts of copper(II) carboxylates with nitrogen donors [1,2]. In the present communication, we report our results on the thermal decomposition of some adducts of morpholine with copper(II) carboxylates of an unusual 1:3 stoichiometry, $Cu(O_2CC_6H_4X\text{-}p)_2 \cdot 3\,C_4H_9ON$ where $X = CH_3$, Cl and OH by thermogravimetry in a static air atmosphere. The work was undertaken in an attempt to isolate corresponding mono- or bis-morpholine complexes of $Cu(O_2CC_6H_4X\text{-}p)_2$ which could not be obtained by conventional methods.

EXPERIMENTAL

Tris-morpholine complexes were prepared and characterized as reported previously [3]. Their purity was established by elemental analyses. The samples taken for thermogravimetry were recrystallized from acetone–morpholine solution before use. TG was recorded on a thermorecording balance (Stanton Instruments, Model No. AD-2) at a heating rate of 4 deg min^{-1}. The amount of each sample taken was ~200 mg. These studies were carried out under as near identical conditions as practicable. TG curves were found to be independent of the amount of sample used. The weight loss data are presented in Table 1 and TG curves are shown in Fig. 1.

RESULTS AND DISCUSSION

Physico-chemical investigations have shown that tris-morpholine complexes are similar to usual binuclear carboxylate bridged species except that they contain four additional uncoordinated molecules of morpholine ligand and they are represented by the formula $[Cu_2(O_2CC_6H_4X\text{-}p)_4 \cdot 2\,C_4H_9ON] \cdot 4\,C_4H_9ON$. The additional four molecules of the morpholine ligand are present in the hollow spaces of the crystals [3].

The TG curve of bis(*p*-methylbenzoato) tris(morpholine) copper(II) (Fig. 1) reveals that the complex is stable up to 360 K and starts decomposing above this

TABLE 1

Weight loss data on the decomposition of tris-morpholine complexes of copper(II) carboxylates

Compound	Intermediates/product-proposed	Temperature (K)	Weight loss (%)	
			Found	Calcd.
1 $[Cu_2(O_2CC_6H_4CH_3\text{-}p)_4\cdot 2\,C_4H_9ON]\cdot 4\,C_4H_9ON$	$[Cu_2(O_2CC_6H_4CH_3\text{-}p)_4\cdot 2\,C_4H_9ON]$	475	30.48	29.29
	$[Cu_2(O_2CC_6H_4CH_3\text{-}p)_4]$	575	42.78	43.93
	CuO	750	86.96	86.63
2 $[Cu_2(O_2CC_6H_4Cl\text{-}p)_4\cdot 2\,C_4H_9ON]\cdot 4\,C_4H_9ON$	$[Cu_2(O_2CC_6H_4Cl\text{-}p)_4\cdot 2\,C_4H_9ON]$	460	26.17	27.40
	$[Cu_2(O_2CC_6H_4Cl\text{-}p)_4]$	545	42.01	41.10
	CuO	730	87.75	87.49
3 $[Cu_2(O_2CC_6H_4OH\text{-}p)_4\cdot 2\,C_4H_9ON]\cdot 4\,C_4H_9ON$	$[Cu_2(O_2CC_6H_4OH\text{-}p)_4\cdot 2\,C_4H_9ON]$	490	30.08	29.09
	$[Cu_2(O_2CC_6H_4OH\text{-}p)_4]$	535	43.41	43.64
	CuO	800	86.57	86.71

temperature. Its TG curve further shows that it decomposes to cupric oxide at 750 K without giving any isolable intermediate. However, the smoothness of the TG curve slackens at 475 and 575 K. These correspond to the formation of two intermediate

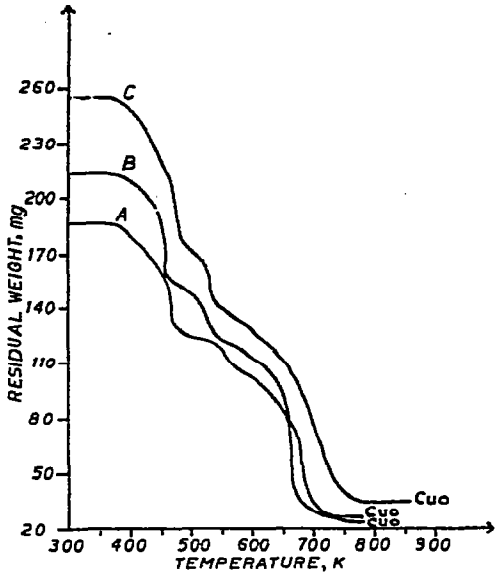

Fig. 1. TG curves of bis(*p*-methylbenzoato) tris(morpholine)-copper(II) (A), bis(*p*-chlorobenzoato) tris(morpholine) copper(II) (B) and bis(*p*-hydroxybenzoato) tris(morpholine) copper (II) (C).

species, $[Cu_2(O_2CC_6H_4CH_3\text{-}p)_4 \cdot 2\,C_4H_9ON]$ and $[Cu_2(O_2CC_6H_4CH_3\text{-}p)_4]$, respectively. Formation of these intermediates has been confirmed by weight loss data (Table 1). The TG curves of bis(*p*-chlorobenzoato) tris(morpholine) copper(II) and bis(hydroxybenzoato) tris(morpholine) copper(II) (Fig. 1) show that the complexes are stable up to 350 and 365 K, respectively, and beyond these temperatures start decomposing slowly and decompose to cupric oxide at 730 and 800 K, respectively, without giving any isolable intermediates. Their curves also depict two pauses each at 460 and 490 K, and 545 and 535 K, respectively, corresponding to the intermediate species $[Cu_2(O_2CC_6H_4X\text{-}p)_4 \cdot 2\,C_4H_9ON]$ and $[Cu_2(O_2CC_6H_4X\text{-}p)_4]$ (where X = Cl or OH). Attempts to isolate their corresponding intermediates were unsuccessful as they are extremely unstable and start decomposing even before their formation is completed.

The close similarity of the TG curves of these complexes further illustrates that the steps involved in the thermal decomposition of these three carboxylate complexes are similar to one another and their decomposition pattern may be represented schematically as under

$$[Cu_2(O_2CC_6H_4X\text{-}p)_4 \cdot 2\,C_4H_9ON] \cdot 4\,C_4H_9ON \xrightarrow{-4\,C_4H_9ON} [Cu_2(O_2CC_6H_4X\text{-}p)_4 \cdot 2\,C_4H_9ON] \quad (1)$$

$$[Cu_2(O_2CC_6H_4X\text{-}p)_4 \cdot 2\,C_4H_9ON] \xrightarrow{-2\,C_4H_9ON} [Cu_2(O_2CC_6H_4X\text{-}p)_4] \quad (2)$$

$$[Cu_2(O_2CC_6H_4X\text{-}p)_4] \rightarrow CuO + \text{volatile products} \quad (3)$$

where $X = CH_3$, Cl and OH.

ACKNOWLEDGEMENTS

The authors wish to thank Dr M.L. Lakhanpal, Professor and Head of the Chemistry Department, Panjab University, Chandigarh (India) for facilities provided for the thermogravimetric studies. A.K.S. thanks the University of Jammu, Jammu for the award of a research fellowship.

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