Thermochimica Acta, 93 (1985) 109-112
Elsevier Science Publishers B.V., Amsterdam

THERMAL PROPERTIES OF COPPER(II) DIMERS WITH UNSATURATED CARBOXYLIC BRIDGES

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ABSTRACT

Thermal decomposition of $Cu_2(RCOO)_4$ and $Cu_2(RCOO)_4L_2$ (where $RCOO^-$ = acrylate, crotonate, methacrylate and 3.3'-dimethylacrylate ions, L = py, quin, acd, pic, lut) type of copper(II) dimers have been studied up 1000^0C in the air. The mechanism of decomposition of these type copper(II) dimers has been proposed.

INTRODUCTION

Dimeric copper(II) carboxylates are since many years the subject to the intensive studies because of their interesting properties. The research are concentrated mainly on searching for correlation between structure and physicochemical properties. Thermal properties of the dimeric copper(II) carboxylates have been broadly investigated, but the compounds with the unsaturated carboxylic acids, e.g. acrylate, crotonate, methacrylate (mcryl) and 3.3'-dimethylacrylate are very little known, still.

EXPERIMENTAL

Thermal stability of the synthetized copper(II) unsaturated carboxylates [1,2] was examined thermogravimetrically on the Paulik-Paulik Derivatograph Q-1500 D using aluminium oxide as a standard. DTG, TG and DTA curves have been recorded up to 1000^0C, by using heating rates of 2.5 and 5^0C/min and samples about 200 mg, the examination were carried out in the platinium sample holder in the air.

RESULTS AND DISCUSSION

The subject to the here presented studies are two groups of copper(II) carboxylates. The first group are the dimeric carboxylates of general formula $Cu_2(RCOO)_4$ having no axial ligands; their polimeric structure in crystal lattice is composed from the dimeric subunits with Cu-Cu distance equal about 2.58 Å [3]. Paramagnetic Cu(II) centres are coupled inside the dimeric units through the

Proceedings of ICTA 85, Bratislava

system of quadrupole triatomic carboxyl bridges (Cu-O-C-O-Cu). To the second group belong the copper(II) carboxylates with the coordinated ligands of the pyridine type (pyridine, quinoline, acridine, picoline, lutidine) of a general formula $Cu_2(RCOO)_4L_2$. In crystal lattice they are the well isolated dimers with the Cu-Cu distance inside a dimer, equal about 2.66 Å [4].

Thermograwimetric analysis TG and DTG and the differential thermal analysis the unsaturated copper(II) carboxylates and their adducts with amines is the provide source for a lot of information about the stability and character of the thermal decomposition of the examined compounds. Characteristic maxima on the DTG curves and related to them shoulders on the DTG curves which register the loss of mass towards the initial complex allowed the identification of the intermediate decomposition products, followed by design of the most probable schemes of their thermal decomposition.

Unsaturated copper(II) carboxylates without axial ligands and their adducts with aromatic amines are stable up to 50 - 70°C. In the range 50, 70 - 200°C the compounds suffer decomposition up to the range 400 - 600°C where the CuO is formed as the final products. Thermal decomposition of the compounds under study is the multistage process. The subsequent splitting off the axial ligands and of the particular carboxyl groups was observed. The loss of the last, fourth carboxyl group proceeds with simultaneous oxidation of copper to CuO. The latter decomposition stage proceeds in some cases through the intermediate product Cu_2O.

Thermolysis of $Cu_2(mcryl)_4$ presented in Fig. 1 is the best example for thermal decomposition of the unsaturated copper(II) carboxylates, having no axial ligands. The derivatogram suggests the following scheme of the copper(II) methacrylate under influence of temperature

$$Cu_2(mcryl)_4 \rightarrow Cu_2(mcryl)_3$$
$$Cu_2(mcryl)_3 \rightarrow Cu_2(mcryl)_2$$
$$Cu_2(mcryl)_2 \rightarrow Cu_2(mcryl)$$
$$Cu_2(mcryl) \rightarrow 2\,CuO$$

The DTG curve presents three well-shaped maxima at 148, 190 and 245°C corresponding to splitting off of three carboxyl groups and one lower maximum at 340°C, related to the reactions·

$$Cu_2(mcryl) \rightarrow Cu_2O \rightarrow 2CuO$$

The DTA curve has only one, broad egsothermic maximum in the range 150 - 250^{0}C with three peaks suggesting the subsequent splitting off of the carboxyl ligands.
The loss of the fourth acidic group with simultaneous formation of CuO , evidenced by the broad maximum on the DTA curve with its centre about 420^{0}C is also the egsothermic transformation. For all examined carboxylate adducts with aromatic amines we have proposed the following scheme of the thermal decomposition:

$$Cu_2(RCOO)_4L_2 \xrightarrow{T_1} Cu_2(RCOO)_4L$$

$$Cu_2(RCOO)_4L \xrightarrow{T_2} Cu_2(RCOO)_4$$

$$Cu_2(RCOO)_4 \xrightarrow{T_3} Cu_2(RCOO)_3$$

$$Cu_2(RCOO)_3 \xrightarrow{T_4} Cu_2(RCOO)_2$$

$$Cu_2(RCOO)_2 \xrightarrow{T_5} Cu_2(RCOO)$$

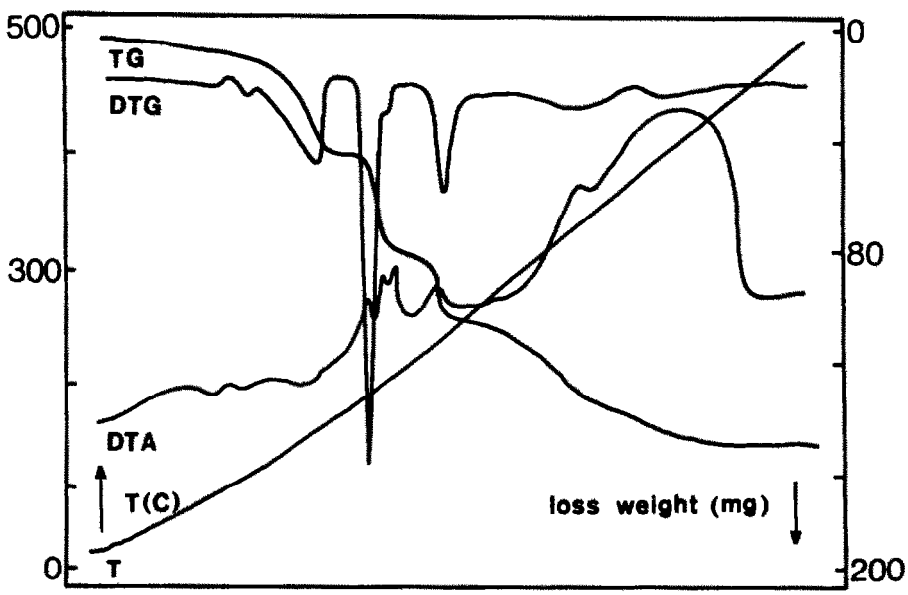

Figure 1. Thermolysis curve of $Cu_2(mcryl)_4$.

$$Cu_2(RCOO) \xrightarrow{T_6} Cu_2O$$

$$Cu_2O \xrightarrow{T_7} 2\,CuO$$

We tried to isolate the discussed stages and the intermediate products from all derivatograms, but we failed in several cases.
In some cases decomposition process is the fluent process, in some cases it is impossible to observe the intermediate products and only the shoulders on the DTG or DTA curves point out to the multistage character of the thermal decomposition.

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