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THERMAL BEHAVIOUR OF THE HOMOPOLYNUCLEAR GLYOXYLATE COMPLEX COMBINATIONS WITH Cu(II) AND Cr(III)

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Abstract

Homopolynuclear complexes of Cu(II) respectively Cr(III) with the glyoxylate dianion, $C_2H_2O_4^{2-}$, have been studied in non-isothermal regime in air and nitrogen.

The results of the non-isothermal analysis performed for the synthesised complexes, $Cu(C_2H_2O_4)\cdot 0.5H_2O$, respectively $[Cr_2(OH)_2(C_2H_2O_4)_2(OH_2)_4]\cdot 2H_2O$, correlated with the results of the IR and TG analysis of the compounds obtained by thermal treatment from the initial complexes and the results of the GLC and XR analysis have led to the establishment of the thermal decomposition mechanisms for the two studied complexes.

The decomposition mechanisms confirm the stoichiometric and structural formulae proposed for the two synthesised homopolynuclear complexes.

Keywords: decomposition mechanisms, glyoxylates, homopolynuclear complexes, thermal analysis

Introduction

The homo- and heteropolynuclear complex combinations in which the cations are located within the same coordination sphere are of a particular theoretical and practical importance. Their study brings contributions to the development of the theory of chemical bond and chemical species structure [1–3]. From the practical point of view such combinations can be used for the generation of simple and mixed oxides and metals with applicability in heterogeneous catalysis, electrocatalysis, obtaining of thermoresistant pigments and various ferrites [4–6].

In this paper are presented studies carried out concerning some homopolynuclear complex combinations with the glyoxylate dianion $C_2H_2O_4^{2-}$ as ligand which may act in double bridge depending on the cation. From these combinations, by an appropriately targeted thermal treatment oxides or mixtures of metal oxides in various oxidation states and crystallinity degrees may be obtained [7, 8].

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The method of obtaining homopolynuclear complex combinations containing as ligand the glyoxylate dianion is based on the hot oxidation reaction in aqueous solution of 1,2-ethanediol simultaneously with the formation in the solid state reaction system of their glyoxylates. The oxidative medium is provided by introducing the cations as nitrates [9, 10].

For this process the synthesis yield is practically 100%.

$$C_2H_4(OH)_2+(2NO_3^-+[M(H_2O)_x]^{2+})\rightarrow MC_2H_2O_4\cdot yH_2O+2NO+(x-y+2)H_2O$$

$$2NO(g)+O_2(g)\rightarrow 2NO_2(g)$$

The thermal decomposition of glyoxylates in order to obtain oxides of remarkable properties presents a series of advantages over other complex combinations or conventional methods.

Thus, the combinations with carboxylic acid anions as ligands decompose at relatively low temperatures and generate highly volatile decomposition products [11, 12].

In this paper the thermal behaviour of glyoxylate homopolynuclear complex combinations formed by Cu(II), respectively Cr(III) is studied.

There are the decomposition mechanisms established using thermal analysis in air and nitrogen, IR spectrometry, gas–liquid chromatography and diffractometric X-ray analysis.

Experimental

The complex homopolynuclear combinations of Cu(II) and Cr(III) have been synthesised according to the previous patent [9] and papers [10] using as reagents 1,2-ethanediol (Fluka), $Cu(NO_3)_2\cdot 3H_2O$ (Merck), and $Cr_2(NO_3)_3\cdot 9H_2O$ (Merck).

After synthesis the Cu(II) and Cr(III) glyoxylates were purified by refluxing in a water–acetone mixture and characterized by elemental analysis [Cu(II), Cr(III), C, H], electronic diffuse reflectance, thermal analysis, IR spectroscopy, assigning the composition formulae $Cu(C_2H_2O_4)\cdot 0.5H_2O$ and $[Cr_2(OH)_2(C_2H_2O_4)_2(OH_2)_4]\cdot 2H_2O$, respectively [10, 13].

The thermal analysis of the obtained compounds has been carried out with a model 1500D derivatograph (MOM, Hungary), in plate-type crucibles, at a heating rate of 5°C min^{-1} in static air atmosphere and flowing nitrogen atmosphere of 100 mL min^{-1}. The mass of the samples taken from each compound was 100.00 mg.

There have been studies for the thermal behaviour of both the initial complexes and the intermediate compounds obtained by heating the glyoxylates at certain temperatures for certain periods of time. The intermediate compounds were stabilized by cooling in nitrogen in a Ugine–Eyraud balance.

The IR spectra of the synthesised complex combinations, intermediate compounds or end-products have been recorded with a Specord M 80 spectrophotometer (Carl Zeiss, Jena) in the range 4000–400 cm^{-1} at room temperature using the KBr pellet technique.

The volatile products resulting from the thermal decomposition were analysed by gas–liquid chromatography with a GCHF 18.3 instrument, on a 3 mm×3 m classical column filled with Porapak Q (80–100 mesh).

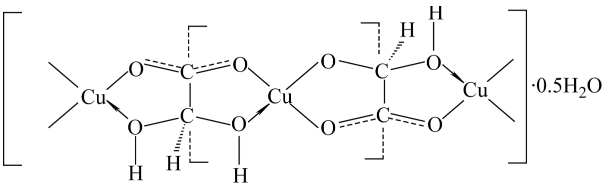
As end-products the metal oxides have been evidenced by diffraction analysis using a Dron 3 X-ray diffractometer with the CoK_α radiation.

Results and discussion

Important information concerning the structure of the complex combinations synthesised have been obtained from the analysis of the diffuse reflectance electronic spectra and IR vibrational spectra, together with the results of the elemental analysis [10].

According to its structure, the glyoxylate dianion $C_2H_2O_4^{2-}$ acts as a double bridge ligand, determining a polynuclear structure of the complex combinations formed.

The studies carried out for the Cu(II) glyoxylate type combination, $[Cu(C_2H_2O_4)\cdot 0.5H_2O]$ led to the following possible structure formula [10]:



Scheme 1

A square-plane coordination geometry has been established for the Cu(II) ion, in good agreement with literature data [14].

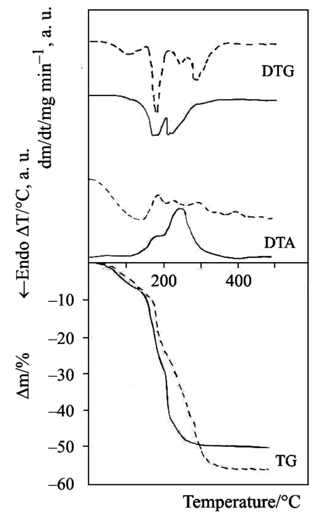


Fig. 1 Thermal curves of the complex combination $Cu(C_2H_2O_4)\cdot 0.5H_2O$; —– air, --- – nitrogen

The study of the thermal decomposition mechanism allowed the confirmation of the stereochemical and structure formulae of the glyoxylate type complex homopolynuclear combination of Cu(II).

In Fig. 1 the thermal conversion curves for the Cu(II) glyoxylate in air respectively nitrogen are presented which supported the delimitation of the steps in the decomposition process in air according to Fig. 2 [15].

From Fig. 1 one may note that:

– irrespective of the working atmosphere, the degradation of the ligand begins after the loss of the crystallization water;

– for the thermal conversion in air, under the working conditions established, the final residue corresponds to the reaction stoichiometry, with the formation of CuO, at the temperature of 300°C;

– in the thermal conversion in nitrogen it is evidenced the reduction of Cu(II) to Cu(I) or even Cu(0).

The samples subjected to thermal analysis (Fig. 2) have been also analyzed by IR spectrometry (Fig. 3), which allowed a better evidence of the steps in the thermal conversion. From the TG curves and IR spectra of the samples treated at 130°C, respectively 160°C, it follows that the crystallization water has been mostly lost up to 130°C and after this temperature the decomposition of the ligand from the superficial strata of the sample begins, according to the reactions:

$$2Cu(C_2H_2O_4)\cdot 0.5H_2O \xrightarrow{120^\circ C} 2Cu(C_2H_2O_4)+H_2O \tag{1}$$

$$2Cu(C_2H_2O_4)\cdot 0.5H_2O \xrightarrow{120-180^\circ C} Cu_2O+3CO+CO_2+2H_2O \tag{2}$$

Both in the 130 and 160°C IR spectra, besides the specific bands for the glyoxylate ligand there occurs a band at 610 cm^{-1} which is assigned to the Cu(I)–O bond from Cu_2O which confirms the occurrence of the reaction (2).

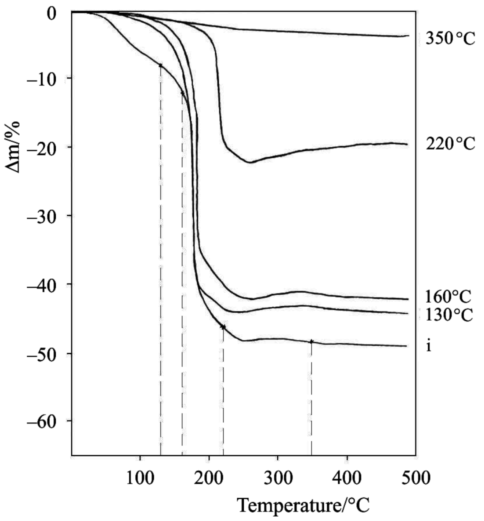


Fig. 2 TG curves of the initial (*i*) and thermally treated (130, 160, 220, 350°C) Cu(II) glyoxylate

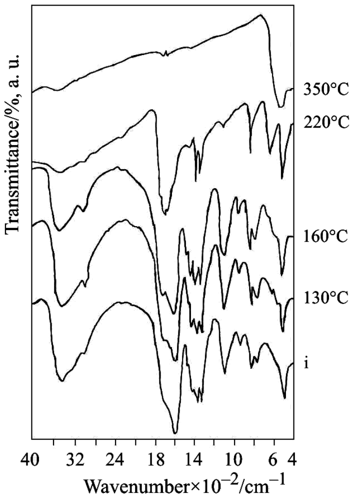


Fig. 3 IR spectra of the Cu(II) glyoxylate: initial (*i*) and thermally treated at 130, 160, 220 and 350°C

The presence of Cu(I) has been also evidenced by the disproportioning reaction:

$$Cu_2O+H_2SO_4\ (conc.) \rightarrow Cu(0)+CuSO_4+H_2O \qquad (3)$$

Within the temperature range up to about 200°C the reactions take place:

$$Cu_2O+CO \rightarrow 2Cu(0)+CO_2 \qquad (4)$$

$$2Cu(0)+O_2 \rightarrow 2CuO \qquad (5)$$

By GLC the presence of CO has been evidenced in the decomposition gases and for the samples treated at temperatures higher than 180°C the presence of CO_2 has been also observed. The exothermal effect with a maximum at about 180°C which is also present in nitrogen atmosphere confirms the proceeding of reaction (4).

The obvious presence in the IR spectra of the sample thermally treated at 220°C of the bands characteristic of copper oxalate and cupreous oxide confirms that the reaction (6) proceeds, it is known that the system Cu^{2+}/Cu^{+} acts as an oxidation catalyst [16]:

$$2CuO+Cu(C_2H_2O_4) \rightarrow Cu_2O+CuC_2O_4+H_2O \qquad (6)$$

For the confirmation of reaction (6) samples of Cu(II) glyoxylate have been subjected to thermal treatment in the range 200–250°C and afterwards have been recorded the TG curves (Fig. 4), respectively the IR spectra (Fig. 5). Compared with the IR spectrum of pure copper oxalate, the IR spectra and TG curves of the samples thermally treated at 200°C for 5 min and 1 h confirm the formation of CuC_2O_4 and Cu_2O from Cu(II) glyoxylate according to reaction (6).

Further, as the temperature rises, the following reactions take place:

$$Cu_2O+1/2O_2 \rightarrow 2CuO \qquad (7)$$

$$CuC_2O_4 \rightarrow CuO+CO+CO_2 \qquad (8)$$

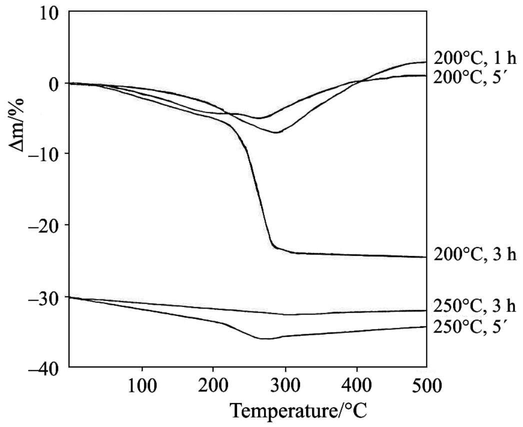


Fig. 4 TG curves of Cu(II) glyoxylate thermally treated at 200°C (5 min, 1 and 3 h) and 250°C (5 min, 1 h)

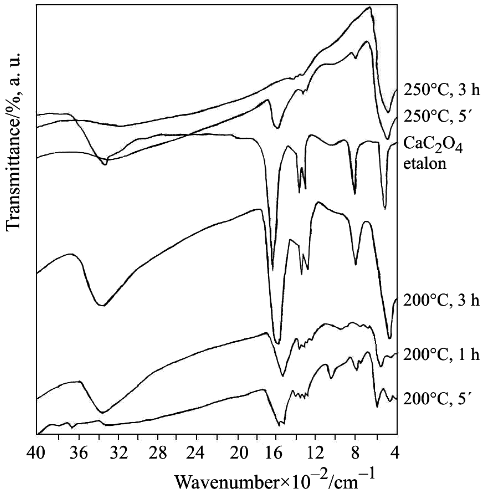
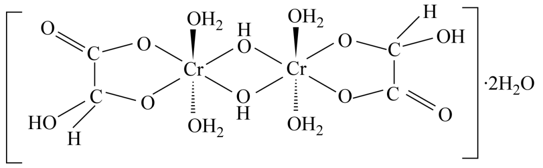


Fig. 5 IR spectra of Cu(II) glyoxylate thermally treated at 200°C (5 min, 1 and 3 h) and 250°C (5 min, 1 h)

Finally at about 350°C the product consists entirely of CuO (Figs 2 and 3) of poor crystallinity, as evidenced also by X-ray diffraction.

For the Cr(III) glyoxylate with the stoichiometric formula $Cr_2(OH)_2(C_2H_2O_4)_2\cdot(H_2O)_6$ has been proposed the following dinuclear structural formula [10]:



Scheme 2

Taking into account the stoichiometry and the hexacoordination of the Cr(III) ion the combination may be formulated with a dimer structure in which the OH groups are placed in the bridge.

Figure 6 shows the thermal curves obtained from the analysis of the complex homopolynuclear combination of the Cr(III) glyoxylate type, in air and respectively nitrogen. The steps of the decomposition process according to Fig. 7 have been delimited from these curves.

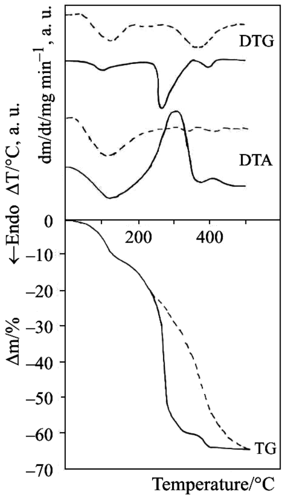


Fig. 6 Thermal curves of the complex combination $Cr_2(OH)_2(C_2H_2O_4)_2\cdot(H_2O)_6$; —– air, --- – nitrogen

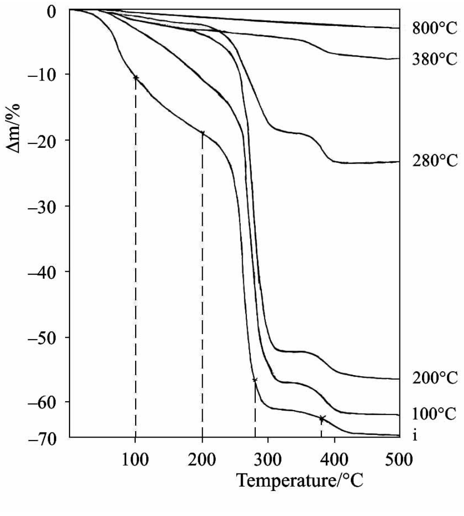


Fig. 7 TG curves of the initial (*i*) and thermally treated (100, 200, 280, 380, 800°C) Cr(III) glyoxylate

In Fig. 6 it can be seen that the crystallization water is eliminated in the temperature range 30–180°C accompanied by an endothermal effect, both in air and nitrogen.

In air, the process of decomposition and burning of the ligand takes place within the range 180–330°C, and within the range 400–420°C occurs the crystallization, α-Cr_2O_3, both processes accompanied by exothermal effects.

In nitrogen, the decomposition takes place within the range 180–480°C, with one only exothermal effect, assigned to the crystallization of amorphous Cr_2O_{3+x} to α-Cr_2O_3 [17]. Both in air and nitrogen the mass of the residue (α-Cr_2O_3) is in agreement with the reaction stoichiometry.

The IR spectra recorded (Fig. 8) for the samples treated at 100, 200, 280, 380, and 800°C as well as the TG curves (Fig. 7) offer useful information for the unraveling of the decomposition mechanism of Cr(III) glyoxylate.

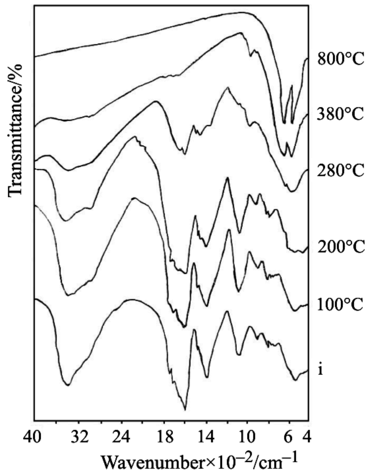


Fig. 8 IR spectra of thermally treated (at 100, 200, 280, 380, 800°C) Cr(III) glyoxylate

From the IR spectra and the TG curves for the samples treated at 100 and 200°C one can ascertain that the organic side of the complex is not affected; during this step it lost the crystallization and coordinated water according to the equations:

$$[Cr_2(OH)_2(C_2H_2O_4)_2\cdot(H_2O)_4]\cdot 2H_2O \xrightarrow{30-180\,^{\circ}C\quad -2H_2O} Cr_2(OH)_2(C_2H_2O_4)_2(H_2O)_4 \quad (9)$$

$$Cr_2(OH)_2(C_2H_2O_4)_2\cdot(H_2O)_4 \xrightarrow{180-230\,^{\circ}C\quad -4H_2O} Cr_2(OH)_2(C_2H_2O_4)_2 \quad (10)$$

Within the range 230–320°C the decomposition of the organic side of the complex occurs according to the equation:

$$Cr_2(OH)_2(C_2H_2O_4)_2 \xrightarrow{230-320\,^{\circ}C\quad +(3+x)/2O_2} Cr_2O_{3+x}+2CO_2+2H_2O \quad (11)$$

From the IR spectrum of the sample at 280°C one notes: the disappearance of the bands at 1070 cm^{-1} corresponding to alcoholic $\nu_{(C-OH)}$ and $\delta_{(MOH)}$ and 900 cm^{-1} for ν_{C-C}; persistency of the bands in the range 1400–1600 cm^{-1} assigned to the carboxylate group (COO^-); the appearance of the bands at 950 cm^{-1} corresponding to the CrO_3 bonds, and at 570 and 620 cm^{-1} corresponding to Cr_2O_3 [18].

These modifications in the IR spectrum show that as the result of the process of breaking the C–C bonds it is formed Cr(III) carbonate besides CO and CO_2 which decomposes at a higher temperature (the TG curve at 280°C exhibits a larger stability domain).

The presence of CO_2 is evidenced in the chromatograms of the samples beginning from 255°C which confirms the starting of the decomposition process of the organic side.

In the IR spectrum of the sample at 380°C one finds only the bands at 950, 560, and 620 cm^{-1} which proves that the glyoxylate was completely decomposed with the formation of $Cr_2O_3{\cdot}CrO_3$ hence (Cr_2O_{3+x}), as is also confirmed by the evolution of the TG curve at this temperature.

The mass loss on the TG curve corresponds to the transformation of the amorphous chrome oxide into crystalline α-Cr_2O_3 according to the equation:

$$Cr_2O_{3+x} \xrightarrow{390-410^\circ C} Cr_2O_3 + x/2O_2 \qquad (12)$$

In the IR spectrum of the sample at 800°C one notes only the presence of the bands characteristic of α-Cr_2O_3 at 560 and 620 cm^{-1} [19] thus confirming the Eq. (12).

The gas-chromatographic analysis of the decomposition of Cr(III) glyoxylate in nitrogen does not evidence the presence of CO_2, thus confirming that the exothermal effect in the decomposition in air was due to the oxidation of CO to CO_2.

Conclusions

The non-isothermal analysis of the complex combinations of Cu(II), respectively Cr(III) with the glyoxylate dianion as ligand, in initial state and after various stages of thermal decomposition, associated with the results of the IR, GLC, and X-ray diffraction analysis enabled the establishment of their decomposition mechanism.

It has been stated that Cu(II) glyoxylate partially decomposes through copper oxalate, while for the Cr(III) the possible intermediate is the carbonate species.

The data of elemental analysis, the diffuse reflectance electronic spectra, and the mechanisms of the complex combination decomposition confirmed the stoichiometric and structural formulae proposed for the homopolynuclear complexes of Cu(II), respectively Cr(III).

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