Journal of Thermal Analysis, Vol. 46 (1996) 263-274

THERMOANALYTICAL INVESTIGATIONS OF THE DECOMPOSITION COURSE OF COPPER OXYSALTS

III. Copper(II) acetate monohydrate

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(Received December 16, 1994; in revised form April 26, 1995)

Abstract

The thermal decomposition course of copper acetate monohydrate (CuAc) was examined on heating up to 600°C at various rates, by TG, DTA and DSC. Non-isothermal kinetic and thermodynamic parameters were determined in air or nitrogen. SEM was used to describe the decomposition course and the solid products were identified by IR and XRD analysis. The results indicated that CuAc was dehydrated at 190°C and then partially decomposed at 220°C, giving rise to CuO in addition to a minor portion of Cu_2O and Cu_4O_3. The last two oxides seemed to facilitate the decomposition of the rest of the anhydrous acetate. Cu_2O and Cu_4O_3 were oxidized in air at >400°C, in a process that did not occur in nitrogen.

Keywords: copper acetate monohydrate, copper oxysalts

Introduction

Metal acetates are useful reagents, particularly in organic synthesis [1] and in the preparation of some industrially important metal and metal oxide catalysts [2]. The thermal decomposition of acetates under various conditions, has attracted attention owing to its importance in several fields of research, in solid-state and surface chemistry and catalysis [1, 3–7].

The aim of the present study is to follow the decomposition course of copper acetate monohydrate. The decomposition course was investigated by thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The kinetic and thermodynamic parameters of the observed events were determined under non-isothermal conditions. The products were analysed by infrared spectroscopy (IR), X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

0368–4466/96/ $ 5.00

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Experimental

Material

Copper acetate (CuAc); $(CH_3COO)_2Cu\cdot H_2O$, used in the present investigation was pure (99.8%) (Prolabo product). Solid products of decomposition were obtained by calcining CuAc at various temperatures (190–600°C) for 2 h, in a static air atmosphere and then kept dry for further analysis. For simplicity, these products are denoted in the text by CuAc followed by the calcination temperature in parentheses. Thus, CuAc(240) indicates the decomposition product of CuAc obtained by heating at 240°C for 2 h.

Apparatus and methods

Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were carried out with a Model 30-H Shimadzu Unit (Kyoto, Japan), by heating up to 600°C at various rates (θ = 5, 10, 20 and 50 deg·min^{-1}), in a dynamic air atmosphere (30 ml·min^{-1}) for TG and DTA while DSC curves were recorded in a dynamic dry nitrogen atmosphere (30 ml·min^{-1}). The techniques adopted and a detailed description of the procedure and equations used to determine the non-isothermal kinetic and thermodynamic parameters have been giving in a previous paper [8]. Analysis of CuAc before, after and at suitable stages of its thermal decomposition course was carried out by scanning electron microscopy, X-ray diffraction and infrared spectroscopy with the apparatus and techniques reported earlier [8].

Results and discussion

TG and DTA curves obtained on heating CuAc in a dynamic air atmosphere (30 ml·min^{-1}) at heating rates of 5, 10, 20 and 50 deg·min^{-1}, are shown in Fig. 1. They indicate that CuAc decomposes via two weight loss processes (thermal events I and II) over the temperature range 100–320°C, leading to the formation of a solid material that slowly gains weight up to 600°C. The IR spectra and X-ray powder diffractograms obtained for CuAc and its solid decompo-

Table 1 Characteristics and non-isothermal kinetic parameters of the thermal events observed (Fig. 1) throughout the decomposition of CuAc based on TG and DTA results

Thermal evvent	Temperature range*/ °C	T^*_{max}/ °C	ΔE / kJ·mol^{-1}	log A/	$k\cdot 10^{-2}$/ min^{-1}	$\Delta T/T$
I	105–165	145	66±2	6.4	1.5	endo
II	255–285	278	227±5	21.2	51.5	exo

* Values obtained from TG and DTA curves recorded at 10 deg·min^{-1} in an air flow

sition products at 190–600°C in a static air atmosphere were used in attempts to identify decomposition intermediates and products. Figure 2 shows TG and DTA curves for CuAc obtained at a heating rate of 10 deg·min^{-1} in a dynamic (30 ml·min^{-1}) nitrogen atmosphere; the corresponding TG and DTA curves re-

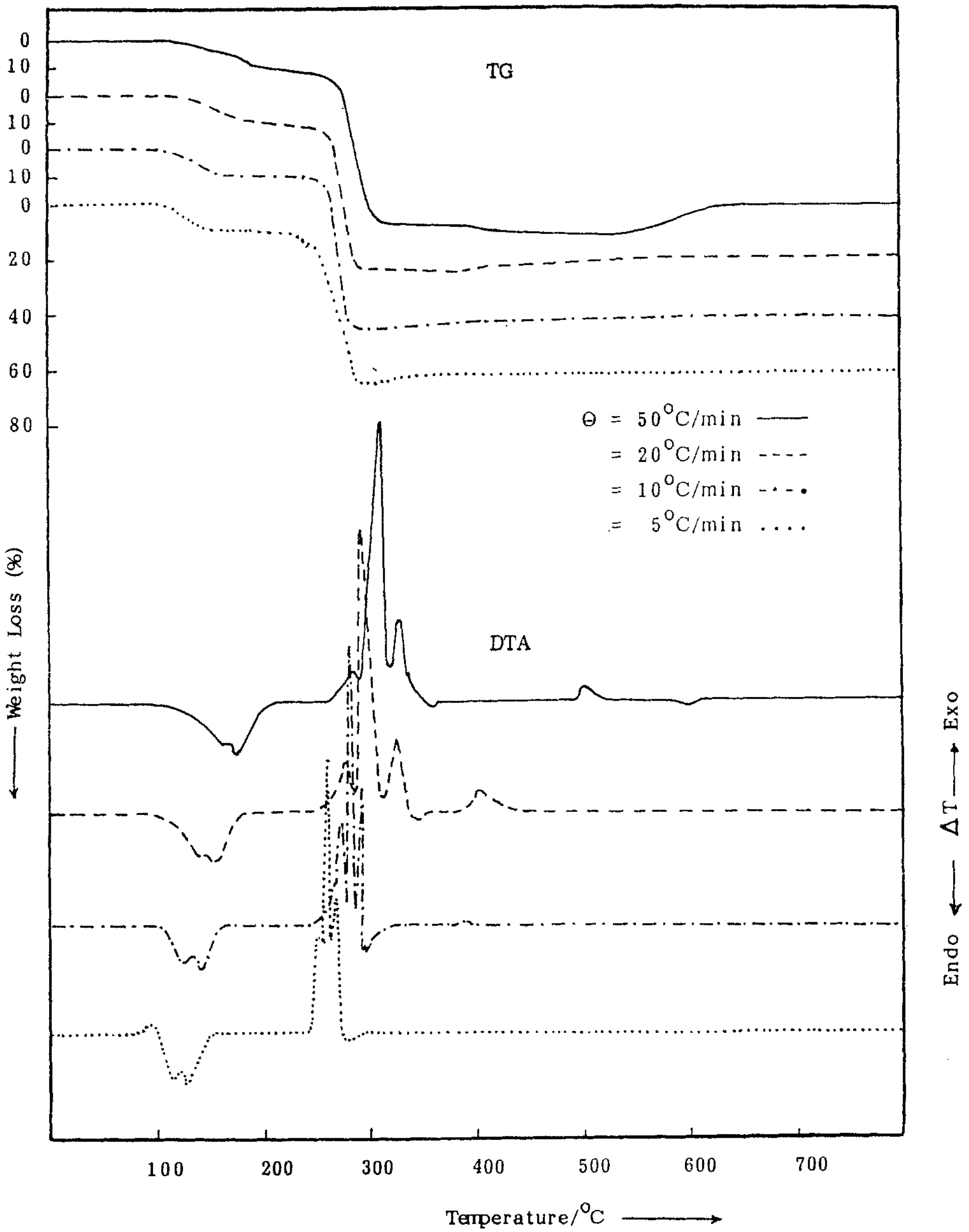


Fig. 1 TG and DTA curves recorded for CuAc in a dynamic (20 ml·min^{-1}) air atmosphere, at the heating rates (θ) indicated

corded in a dynamic (30 ml·min^{-1}) air atmosphere are also shown for comparison. Logθ *vs.* $1/T_{max}$ plots, constructed on the basis of the TG results (Fig. 1), were used to calculate the values of ΔE, k and log$A$ that are listed in Table 1. DSC curves recorded at 5, 10 and 20 deg·min^{-1} are shown in Fig. 3. Table 2 compiles the non-isothermal kinetic and thermodynamic parameters of the thermal events that have been determined on the basis of DSC measurements.

Figures 1 and 3 show that an increase in the heating rate resulted in an increase in T_{max}. For convenience, the description of the decomposition course will be done with reference to the results obtained at a heating rate of 10 deg·min^{-1}.

Table 2 Non-isothermal kinetic and thermodynamic parameters of the thermal events revealed by DSC measurements throughout the decomposition of CuAc (in a nitrogen flow)

Thermal events	Temp. range* / °C	ΔE / kJ·mol^{-1}	ln$A$	$k\cdot10^{-1}$ / min^{-1}	ΔH / kJ·mol^{-1}	C_p J·K^{-1}g^{-1}	ΔS / J·K^{-1}g^{-1}	$\Delta T/T$
I	96–175	84	23	5.7	49	3.02	0.586	endo
a	258–277	182	20.1	7.5	5	1.48	0.037	endo
II b	276–290	273	30	10.7	10	4.55	0.052	endo
c	290–320	424	30	15	8	0.46	0.011	endo

* Values obtained from a DSC curve recorded at 20 deg·min^{-1} in a nitrogen flow

Characterization of the observed thermal events

Event I

It can be seen from the TG and DTA curves (Fig. 1) that thermal event I is an endothermic weight-loss process, with maximum at 125 → 175°C, depending on the heating rate.

The IR spectrum taken of CuAc(190) is similar to that obtained for untreated CuAc. It exhibits almost all the characteristic absorption bands of the acetate anion (at 1585–640 cm^{-1}) and a weak band at 3440 cm^{-1}, indicating the presence of some residual water [9, 10].

The total weight loss accompanying this event (9.1%) is fairly close to that expected (ca. 9.0%) for the dehydration of CuAc. Hence, from this result and the IR spectrum, it may be suggested that thermal event I involves the following reaction:

$$Cu_2(CH_3COO)_4\cdot2H_2O \rightarrow 2Cu(CH_3COO)_2 + 2H_2O$$

This conclusion agrees with reported data [11, 12]. It is to be noted that part of the released water seems to be retained in the solid product which could be in the form of adsorbed species. Moreover, the activation energy (ΔE) calculated for this event (Table 1) is close to the reported values [11].

Event II

The TG And DTA curves (Fig. 1) show that thermal event II commences exothermally in the temperature range 220–320°C. This event brigs the total weight loss up to 66% which is higher than that predicted for the formation of CuO (60.0%), and lower than that for the formation of metallic copper (68.1%). DTA curves (Fig. 1) indicate that the decomposition process is complicated.

The IR spectrum of CuAc(240) shows marked decreases in the ν_{as} and ν_s absorptions of the COO^- group at 1595 and 1445 cm^{-1}. It also reveals bands due to Cu_2O [10]. The XRD of this product at 240°C exhibited the characteristic lines of Cu_2O [ASTM card no. 5-667] as a major component as well as ill-defined lines characteristic of CuO (ASTM card no. 5-661) and Cu_3O_4 [ASTM card no. 3-879]. The diffractogram indicated the domination of the created oxides over the parent acetate. The IR spectrum of CuAc(320) indicated the complete disappearance of the acetate ion. It displayed the bands of Cu_2O and CuO in the range 700–300 cm^{-1} [10].

It could be concluded from these results that the decomposition reaction of the anhydrous acetate intermediate commences slowly in the temperature range 220–260°C, and then the decomposition was completed immediately (c.f. Fig. 1). The weight loss accompanying this event being greater than that anticipated for the CuAc → CuO transformation could be attributed to the formation of Cu_2O and Cu_4O_3 during this process, in addition to CuO. The activation energy (ΔE) calculated for this step (Table 1) was also found to be close to published data [11].

As already clear from Fig. 1, the decomposition product started to slowly gain weight with rising temperature. The temperature at which the weight gain process begins is higher, the higher the heating rate applied. Considering the weight increase, the total weight loss of CuAc by the end of this process amounts to 60%, no matter what the heating rate is. This weight loss is equal to the value calculated for the presumed CuAc → CuO transformation, i.e. it is equal to percent weight difference between the parent CuAc and the CuO product, regardless of the reaction pathways. The IR and XRD analysis results obtained for the solid decomposition product CuAc(600) revealed that is was composed of CuO only, with no sign of either Cu_2O nor Cu_4O_3. Here, it could be presumed that the latter two oxides had undergone an oxidation process with the oxygen in the air flow. Hence, such oxidation process could explain the observed gain in weight especially at high heating rates and at elevated temperatures.

It is worth mentioning that Cu_2O was detected at the early stages of thermal event II. Hence, it may be suggested that Cu_2O is the first decomposition product. It seems that the formation of Cu_2O nuclei facilitates the decomposition process of CuAc, giving rise to CuO and hence Cu_4O_3.

Figure 2 demonstrates that the decomposition of CuAc under a dynamic nitrogen atmosphere also begins with two steps. The first step is endothermic and involves dehydration. The second one brings the weight loss to 72% which is higher than that expected for the formation of CuO or Cu. On the other hand, no weight gain is observed for the decomposition products under these conditions. The greater weight loss than that expected for the formation of Cu could

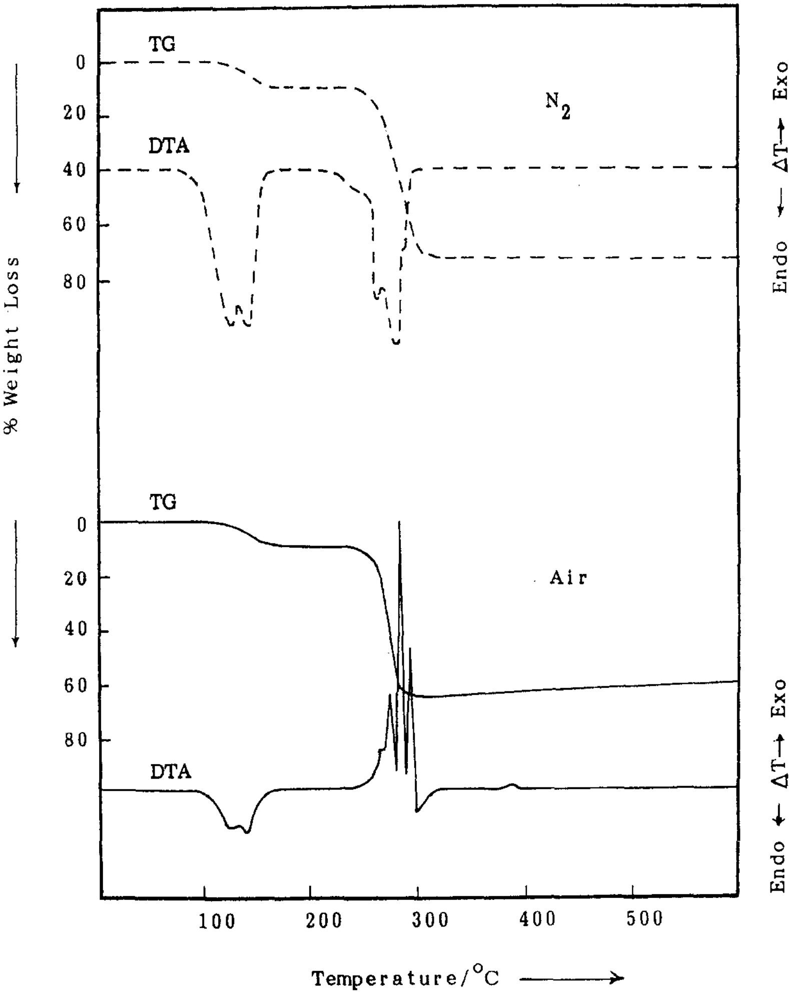


Fig. 2 TG and DTA curves recorded for CuAc at 10 deg·min^{-1} in a dynamic (20 ml·min^{-1}) nitrogen (– – –) and air (—) atmosphere

be attributed to the formation of volatile intermediates during the decomposition. Such finding has been reported by Judd *et al.* [12] who stated that during the decomposition of CuAc in an inert atmosphere, part of the material has been volatilized. Such volatile material was identified as cuprous acetate [12]. It is worth noting that this compound has not been detected in decompositions conducted under an air atmosphere. Furthermore the absence of the process with weight gain in a nitrogen atmosphere, unlike that in an air flow (Fig. 2) may support the assumption of an oxidation process and the nature of the decomposition product in a dynamic air atmosphere.

It is worth noting that the second process (the decomposition of acetate) is endothermic in nitrogen, while it is exothermic in air. This could be explained by assuming that removal of gaseous products by a nitrogen stream would favour the formation of copper metal, whereas in air the presence of atmospheric oxy-

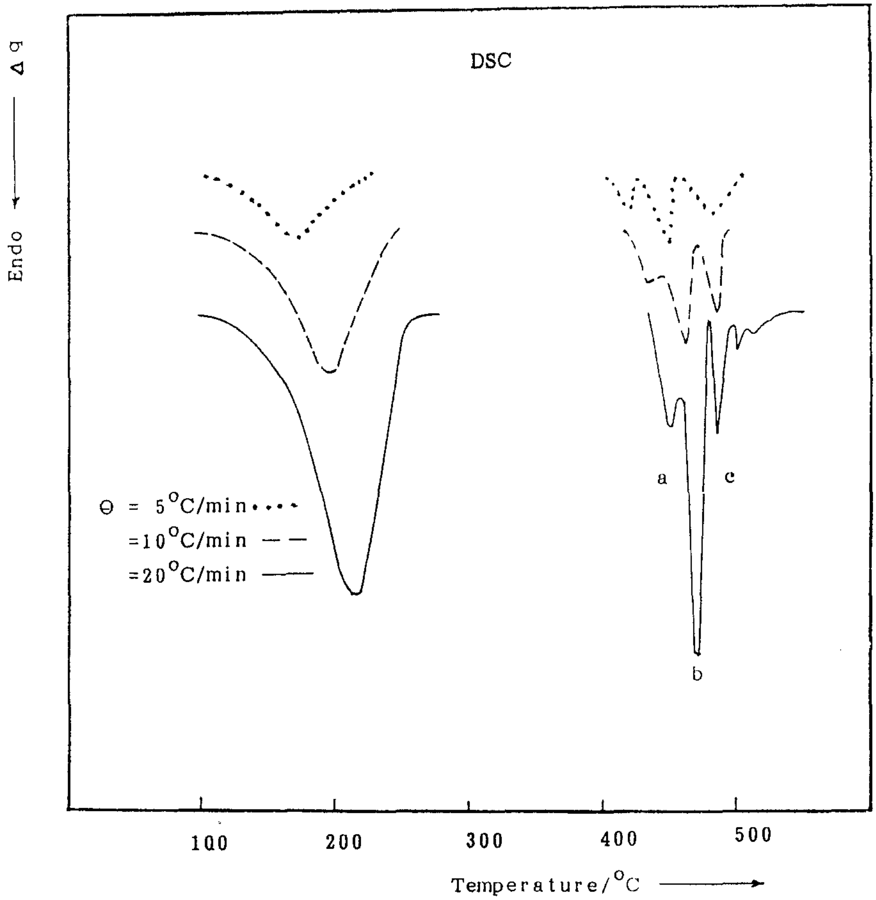


Fig. 3 DSC curve recorded for CuAc at the heating rates (θ) indicated, in a dynamic (20 ml·min^{-1}) nitrogen atmosphere

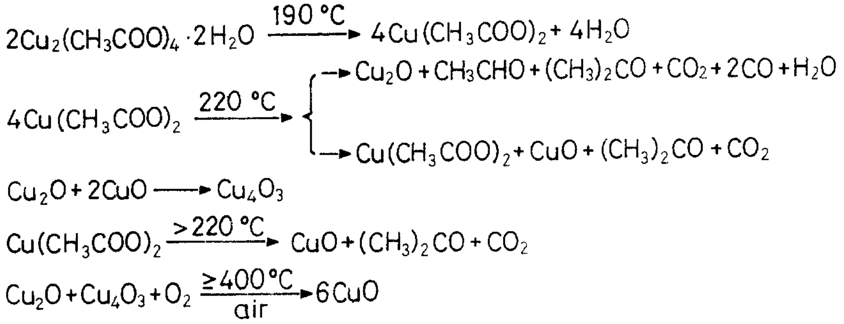
gen would lead to the oxidation of the produced metal, which is an exothermic process. The complicated shape of the DTA peak representing event II in air could be attributed to such oxidative decomposition [13].

Figure 3 shows typical DSC curves obtained by heating CuAc in nitrogen up to 500°C at heating rates of 5, 10 and 20 deg·min^{-1}. The curves show the endothermic peak for the dehydration process in the temperature range 95–189°C. A composite endothermic response is obvious for the decomposition process which could be resolved into three peaks (viz. a, b and c). The curves were analyzed by means of Ozawa's [14] method and the estimated activation energies (ΔE) are listed in Table 2. The Table also contains the corresponding k, ln A, ΔH, C_p and ΔS values for the resolved peaks (viz. I for thermal event I and a, b and c for the DSC response implied in thermal event II).

The ΔE value calculated for the dehydration process (Table 2) was found to be higher than that calculated from TG measurements (Table 1), which may be attributed to the difference in the atmosphere used. The high values of ΔS and the enthalpy change (ΔH) may reveal the formation of a less ordered solid product.

In terms of the DSC responses, thermal event II seems to involve three steps (termed a, b and c). The first two processes, a and b, are slow with activation energies (ΔE) of 182 and 273 kJ·mol^{-1}, respectively (Table 2). The corresponding ΔH and ΔS values are higher for b than for a, which indicates the increase in the disorder as the reaction proceeds in b. The third process c occurs with high ΔE value indicating a largely deceleratory process. The estimated ΔS value is far less than that for a and/or b revealing the decrease in the disorder of the solid product which is expected, since the decomposition under a nitrogen flow would, as stated earlier, favour the formation of solely Cu metal as a final product.

In view of the above-described and discussed results of the thermal events and product analysis, the following reaction sequence may be suggested to describe the decomposition of CuAc in air:



$$2Cu_2(CH_3COO)_4\cdot 2H_2O \xrightarrow{190\ °C} 4Cu(CH_3COO)_2 + 4H_2O$$

$$4Cu(CH_3COO)_2 \xrightarrow{220\ °C} \begin{cases} \rightarrow Cu_2O + CH_3CHO + (CH_3)_2CO + CO_2 + 2CO + H_2O \\ \rightarrow Cu(CH_3COO)_2 + CuO + (CH_3)_2CO + CO_2 \end{cases}$$

$$Cu_2O + 2CuO \longrightarrow Cu_4O_3$$

$$Cu(CH_3COO)_2 \xrightarrow{>220\ °C} CuO + (CH_3)_2CO + CO_2$$

$$Cu_2O + Cu_4O_3 + O_2 \xrightarrow[air]{\geq 400\ °C} 6CuO$$

Acetone was found to be the main product of decomposition of CuAc [13] like other acetates [7]. On the other hand, acetaldehyde, water and carbon monoxide were also reported to be formed during the thermal decomposition of CuAc [11].

Electron microscopic examinations

Examination of the parent copper acetate (CuAc) by scanning electron microscopy revealed a narrow size-range of well formed crystals with flat surfaces containing a small number of pits. Most of the crystals are of a regular habit (Fig. 4a); the pits are superficial.

Heating to 190°C resulted in the appearance of surface wrinkling (Fig. 4b). Such wrinkling was considered as the first structural feature indicative of the onset of the dehydration process. At 240°C, marked changes in the morphology were evident, the most significant features being the appearance of a remarkable roughness of the surface while the crystals remained coherent (Fig. 4c). Such structures of coherent particles and rough surfaces are supposed to crumble readily, which explains the departure of the parent salt from the crystalline structure. At this stage the results of thermal and physicochemical analyses (TG, DTA, IR and XRD) indicated the development of the decomposition process and the appearance of a new solid product which may be CuO in addition to the appearance of a small portion of other solid nuclei which are assumed to be Cu_2O and/or Cu_4O_3. This product exhibited an X-ray diffractogram suggesting an amorphous nature which could account for the electron-micrographs shown in Fig. 4c.

The electron micrograph of the calcination product at 320°C, where the decomposition of acetate has been nearly completed, indicated the occurrence of a progressive modification of the surface, with appearance of smooth circular pits which could be due to a fusion of CuO crystals (Fig. 5a). The Figure indicates the presence of two crystal structures: the dominating one with smooth surfaces could be assigned to CuO, whereas the other one with a froth-like structure could be assumed to be aggregates of Cu_2O and/or Cu_3O_4.

On completion of the decomposition course, the produced CuO (the sole component at 600°C) appeared as aggregates of irregular crystals with rounded edges in a wide size range (Fig. 5b).The surfaces of these crystals were smooth, however the presumed fusion process could accompany the oxidation process of Cu_2O and Cu_4O_3 and then resulted in the appearance of some crystals of slightly protuberated surfaces as seen in Fig. 5c.

Conclusions

The results of the present investigation led to the following conclusions:

– The decomposition of CuAc is greatly affected by the ambient atmosphere.

– Small amounts of Cu_2O and Cu_4O_3 are found during the decomposition course.

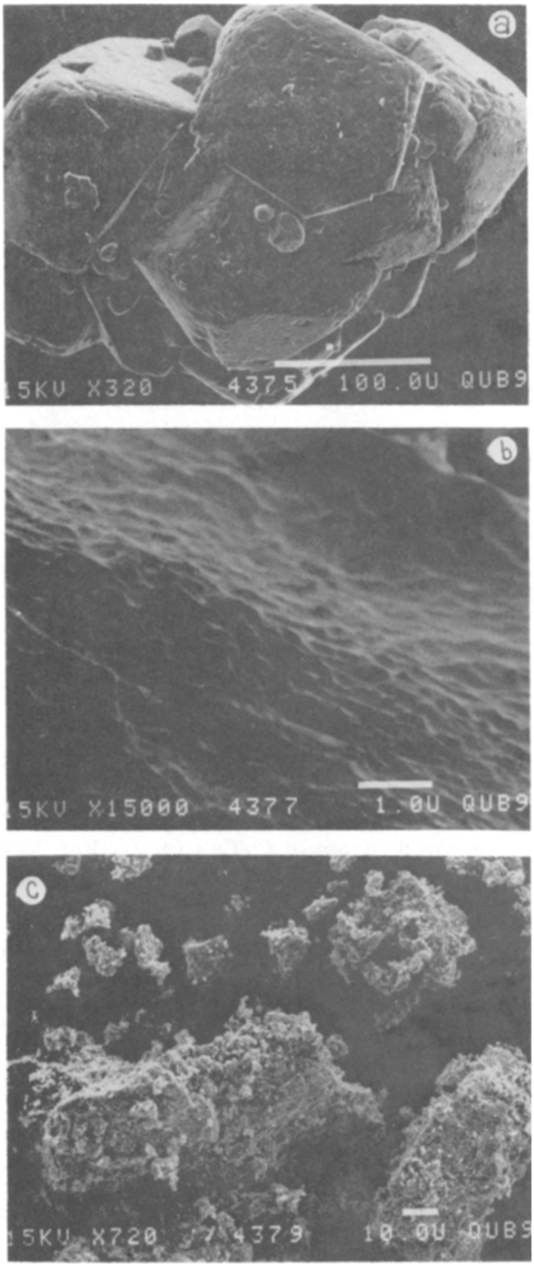


Fig. 4 a) SEM (Scanning Electron Micrograph) of the reactant CuAc, typical crystals which are of almost the same size with pits which are clearly superficial; b) SEM of CuAc heated at 190°C, the onset of dehydration; c) SEM of CuAc calcined at 240°C showing the surface roughness while the crystals remained coherent

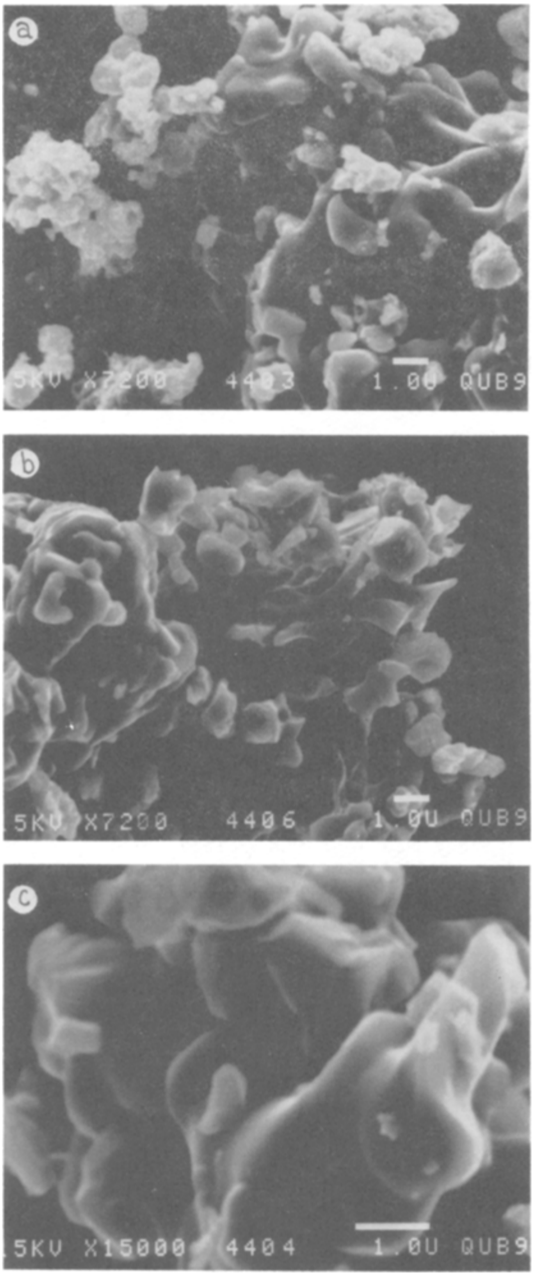


Fig. 5 a) SEM of CuAc calcined at 320°C showing the generation of circular pits on the decomposition product. Two crystal structures are obvious; b and c) SEM of the final product at 600°C consisting of irregular crystals (b) with slightly protuberated surfaces (c)

– Cu_2O and Cu_4O_3 are oxidized in air giving rise to CuO as a final decomposition product, while in nitrogen metallic Cu is the final product.

– The temperature of the last oxidation process in air depends on the heating rate.

– Morphological and structural modifications have been described by the aid of SEM examinations.

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It is a pleasure to thank the Queen's University of Belfast, particularly the staff of the Electron Microscope Unit for assistance in obtaining the electron micrographs. Thanks are also due to the Egyptian Government for the granted fellowship.

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