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THERMAL DECOMPOSITION OF COPPER(II) GLUTARATE TRIHYDRATE. PART I. THE MECHANISM OF DEHYDRATION OF COPPER(II) GLUTARATE TRIHYDRATE

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ABSTRACT

The mechanism of thermal dehydration of copper(II) glutarate trihydrate has been determined from the analysis of the kinetic data for isothermal and non-isothermal dehydration experiments Microscopic investigations for the dehydration process of a single crystal of copper(II) glutarate trihydrate have been carried out to support the mechanism. The simultaneous DTG—DTA—TG curves of the salt are also described.

INTRODUCTION

The mechanism of thermal dehydration and decomposition of metal carboxylates is the subject of much current interest [1—7]. Efforts have been made to determine the mechanism of a thermal process from the determination of kinetic parameters. Thus, in order to study the mechanism, equations conforming to various mechanisms are tried on kinetic data. However, obedience to a particular kinetic equation is not always sufficient to identify the mechanism [1,8]. Recently, Criado and Morales [9], Dharwadkar et al. [10] and others [11—13] have shown that non-isothermal kinetic equations alone do not determine the mechanism of a decomposition process unless the mechanism is also supported by isothermal analysis.

In these investigations, their technique for determining the mechanism is applied. However, it becomes very difficult to determine the mechanism in certain border-line cases when the various equations hold equally well both to the isothermal and non-isothermal data. In such cases, therefore, the mechanism may be further supported from microscopic studies of the reacting substances.

EXPERIMENTAL

Copper(II) glutarate trihydrate was prepared by a previously described method [14]. Basic copper carbonate (BDH) was added to a gently warmed, ~333—343 K, glutaric acid (BDH) (one part) solution in water (50 parts) until effervescence ceased. The solution was filtered to remove excess solid carbonate. The resulting clear solution was concentrated to small bulk and set aside. The blue crystalline product formed on standing was filtered off, washed with water, recrystallized and finally air-dried. The results of elemental analysis of the trihydrate were: found Cu 25.2, C 23.9 and H 4.5%; calculated Cu 25.6, C 24.2 and H 4.8%.

For isothermal dehydration, a known amount of the sample was taken and the reactions were carried out in a manually operated thermobalance [15]. Simultaneous DTG—DTA—TG curves were recorded by means of a Paulik—Paulik—Erdey MOM derivatograph (Hungary). Reflectance spectra of hydrated and partially dehydrated species were measured on a spectrophotometer VSU-2P in the range 1000—220 μm using MgO as the reference. A polarizing microscope was used for microscopic studies of the crystals.

RESULTS AND DISCUSSION

Reflectance spectra

The appearance of a new species upon dehydration is revealed from the difference in the positions and absorbance of the two bands in the reflectance spectra. The reflectance spectra (Fig. 1) of copper(II) glutarate trihydrate and its dehydration derivative display absorption bands around 475—400 and 525—400 μm, respectively. It was also noted that the absorbance of monohydrate was lower in the near-IR region and higher in the UV region than that of trihydrate.

Kinetics of dehydration

The dehydration of copper(II) glutarate trihydrate occurs in two stages, i.e. nucleation and growth.

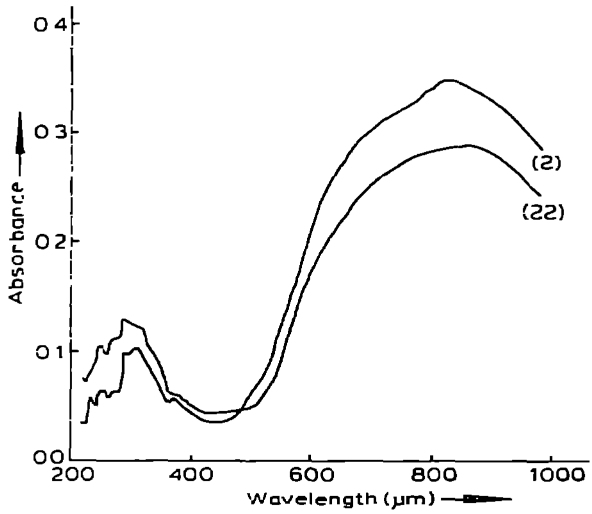

Fig. 1. Reflectance spectra of (i) copper(II) glutarate trihydrate and (ii) copper(II) glutarate monohydrate.

Nucleation

On heating the crystals at 423 K in an oven at a constant temperature and observing under a polarizing microscope at different intervals of time, there appeared certain specks on the large faces and inside the crystal but their growth was extremely slow, whereas the nuclei formed on the corners and edges of smaller faces quickly grew inwards from all the sides as shown in Fig. 2. These observations show that the process of dehydration follows a phase-boundary controlled mechanism. The colour of the product nuclei was dark blue. The growth front was initially macroscopically non-faceted and the product was opaque. Although nucleation occurred at a high temperature (423 K), after 2—3 min the growth continued even as the temperature decreased.

Isothermal dehydration

The isothermal dehydration of copper(II) glutarate trihydrate was studied at 393—423 K. The weight loss at 423 K (~0.0148 g against the expected weight loss of 0.0145 g) corresponds to the formation of copper(II) glutarate monohydrate. The kinetic data were analyzed for the Erofeev—Avrami mechanism [16,17], i.e.

$$[-\log(1-\alpha)]^{1/n} = Kt \qquad (1)$$

and the phase-boundary controlled mechanism, i.e.

$$[1-(1-\alpha)^{1/n}] = K't \qquad (2)$$

With eqn. (1) the best fit was for $n = 3$ followed by $n = 2$ (Figs. 3 and 4). The corresponding apparent activation energies were 46.4 and 42.6 kJ mole^{-1}, respectively. With eqn. (2) (Figs. 5 and 6) for $n = 3$ and $n = 2$ the apparent activation energies were 40.5 and 43.6 kJ mole^{-1}, respectively.

Thermoanalytical studies

Figure 7 gives the simultaneous DTG—DTA—TG curves of copper(II) glutarate trihydrate at the heating rate of 5°C min^{-1}.

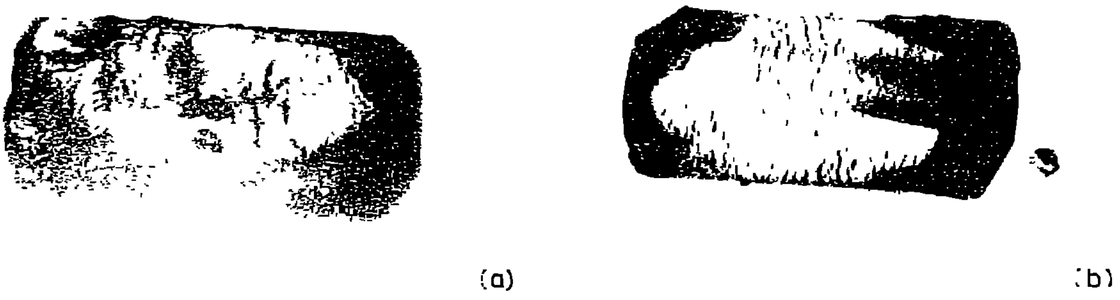

Fig. 2. Photomicrographs of a single crystal of copper(II) glutarate trihydrate.

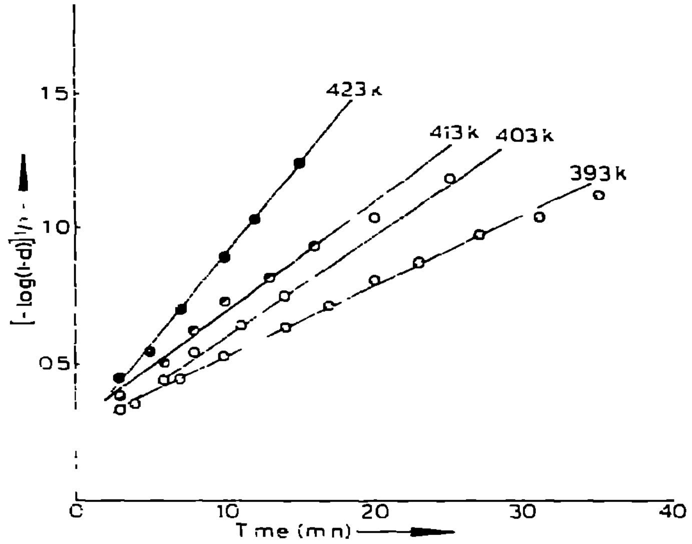

Fig. 3. Plots of $[-\log(1-\alpha)]^{1/3}$ vs time for the isothermal dehydration of copper(II) glutarate trihydrate.

All the thermal curves are accompained by weight losses. The decomposition consists of three steps, the probable reactions being dehydration to give a monohydrate, decomposition of the monohydrate to give copper(II) oxalate as an intermediate, and a two-step decomposition of the oxalate to yield a mixture of CuO and Cu. The nature of these three main events remains uneffected by the change in heating rate. DTA shows that dehydration of trihydrate is an endothermic process and takes place from 403 to 493 K. The initial weight loss temperature, T_i, and the DTG peak tempera-

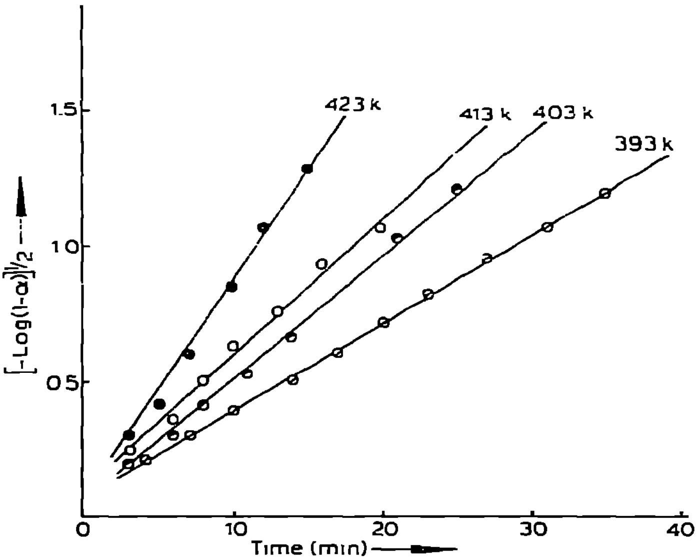

Fig. 4. Plots of $[-\log(1-\alpha)]^{1/2}$ vs. time for the isothermal dehydration of copper(II) glutarate trihydrate.

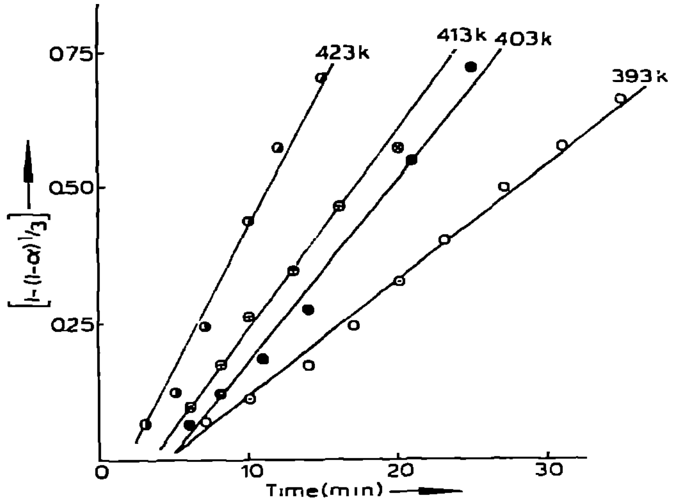

Fig. 5. Plots of $[1-(1-\alpha)^{1/3}]$ vs. time for the isothermal dehydration of copper(II) glutarate trihydrate.

ture, T_m, for the loss of two molecules of water are 403 and 458 K, respectively. These are relatively higher than ordinary values for the elimination of crystalline water and this compared with those given for malonates and succinates of metals [3,18], shows that all the water molecules are coordinated. The TG curve weight loss in the first stage is 0.0291 g; the calculated value for monohydrate is 0.030 g. The decomposition of monohydrate is a complicated multi-step process. The first step of decomposition occurs

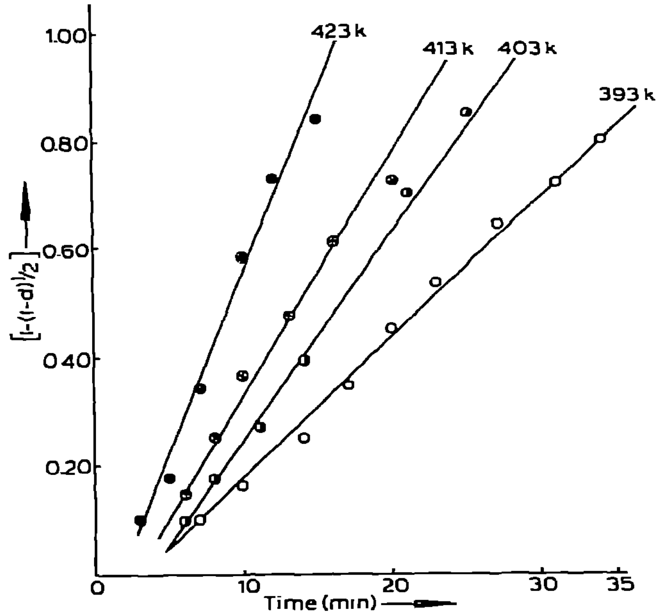

Fig. 6. Plots of $[1-(1-\alpha)^{1/2}]$ vs. time for the isothermal dehydration of copper(II) glutarate trihydrate.

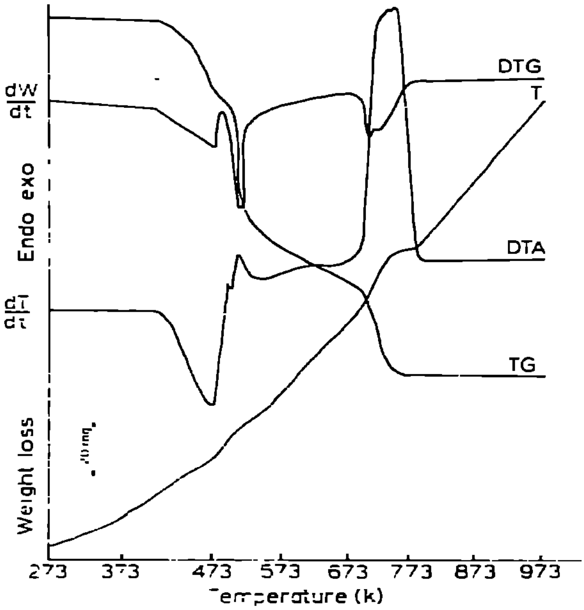

Fig. 7. Simultaneous DTG—DTA—TG curves of copper(II) glutarate trihydrate at a heating rate of 5°C min^{-1}.

at 513 K. and has a distinct small exo peak. There is no definite arrest in the TG curve, although there is a change in the slope of the curve at this point. The reaction occurs with a weight loss of 0.0786 g; the expected loss is 0.0775 g for oxalate, corresponding to the DTG peak at 508 K. The final step in DTA is an exothermic process with a dual character between 673 and 783 K. The corresponding DTG also shows a dual character, thereby indicating that the decomposition of oxalate to final product involves two steps. The loss in weight from the TG curve, 0.104 g, where the nature of the slope shows a downward thrust at 693 K, is in agreement with the expected value of 0.101 g for $CuCO_3$ formation. The TG curve, however, does not show an arrest at this temperature, indicating that the species at this stage is unstable and hence not separable. This carbonate intermediate decomposes further giving a mixture of CuO and Cu. The composition of the final product is confirmed by the X-ray diffraction pattern of the black residue from the reaction.

Mechanism of dehydration

The determination of the mechanism of a decomposition process from the analysis of the TG curves or isothermal dehydration studies is a very difficult problem. First. it must be established whether a given process is phase-boundary or nucleation-growth controlled, or some other mechanism applies. Several workers have treated the experimentally recorded TG curves of the decomposition reactions of standard or known substances, such as $CdCO_3$ or $CaC_2O_4 \cdot H_2O$, to extract kinetic parameters [10,19]. In the present work, the methods of kinetic analysis have been applied to study the mode of dehydration of copper(II) glutarate trihydrate to monohydrate. The non-isothermal data gave different orders for different heating rates and with different kinetic equations. The values of reaction order (n) from the Horowitz—Metzger equation [20] at the heating rates of 5 and 10°C min^{-1} were less than 0.5

$$C_s = (n)^{1/1-n} = \frac{W_s - W_f}{W_0 - W_f} \tag{3}$$

where W_s = weight fraction at T_s, i.e. the DTG peak temperature, W_0 and W_f are the initial and the final weights of the substance.

The Freeman—Carroll equation [21] gave the order to be 0.25 and 0.6 for the heating rates of 5 and 10°C min^{-1}, respectively

$$\frac{(-E/2.3\,\mathrm{R})\Delta(1/T)}{\Delta\log(W - W_f)} = -n + \frac{\Delta\log(\mathrm{d}W/\mathrm{d}t)}{\Delta\log(W - W_f)} \tag{4}$$

where W = sample weight at temperature T. The apparent activation energies from this equation are 60.0 and 76.6 kJ mole^{-1}, respectively.

The Brochardt and Daniels equation [22] was tried, assuming $g = n$. for different closely varying values of n

$$\frac{\mathrm{d}W/\mathrm{d}t}{M^{1-g}(W_0 - W_t)} = z\exp(E/RT) \tag{5}$$

where M = molecular weight of the substance, W_0 and W_t are the total weight loss and weight loss up to time t, respectively, and g = the geometrical factor. The best fit was for $n = 0.75$, followed by $n = 0.67$ (contracting volume equation) and $n = 0.5$ (contracting area equation).

The Coats—Redfern equation [23] has also been applied to deduce kinetic parameters

$$\log\frac{g(\alpha)}{T^2} = -\frac{E}{2.3RT} + \log\frac{ZR}{\beta E}\ 1 - \frac{2RT}{E} \tag{6}$$

with

$$g(\alpha) = [-\log(1-\alpha)]^{1/n} \text{ (Erofeev—Avrami mechanism)} \tag{a}$$

and

$$g(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n} \text{ (phase-boundary mechanism)} \tag{b}$$

It becomes very difficult to distinguish between the plots (Figs. 8 and 9) having values of $n = 2$ and 3 (for $n = 1$ the plot is not good). The apparent energies of activation found from eqn. (6a) (Fig. 8) with values of $n = 2$ and 3 are 95.4 and 31.9 kJ mole^{-1}, respectively, and for eqn. (6b) (Fig. 9) with values of $n = 0.5$ and 0.67 are 86.6 and 102.2 kJ mole^{-1}, respectively.

The different values for apparent activation energies with different equations do not agree with the theoretical prediction of Criado and Morales [9], but are very well in accord with the recent observations of Fong and Chen [11], Dharwadkar et al. [10], Šesták et al. [12] and Ozawa [13].

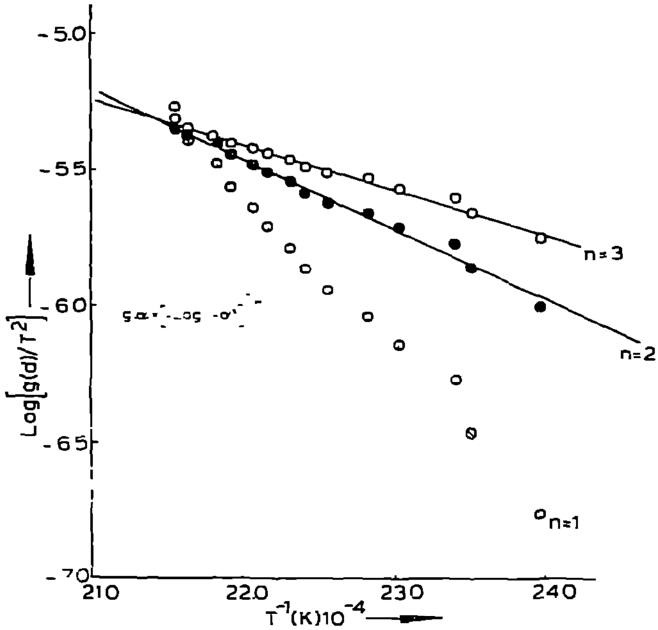

Fig 8. Plots of $\log[g(\alpha)/T^2]$ vs. T^{-1} for the dehydration of copper(II) glutarate trihydrate.

Since the determination of kinetic parameters from the TG curve or even from isothermal studies should always be done very carefully, large variations occur in the literature for different compounds. It is therefore concluded that before estimating the kinetic parameters the mechanism should be established by observing the solid specimen through a microscope or otherwise. We support that, in deciding the mechanism of the decomposi-

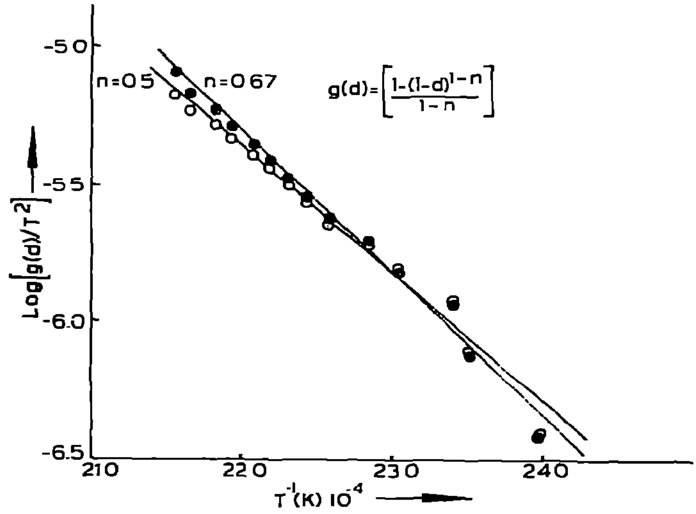

Fig. 9. Plots of $\log[g(\alpha)/T^2]$ vs. T^{-1} for the dehydration of copper(II) glutarate trihydrate.