Thermochimica Acta, 30 (1979) 339–350

THE THERMAL DECOMPOSITION OF METAL FORMATES. II. SOLID STATE THERMAL DECOMPOSITION STUDIES ON MAGNESIUM FORMATE DIHYDRATE

D. DOLLIMORE
The University of Salford, Salford M53WT (Gt. Britain)
J. P. GUPTA AND D. V. NOWELL
School of Natural Sciences, The Hatfield Polytechnic, Hatfield, Hertfordshire AL10 9AB (Gt. Britain)
(Received 27 June 1978)

ABSTRACT

Magnesium formate dihydrate has been synthesized by the action of formic acid on anhydrous magnesium oxide. This product analysed as $Mg(COOH)_2 \cdot 2H_2O$. Its mode of thermal decomposition has been studied by thermal methods of analysis including simultaneous DTA/mass spectrometry. Nitrogen adsorption surface area of the solid products at various stages of its decomposition have been obtained. X-Ray diffraction and scanning electron micrographs have also been used to interpret the results. The decomposition of magnesium formate took place in three stages, which includes a phase change, at 265 °C. The endotherm at 430 °C changed to an exotherm in the presence of air; it corresponded to the decomposition of a new anhydrous phase of magnesium formate. The effect of the sample holder and changing atmospheres on the DSC analysis has been investigated. A scheme is presented for the thermal decomposition.

INTRODUCTION

Recently, we have been concerned with the development of various methods for studying the solid state thermal decomposition of various salts[1–3]. Considerable interest exists in the study of changes which occur in solid inorganic compounds as they are uniformly heated. By studying such changes, information can be gained concerning the mode of decomposition, phase changes, energy of transition, heat of decomposition and also novel methods of preparing compounds.

In spite of its simplicity, very little is reported about magnesium formate. A conclusion that magnesium formate decomposed soon after dehydration is reported by Zeppletal et al.[4] on the basis of TG and DTA studies. They have also investigated Cu, Ni, Co, Zn, Cd, Mn, Ca, Sr and Ba formates. Rienacker and Toursel[5] have concluded that the decomposition of magnesium formate resulted in the evolution of CO, CO_2 and H_2 leaving a product of magnesium oxide. They have also studied its decomposition when mixed with Ni, Co and Cu formates. However, features of the decomposition of magnesium formate remain incompletely understood. Barium and calcium formates have been studied extensively as far as their thermal decomposition is concerned[6–10]. Alkali metal formates have also been investigated by Meisel et al.[11].

In this study, we have therefore examined the mode of thermal decomposition of magnesium formate by TG, DTG, DSC, DTA together with simultaneous DTA/mass spectrometry techniques. The results have also been supported by X-ray diffraction, and electron microscopy studies together with nitrogen adsorption surface area determinations.

EXPERIMENTAL

Reagents

Analar grade magnesium oxide was used and the other chemicals were of laboratory reagent grade.

Synthesis of magnesium formate

To 50 cm^3 of formic acid (90% w/w) was added 5 g magnesium oxide. A vigorous reaction took place resulting in a turbid reaction mixture. This solution was boiled until a thick precipitate formed. After cooling and washing, first with cold formic acid followed by dry ether, the product was dried at 40°C under vacuum.

Analytical procedure

A hydrated sample was dried at 260°C for 1 h before analysis. Magnesium was determined volumetrically by EDTA using Eriochrome Black T and samples were submitted for carbon and hydrogen analysis.

Thermal analysis

(a) DSC and TG analyses were carried out using a Dupont 900 thermal analyser together with a 950 TG Cell in an atmosphere of air, nitrogen and helium (400 cm^3 min^{-1}). The heating rate was 5°C min^{-1} throughout the experiments. DTG was obtained from the TG curve.

(b) DTA/MS studies were carried out using a Micromass Quadrupole (Q801) mass spectrometer linked to a Stanton 501 B DTA unit by a heated capillary. The MS inlet and capillary were maintained at 150°C. Residual water was minimised by degassing the MS traps and by heating the DTA cell to approximately 300°C and allowing to cool under a 400 cm^3 min^{-1} flow of dry helium. A 25–30 mg sample was placed in the sample holder with an equal weight of reference material (alumina) in the reference. Aluminium or copper pans were used according to the experiment. The MS was set to scan the range 10–50 (*m*/*e*) units at a scan speed of 0.03 sec. The trace was triggered by the shutter of a camera mounted on a remote oscilloscope. During the experiment, a helium flow rate 100 cm^3 min^{-1} and a heating rate of

10 °C min^{-1} were used. The mass spectrum was monitored by taking photographs every 30 sec.

X-Ray diffraction and infrared studies

The X-ray diffraction patterns of samples, heated at various temperatures, were taken by a Philips X-ray unit using Nickel filtered Cu K_α radiation.

Surface area determination

The nitrogen adsorption surface area of the samples heated at various temperatures was determined by a single point apparatus[12]. The results were evaluated using a computer programme.

Scanning electron microscopy

Electron micrographs of the samples were taken by a Cambridge stereoscan microscope interfaced with an X-ray microprobe analysis unit.

RESULTS AND DISCUSSION

The chemical analysis of synthetic magnesium formate is presented in Table 1; it is in good agreement with the values required by theory.

TABLE 1

CHEMICAL ANALYSIS OF ANHYDROUS MAGNESIUM FORMATE

Carbon (%)		*Hydrogen (%)*		*Magnesium (%)*	
Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
21.01	20.92	1.75	1.74	21.01	20.67

The thermogravimetric analysis of magnesium formate in a nitrogen atmosphere are given in Fig. 1. The effect of different heating rates from 0.2 to 10 °C min^{-1} produced identical results. The DTG curve and DSC (in nitrogen and in air) curves are also presented in Fig. 1. It can be seen from the TG curve that a weight loss beginning at 160–220 °C corresponded to the removal of the water molecules contained in this salt. The DSC and DTA curves also produced broad endothermic peaks, as being the dehydration peak, in this temperature range. An exothermic peak at 265 °C was seen in the DSC/DTA curves while there was no indication of weight loss or the appearance of a peak in TG and DSC, respectively. This peak in DTA/DSC was unaltered even when the atmosphere of flowing gas was changed. Also, this peak did not change to an endothermic peak upon cooling. The effect of holding time at 200 °C shows (see Fig. 2) that this peak disappeared after holding for 3 h. Scholten et al.[13] have indicated that 5% of a basic magnesium formate salt decomposed between 214 and 255 °C. However, we were unable to detect any volatile product under

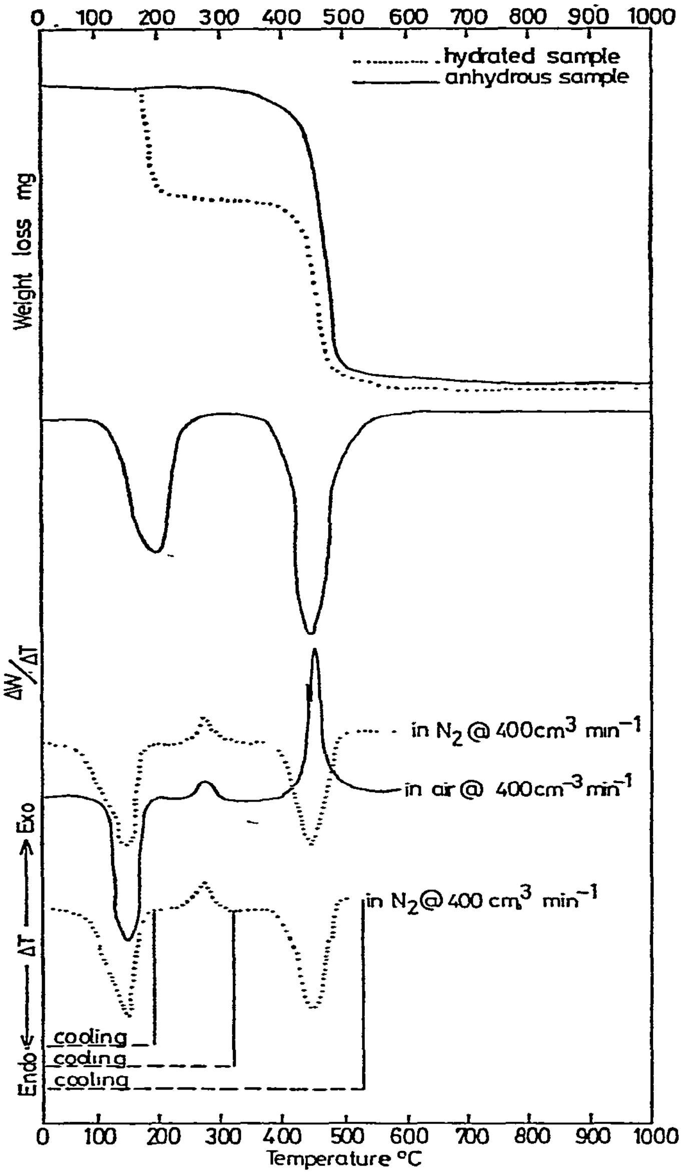


Fig. 1. TG, DTG and DSC of magnesium formate dihydrate.

this temperature range in the mass spectroscopic scans (see Fig. 6). Our observations seem to indicate that the anhydrous salt, immediately after dehydration, was poorly crystalline and recrystallized at 265 °C. To confirm this, X-ray diffraction and scanning electron microscope studies were carried out. Figure 3 shows the comparative X-ray diffraction spectra of magnesium formate heated at various temperatures. The dihydrate sample was very crystalline and the anhydrous sample lost its crystallinity while the sample heated to 265 °C recrystallized again. Plates (a)–(d) (Fig. 4) of the scanning electron micrographs followed X-ray diffraction results. The nitrogen adsorption surface area of these samples was also determined. The results are tabulated in Table 2 and show that the surface area of the dihydrate was very low. It increased

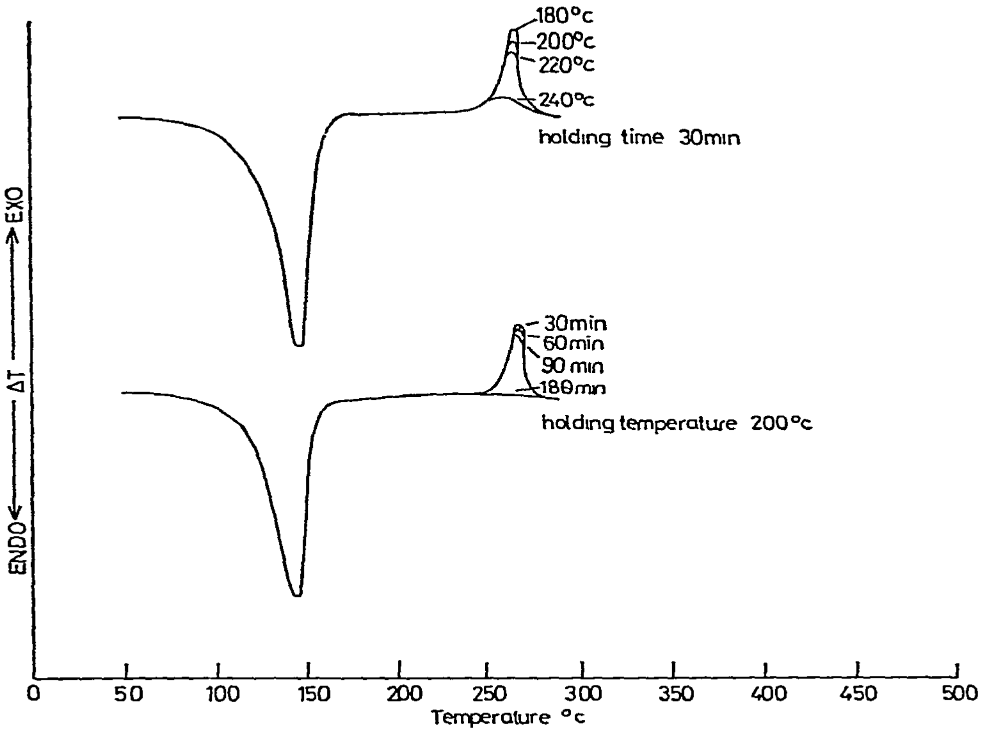


Fig. 2. Effect of holding time and holding temperature on the exotherm (265 °C) in the DSC curve of magnesium formate dihydrate.

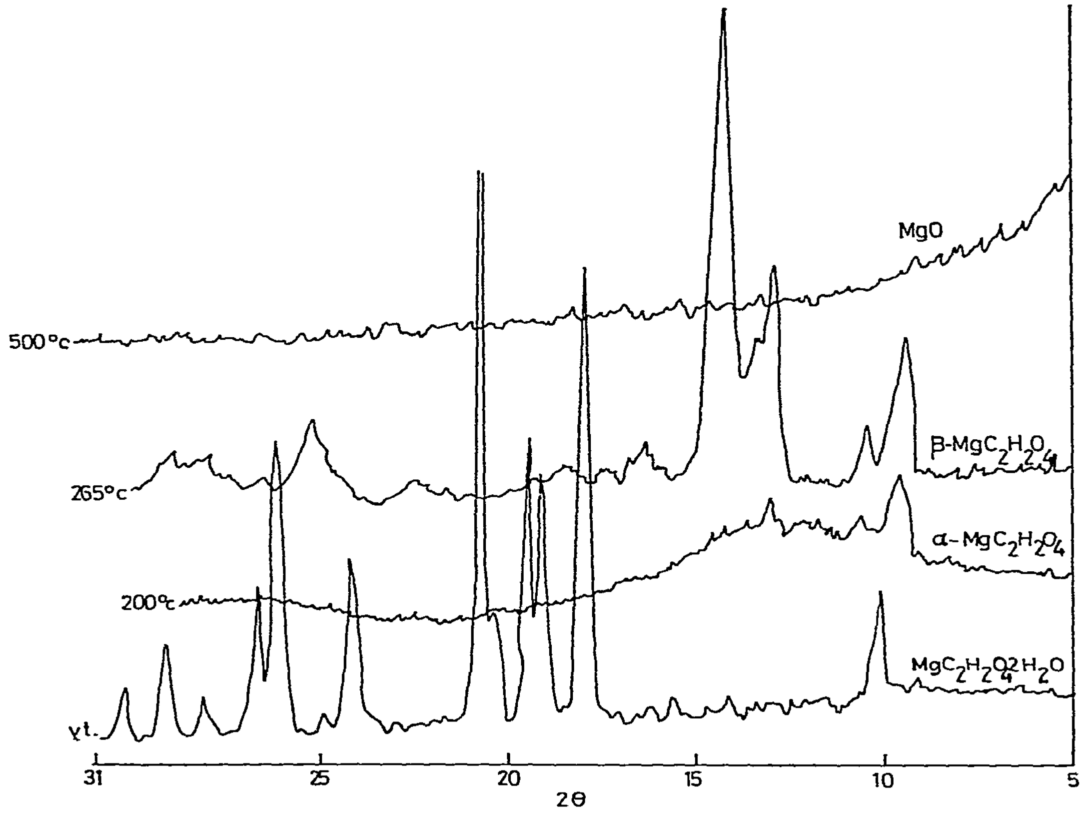
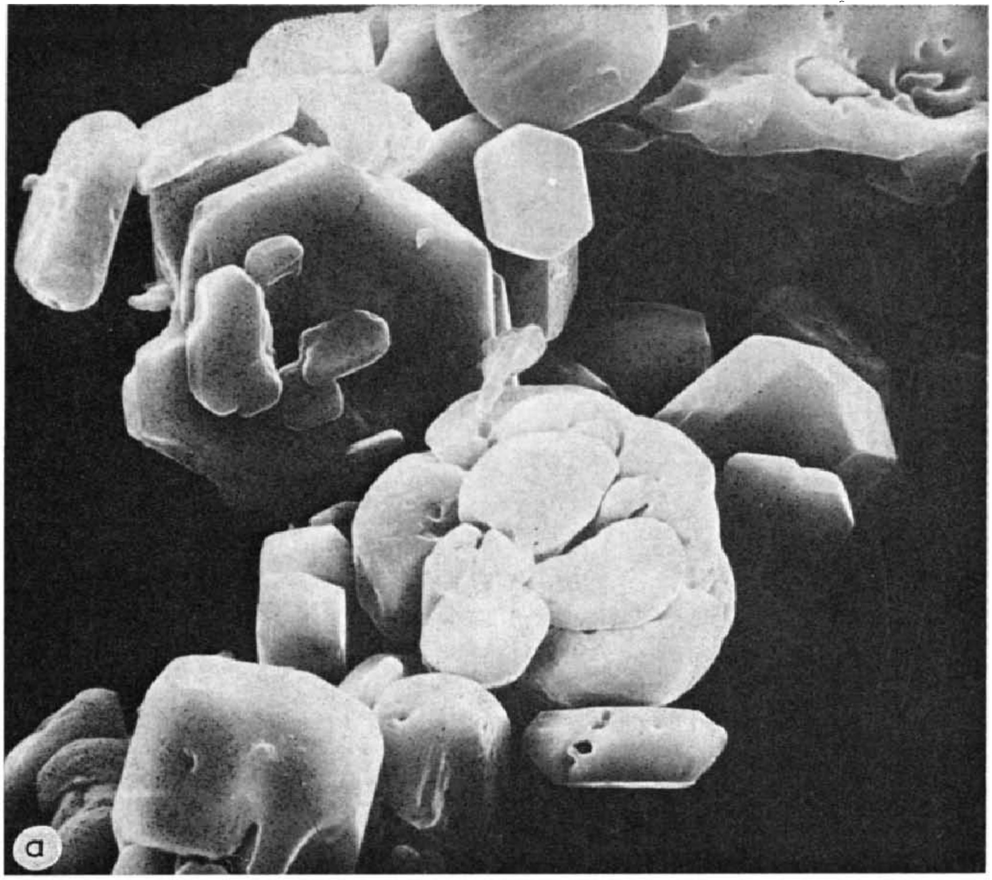


Fig. 3. X-Ray diffraction patterns of magnesium formate dihydrate at various temperatures.


a


b

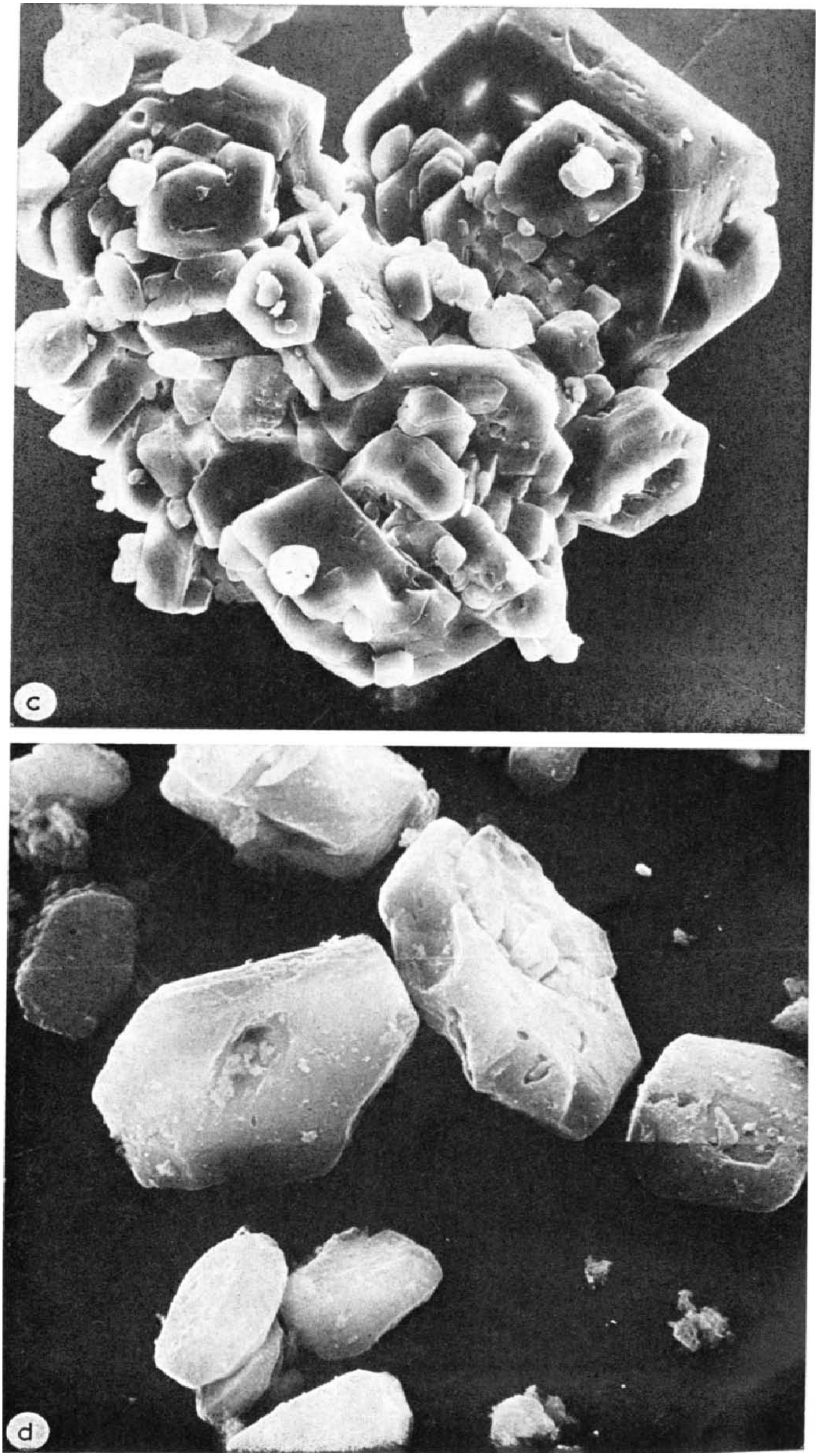


Fig. 4. Scanning electron micrographs of magnesium formate at various temperatures. (a) Magnesium formate dihydrate, × 1000; (b) magnesium formate heated at 200 °C, × 1000; (c) magnesium formate heated at 265 °C, × 500; (d) magnesium formate heated at 500 °C (i.e. MgO), × 1000.

TABLE 2

SURFACE AREA OF MAGNESIUM FORMATE AT VARIOUS TEMPERATURES

Possible compound	*Temperature (°C)*	*Surface area ($m^2 g^{-1}$)*
$MgC_2H_2O_4 \cdot 2H_2O$	105	1
$MgC_2H_2O_4$ (α)	200	6
$MgC_2H_2O_4$ (β)	265	1
MgO	500	18.5

upon dehydration and decreased again due to recrystallization at 265 °C, confirming X-ray and electron microscope studies.

The TG curve also suggests that the decomposition of crystalline anhydrous magnesium formate (β-$MgC_2H_2O_4$) began at 360 °C and finished at 520 °C. The DSC curve also records the decomposition temperature as 452 °C. The endotherm produced in DSC/DTA at the decomposition temperature in the atmosphere of nitrogen or helium changed to an exotherm in the oxygen or air atmospheres indicating the oxidation reaction. The weight loss corresponded to either the removal of 2 moles of CO and 1 mole of H_2O or 1 mole each of CO, CO_2 and H_2, leaving the material as MgO. The X-ray diffraction studies and the chemical analysis showed that the final decomposition residue of the substance was amorphous magnesium oxide. The

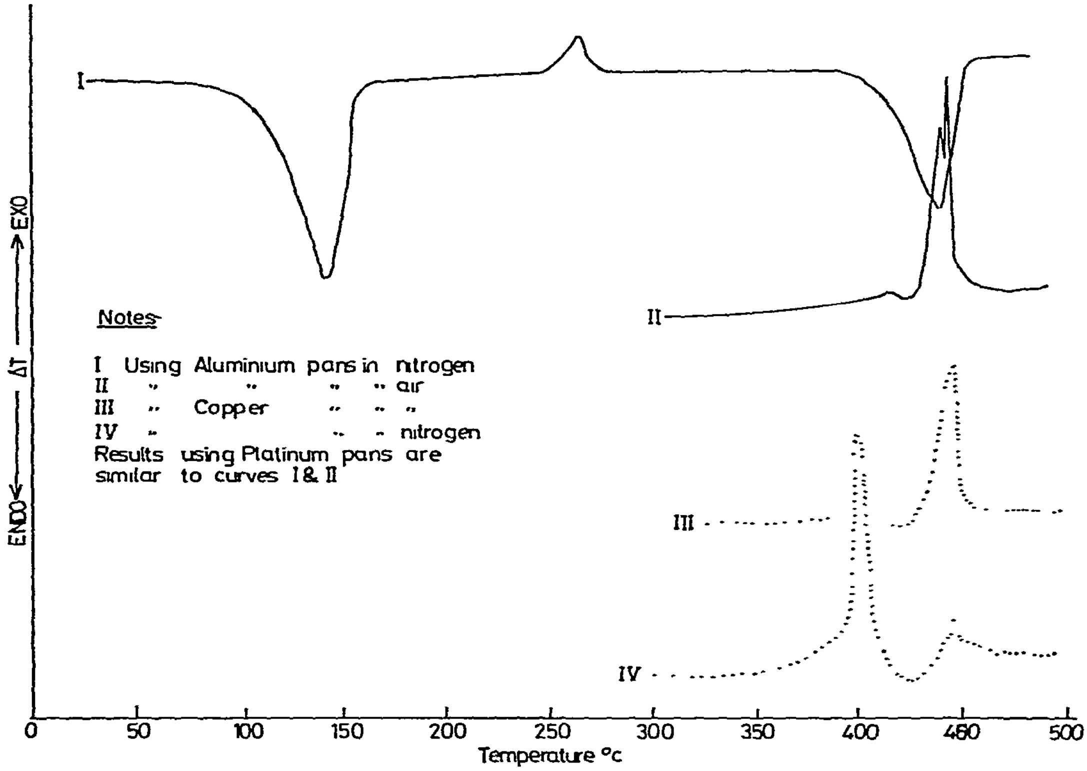


Fig. 5. Effect of sample holders in the thermal decomposition of magnesium formate dihydrate.

final product was shown by chemical analysis to contain carbon. The presence of carbon is most likely due to the chemisorption of CO and CO_2 on to the MgO. The effect of the sample holders on the decomposition of this substance was studied. Aluminium and platinum holders gave identical results. Copper holders in the atmosphere of helium also produced an endotherm at the decomposition temperature (see Fig. 5). Careful inspection of the DSC curve when copper sample holders were used with nitrogen as carrier gas showed that, not only did the decomposition peak change (exotherm from endotherm), but also the peak temperature shifted to a lower value. This may be due to the fact that, in the cases of curves II and III of Fig. 5, there is a slow build up of magnesium oxide. Perhaps the sintering of magnesium oxide and also the influence of foreign carbon reduced the decomposition activity as has been found in the thermal decomposition processes of zinc and nickel oxalates[14]. The effect of copper, silver, nickel and gold powder, when mixed with

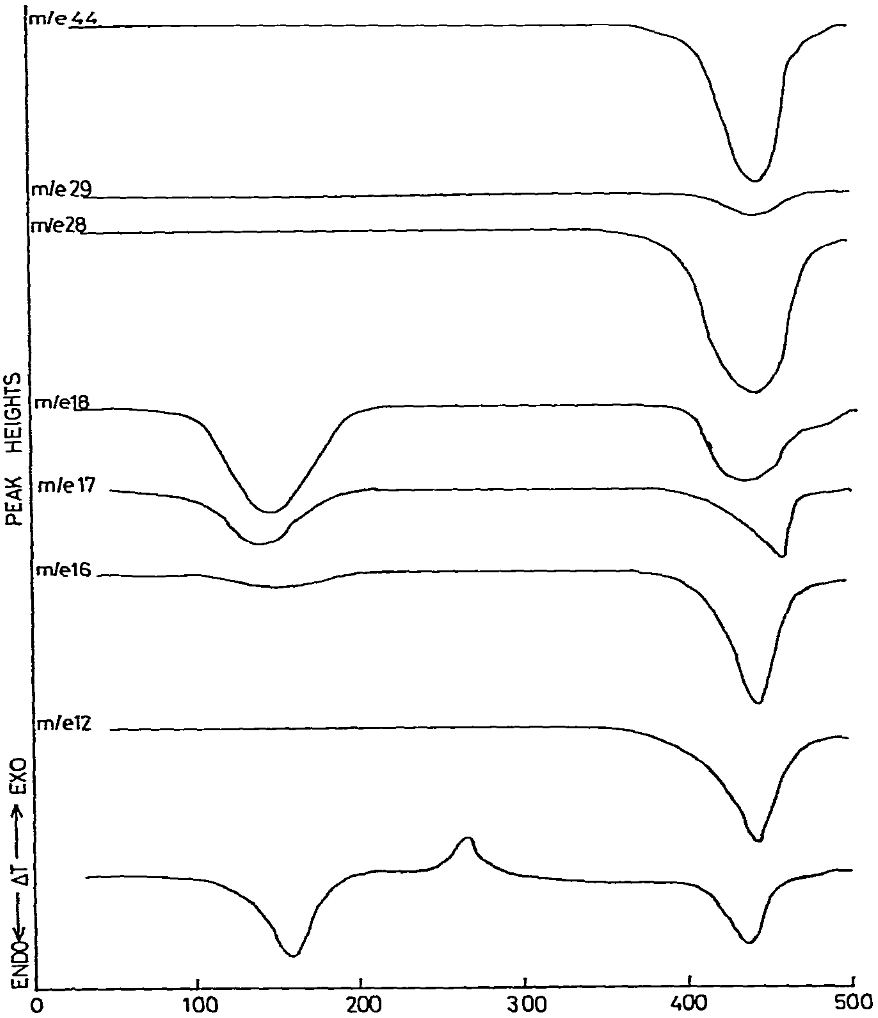


Fig. 6. Simultaneous DTA/MS scan of the thermal decomposition of magnesium formate using an aluminium sample holder.

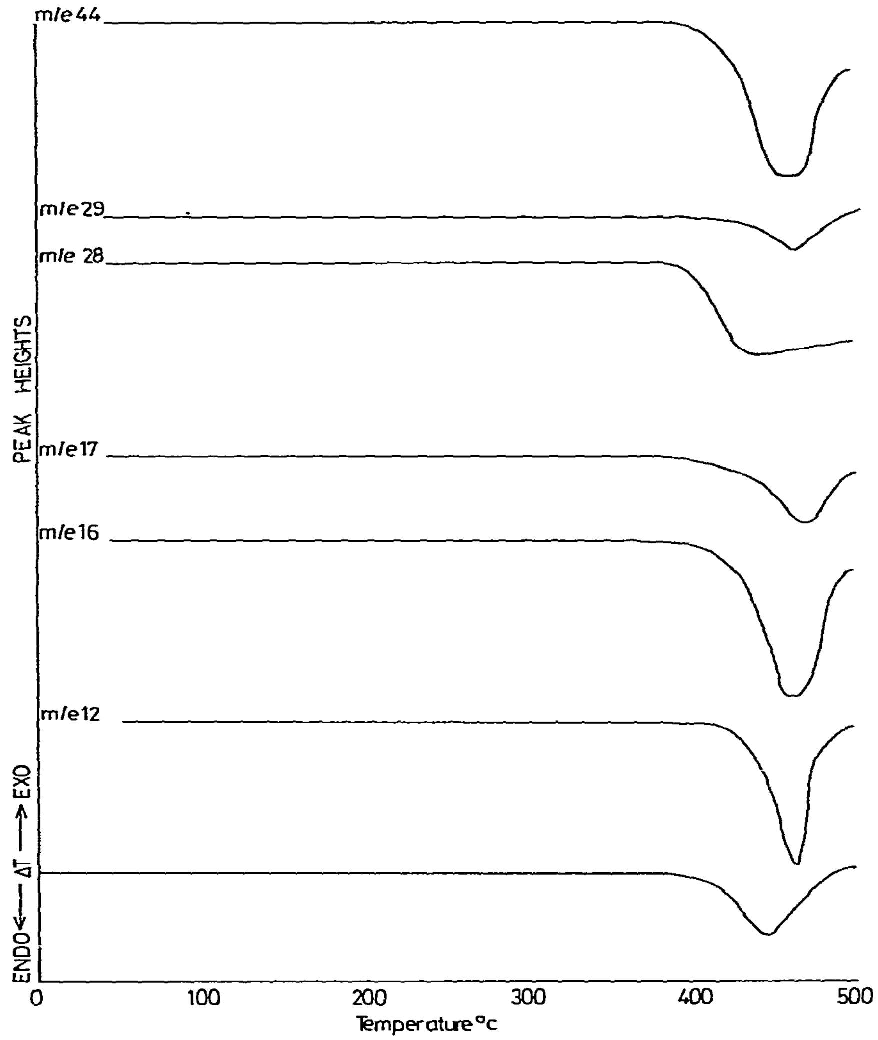


Fig. 7. Simultaneous DTA/MS scan of the thermal decomposition of anhydrous magnesium formate using a copper sample holder.

magnesium formate, produced identical results to those shown in Fig. 1 using aluminium samples holders.

DTA/MS results on the decomposition of this compound are shown in Figs. 6 and 7. It can be seen from Fig. 6 that, at the first stage of decomposition, reaction peaks due to (*m/e*) 16, 17 and 18 were seen, which confirm our TG results (removal of interstitial water molecules). The endotherm produced at 452°C shows (*m/e*) 12, 16, 17, 18, 28, 29 and 44 in the MS scan. These masses seem to indicate the presence of carbon (*m/e* 12), oxygen (*m/e* 16; from the cracking of CO_2), water (*m/e* 16, 17 and 18), carbon monoxide (*m/e* 28), formaldehyde (*m/e* 29), and carbon dioxide (*m/e* 44). When the sample was subjected to MS/DTA analysis using a copper sample holder, the spectrum remained almost the same as with an aluminium sample holder. However, peak (*m/e* 18) was not identified in this case (Fig. 7). It was thought that the decomposition products using copper samples holders may be different. The

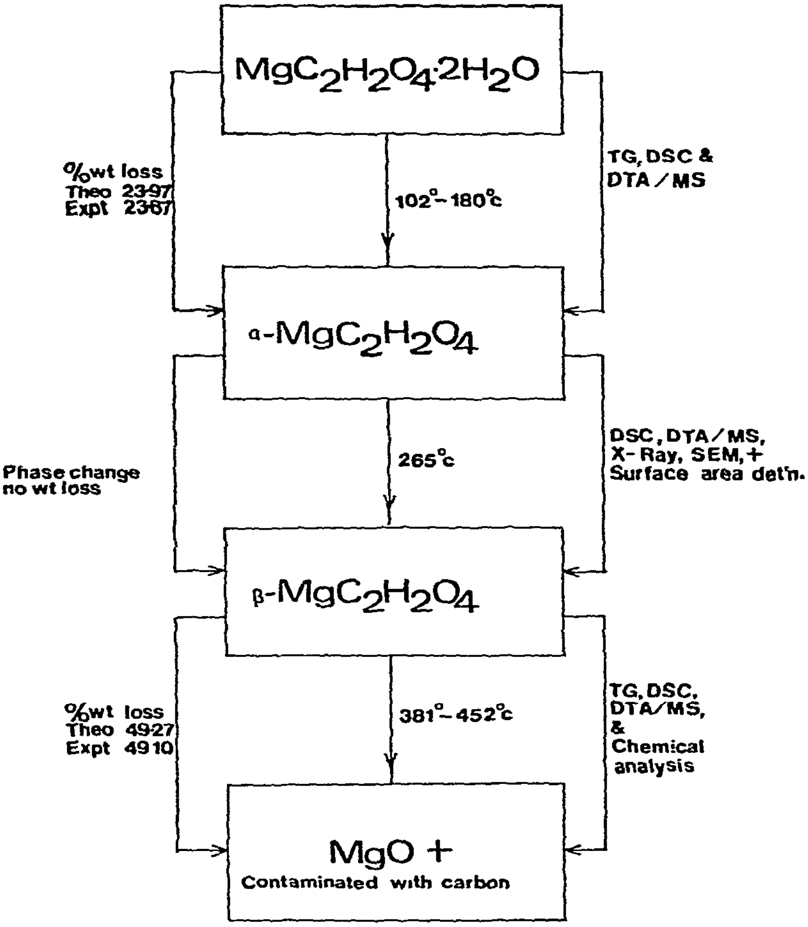


Fig. 8. Schematic diagram of the thermal decomposition of magnesium formate dihydrate.

experiment was also repeated in a nitrogen atmosphere to establish the presence of any hydrogen in the MS spectrum. The spectrum did not confirm hydrogen. These results indicate that magnesium formate does not undergo decomposition soon after dehydration as found by Zepletal et al.[4], but an irreversible phase change takes place at about 265 °C. Ca, Sr and Ba formates do not follow this trend[15]. Figures 6 and 7 indicate that the production of formaldehyde did not take place immediately decomposition began. This could proceed by the removal of water gas which produces formaldehyde in the presence of MgO as catalyst. The production of CO and H_2O commences at approximately 400 °C from the MS results. The following reactions on the decomposition of this salt can be suggested on the basis of above studies.

$$\mathrm{Mg(COOH)_2 \cdot 2H_2O} \xrightarrow[\text{endo}]{} \mathrm{Mg(COOH) + 2\,H_2O}\uparrow \tag{1}$$

α-magnesium formate

$$\mathrm{Mg(COOH)_2} \xrightarrow{265\,^{\circ}\mathrm{C}} \mathrm{Mg(COOH)_2} \tag{2}$$

α-magnesium formate β-magnesium formate

$$\underset{\beta\text{-magnesium formate}}{\mathrm{Mg(COOH)_2}} \xrightarrow{452\,^\circ\mathrm{C}} \mathrm{2\,CO + H_2O + MgO} \tag{3}$$

$$\mathrm{2\,CO_2 \rightleftharpoons 2\,CO + O_2} \tag{4}$$

$$\underset{\beta\text{-magnesium formate}}{\mathrm{Mg(C_2H_2O_4)}} \xrightarrow[\mathrm{Cu}]{400\text{–}450^\circ\mathrm{C}} \mathrm{CO_2 + H_2CO + MgO} \tag{5}$$

$$\mathrm{H_2O + 2\,CO} \xrightarrow{\mathrm{MgO}} \mathrm{H_2CO + CO_2} \tag{6}$$

$$\mathrm{2\,CO} \xrightarrow[\mathrm{Cu + Ar}]{\mathrm{N_2 + Ar}} \mathrm{CO_2 + C} \tag{7}$$

Reactions (1)–(4) and (6) support the reaction occurring when the aluminium sample holders are used. Reactions (1), (2), (4), (5) and (7) may be true in the case of a copper sample holder.

A schematic diagram for the decomposition pattern of this salt is presented in Fig. 8.

REFERENCES

1 D. Dollimore, J. P. Gupta and D. V. Nowell, *Proc. First Eur. Symp. Therm. Anal.*, Heyden, London, 1976, pp. 233–236.
2 N. J. Manning and D. V. Nowell, *Proc. First Eur. Symp. Therm. Anal.*, Heyden, London, 1976, pp. 317–320.
3 J. P. Gupta and D. V. Nowell, paper presented at the *Symposium of Thermal Analysis and Calorimetry*, Plymouth, 19–21 Sept. 1977.
4 V. Zepletal, J. Jedlicka and V. Ruzicka, *Chem. Listy*, 50 (1956) 1406.
5 V. G. Rienacker and W. Toursel, *Z. Anorg. Allg. Chem.*, 307 (1961) 235.
6 C. Comel and B. F. Mentzen, *Proc. First Eur. Symp. Therm. Anal.*, Heyden, London, 1976, pp. 75–76.
7 B. Claudel, C. Comel, B. F. Mentzen and J. Veron, *Thermal Analysis. Proc. 3rd ICTA*, Vol. 2, Birkhauser, Basel, 1972, p. 365.
8 M. D. Judd, M. I. Pope and C. G. Wintrell, *J. Appl. Chem. Biotechnol.*, 22 (1972) 679.
9 R. Canning and M. A. Hughes, *Thermochim. Acta*, 6 (1973) 399.
10 K. O. Hartman and I. C. Hisatsune, *J. Phys. Chem.*, 69 (1965) 583.
11 T. Meisel, Z. Halmos, K. Seybold and E. Pungor, *J. Therm. Anal.*, 7 (1975) 73.
12 N. J. Manning, *Ph. D. Thesis*, University of Salford, in preparation.
13 J. J. F. Scholten, P. Mars, P. G. Menon and R. V. Hardeveld, *Proc. 3rd Int. Congr. Catal., Amsterdam*, Vol. 2, 1964, pp. 881–890.
14 D. Dollimore, *J. Therm. Anal.*, 11 (1977) 185.
15 D. Dollimore, J. P. Gupta and D. V. Nowell, unpublished work.