Thermochimica Acta, 35 (1980) 239—245

THERMAL AND X-RAY POWDER DIFFRACTION STUDY OF MAGNESIUM SULPHITE HYDRATES: EVIDENCE FOR A NEW CRYSTALLINE PHASE OF LOW WATER CONTENT

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(Received 10 May 1979)

ABSTRACT

Four samples of magnesium sulphite in different hydration states were prepared and characterized by thermal (TG/DTG/DTA) analysis and X-ray powder diffraction. Evidence was derived for the existence of a previously unreported crystalline phase of approximate composition $MgSO_3 \cdot H_2O$. The other samples were the hexa-, tri-, and dihydrates. The temperature of dehydration was found to increase with decreasing water content. The endothermicity of dehydration, on the other hand, decreased steadily for the lower hydrates.

INTRODUCTION

Magnesium sulphite finds its most important use in the manufacture of wood pulp [1], and may also serve as a possible route for the production of high grade magnesia from impure magnesite (S. Afr. Patent No. 74/1871). It is commonly separated from solutions as hydrates (the anhydrous form not being known). Three hydrates have been described in the literature: $MgSO_3 \cdot 6\ H_2O$, $MgSO_3 \cdot 3\ H_2O$ and $MgSO_3 \cdot 2\ H_2O$.

Crystallographic and X-ray powder diffraction data for the hexa- and trihydrates are well established [2,3]. Thermal analyses (TG, DTG, DTA) of these hydrates have also been reported [4,5]. The dihydrate has been less well studied. Interplanar ("*d*") spacings for the dihydrate have been reported [6] but it has not been studied by the technique of thermal analysis. Neither crystallographic nor thermal analytical data are available for lower hydrates which may possibly exist.

This paper presents a comparative TG/DTG/DTA study of four hydrates of magnesium sulphite. One of these displayed a nominal composition of $MgSO_3 \cdot 1.2\ H_2O$. X-ray powder diffraction data are presented for this sample, and it is argued that the sample is an impure monohydrate.

EXPERIMENTAL

Sample preparation

Four hydrates of $MgSO_3$ were prepared (A—D). Samples A and B were derived from magnesium bisulphite solution by thermal precipitation at 25—

TABLE 1

Experimental conditions for thermal analysis

Sample mass	100—160 mg
Sample pretreatment	Lightly crushed
Sample holder	Cylindrical Al_2O_3; height 20 mm, diameter 8 mm
Packing density	Loosly-packed, bulk density ca. 0.25 g cm^{-3}
Thermocouples	Pt/Pt_{90}—Rh_{10} in contact with crucible
Heating rate	4°C min^{-1}
Furnace atmosphere	Argon (84 kPa); flow rate = 50 ml min^{-1}
Reference material	150 mg annealed Al_2O_3

30°C (sample A) and at 90—95°C (sample B). These were shown by subsequent X-ray diffraction analysis to be $MgSO_3 \cdot 6\,H_2O$ (sample A) and $MgSO_3 \cdot 3\,H_2O$ (sample B). The other two samples were precipitated under pressure in a mild-steel bomb from trihydrate in excess water. Sample C was derived at 150°C under a pressure of 450 kPa: this was identified by X-ray diffraction as $MgSO_3 \cdot 2\,H_2O$. Sample D was precipitated at 200°C at a pressure of 1550 kPa. The sample was found to be crystalline and yielded a set of X-ray diffraction lines which was, however, not recorded in the JCPDS powder diffraction file (1977). This suggested that the sample may be a new phase of magnesium sulphite.

Measurements

Simultaneous TG, DTG, DTA measurements were performed with a Mettler Thermoanalyzer. Sample characteristics and instrumental parameters are listed in Table 1.

X-ray diffractometric traces of powdered samples were made with a Philips PW 1050 diffractometer using CoK_α radiation and Fe filter. The scanning speed was 1° min^{-1} for accurate measurements of d-values. 2θ angles were corrected for recorder error by using silicon as internal standard. Routine identification of samples were performed at a scanning speed of 4° min^{-1}.

RESULTS

Figure 1 summarises the results of DTG analysis of the dehydration of hexa-, tri-, and dihydrates of magnesium sulphite. The corresponding TG data (up to 400°C where the decomposition of anhydrous $MgSO_3$ begins) are presented in Table 2. The Table lists the temperatures at which dehydration is initiated (T_i), attains maximum rate (T_p) and reaches 90 per cent completion ($T_{0.9}$), as well as the accompanying mass losses, ΔW.

Figure 2 shows the DTG curve derived for the dehydration of sample D, together with the observed mass losses. It is seen that the TG results confirm the X-ray diffraction finding that the sample is a possible new hydrate of magnesium sulphite since, taken at face value, the mass loss indicates a com-

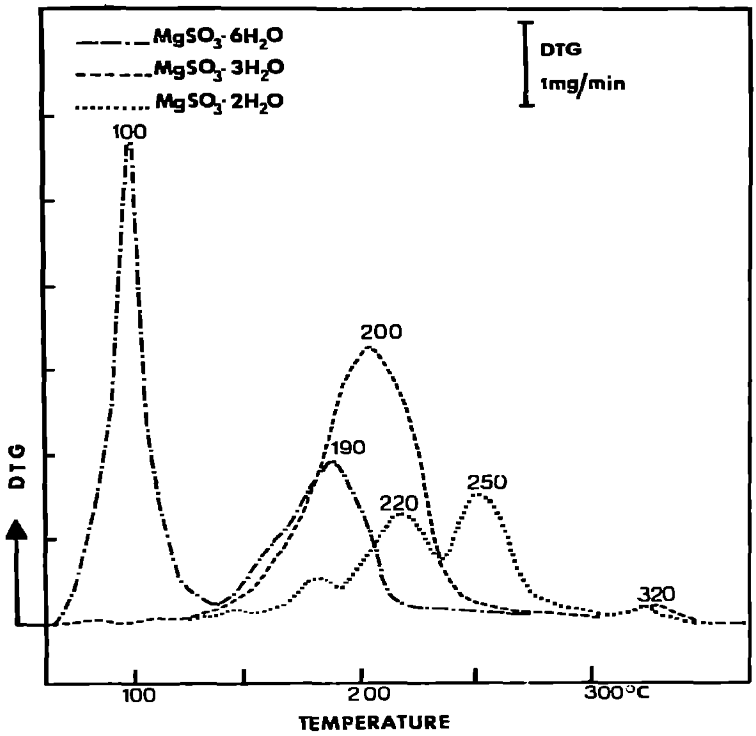

Fig. 1. DTG curves for the dehydration of magnesium sulphite samples (A, B, C). Sample masses: A, 104 mg; B, 155 mg; C, 142 mg.

position of $MgSO_3 \cdot 1.2\ H_2O$. (By chemical analysis for magnesium, a composition of $MgSO_3 \cdot 1.1\ H_2O$ was inferred.) The simplest interpretation of these observations is that the sample is a "monohydrate" which contains higher hydrates as impurities. The broad DTG peak at 100—200°C (Fig. 2) is then identified with the dehydration of these impurities.

Table 3 lists the *d*-spacings measured for sample D. The diffractometric (2θ) trace is shown in Fig. 3.

The DTA curves measured concurrently with the DTG curves of Figs. 1

TABLE 2

Summary of TG data for the dehydration of magnesium sulphite samples [a]

Sample	T_i	T_p	$T_{0.9}$	ΔW ($T_i - T_{0.9}$)	ΔW (25—400°C) Meas.	ΔW (25—400°C) Calc.
$MgSO_3 \cdot 6\ H_2O$	70	100	125	26.0		
	<140	190	235	21.4	49.8	50.9
$MgSO_3 \cdot 3\ H_2O$	100	200	240	29.5	32.4	34.2
$MgSO_3 \cdot 2\ H_2O$	<190	220	>230	>8.4		
	<230	250	310	9.1	25.0	25.7

[a] T in °C; ΔW in mass %.

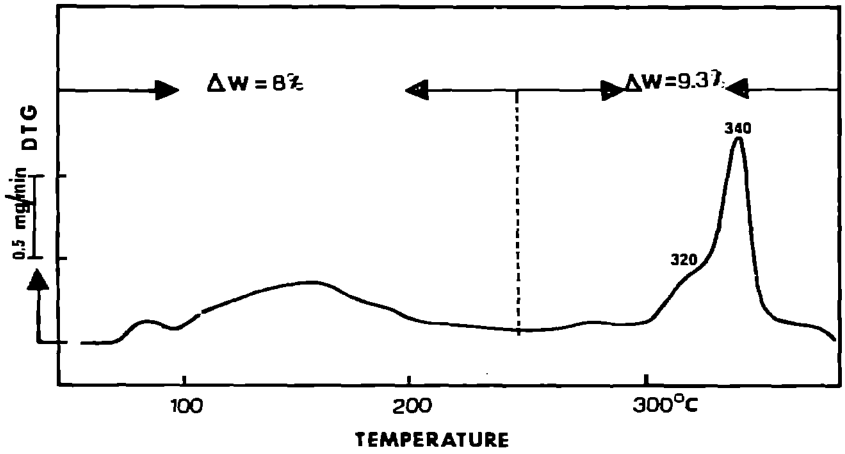

Fig. 2. DTG curve for the dehydration of magnesium sulphite sample D. Sample mass 110 mg.

TABLE 3

d-Spacings and relative intensities of X-ray diffraction lines of samples D ("monohydrate of magnesium sulphite")

d (Å)	I/I_0 [a]
6.40	100
3.35	<1B
3.20	75
2.75	1B
2.38	<1B
2.26	<1B
2.12	<1B
1.99	<1B
1.598	5

[a] *B* denotes a broad or diffuse line. I/I_0 is relative intensity.

TABLE 4

DTA data for the dehydration of magnesium sulphite samples

Sample	DTA peak area/mole (arbitrary units)	DTA peak area/molecule-H_2O
Hexahydrate	330	55
Trihydrate	130	43
Dihydrate	72	36
"Monohydrate"	23	23

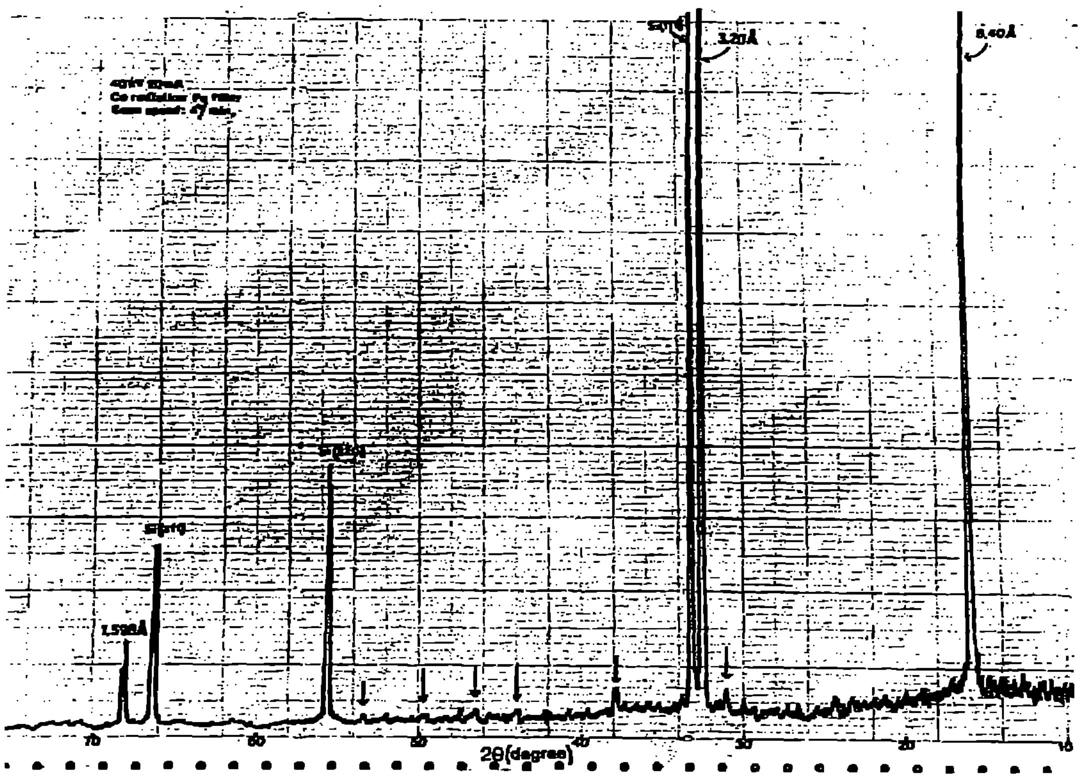

Fig. 3. X-ray powder diffraction pattern of magnesium sulphite sample D using silicon (Si) as internal standard. Approximate positions of weak and diffuse lines are indicated by arrows.

and 2 all exhibited an endothermic character. The relative peak areas are listed in Table 4.

DISCUSSION

Since a general feature of heterogeneous decomposition reactions is the dependence of the rate of product formation upon the prevailing product gas pressure, it is of importance to define the water vapour pressure under which the present analyses were carried out. It has been established [7] that for the crucible geometry used and at the rate of product gas formation observed (>1 mg min^{-1} in general), the dilution of the self-generated reaction atmosphere by the furnace purge gas is negligible. Hence the dehydration reactions described here occurred essentially under a water vapour pressure equal to ambient pressure (ca. 84 kPa).

Measured mass losses up to 400°C are, in all cases, close to the calculated values for hydrates of stoichiometric composition. Deviations from these values are probably caused by adsorbed moisture and small amounts of lower and/or higher hydrate impurities. The small DTG peak seen at temperatures below 200°C during the dehydration of the dihydrate is probably due to the incomplete conversion of the original trihydrate material.

The DTG patterns for hexa- and trihydrates are in general agreement with those reported previously [4,5]. The decomposition of hexahydrate occurs in two stages with the intermediate formation of trihydrate. Whether derived by thermal decomposition or by precipitation from solution, the trihydrate undergoes a single stage decomposition at 190° C. The relatively broad DTG peak associated with this stage would seem to suggest, however, the occurrence of a number of unresolved intermediate reaction steps.

In a similar way to the hexahydrate, DTG indicated a two-stage process for the dehydration of dihydrate. Since the mass losses in both stages — centred on 220° C and 250° C — are approximately the same, thermal analysis suggests that dehydration proceeds via the formation of an intermediate compound of composition $MgSO_3 \cdot H_2O$. Direct verification of this by X-ray diffraction analysis proved to be impossible. In all cases, thermal decomposition products of the samples were amorphous.

Thermal analysis in conjunction with chemical and X-ray powder diffraction analysis provides definite evidence for the existence of a new phase of magnesium sulphite with a low (probably 1) hydration number. The observed temperature of dehydration of this phase may also be adduced as indirect evidence for a low water content. The temperature of 320—340° C conforms to a trend established by the higher hydrates — temperature of dehydration increases as the water content decreases.

The dehydration of the "monohydrate" at 320—340° C does not contradict the hypothesis that the dihydrate decomposes via the formation of $MgSO_3 \cdot H_2O$, the decomposition of which was identified with the 250° C DTG peak in Fig. 1. However, this material would be amorphous, whereas the decomposition temperature of 320—340° C was determined for a crystalline material. That the degree of crystallinity may strongly influence thermal stability is well known. Thus, it has been reported [8] that the dehydration of highly disordered kaolinite occurs at $<530°$ C, that of well-ordered crystals at $>575°$ C.

Comparison of *d*-spacings of the new phase (Table 3) revealed no similarities with those of the higher hydrates.

The powder diffraction pattern for the "monohydrate" appears to be relatively simple, comprising 3 main diffraction lines (Fig. 3). It is possible that some of the diffuse minor lines recorded in the figure derive from impurities. Under a binocular microscope the "monohydrate" was seen to occur mainly as transparent, platy crystals which exhibited well-developed cleavages. It was also noted that the material is unstable at ambient temperatures and pressures. Three days after its preparation, X-ray diffraction analysis revealed the conversion of a substantial fraction of the material into hexahydrate. After a month, the *d*-spacings listed in Table 3 were no longer detected, and only diffraction lines corresponding to hexa- and trihydrates were recorded. It is therefore probable that the higher hydrate impurities (whose presence was inferred from the low temperature DTG peak in Fig. 2) were derived by conversion of "monohydrate".

It is interesting to note that although the endothermicity of dehydration decreases steadily for the lower hydrates (Table 4), increasingly higher temperatures are required for the reaction to proceed. This may be interpreted as indicating that while the enthalpy of dehydration decreases, there is an increase in the activation energy required for the formation of the activated complexes that mediate thermal decomposition.

ACKNOWLEDGEMENTS

Mr. J.H. Selby prepared all magnesium sulphite samples. We thank the Management of Anglo American Research Laboratories for permission to publish the results of this investigation.

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