

MECHANISM OF DEHYDRATION OF MAGNESIUM OXALATE DIHYDRATE

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ABSTRACT

The isothermal dehydration of magnesium oxalate dihydrate has been studied at various temperatures between 190 and 260°C in the presence of air. The isothermal dehydration curves show the usual sigmoidal character and display an induction period which is highest at 190°C. The dehydration velocity constant (k) values (obtained by the application of Mampel's equation) plotted vs. $1/T$ according to the Arrhenius equation gave a plot in which two linear sections intersect at $\sim 215^\circ\text{C}$ with activation energies of 12.3 and 18.3 kcal mole⁻¹ for the lower- and higher-temperature sections, respectively. This behaviour is tentatively explained in terms of a change in the mechanism of dehydration, and not the formation of some new phase other than the dihydrate and the anhydrous oxalate phases present in both the original crystalline oxalate and the sample heated at 200°C for 120 min. X-Ray patterns of the heated oxalate sample left for a few days at room temperature showed a marked sensitivity for rehydration of the anhydrous oxalate phase.

INTRODUCTION

The complexity of the mechanism by which dehydration of metals and heavy metal salt hydrates can take place has been realised by many investigators, especially those working with the dehydrated sulphates [1,2], oxides [3] and hydroxides [4]. Contradictory studies, probably due to different operating conditions, have suggested the formation of the trihydrate [5,6], dihydrate [7] and monohydrate [7–12] on thermal decomposition of hydrated metal hydroxides. Nevertheless, in spite of the widespread use of metal oxalates, very little attention has been devoted to the study of their thermal and isothermal decomposition.

Recently, the decomposition of magnesium oxalate has been followed by Rao and Gandhe [13], who showed that thermal treatment of such an oxalate results in the production of CO and CO₂. Analysis of the gaseous products indicated that the oxalate decomposes to MgCO₃ + CO, followed by further decomposition of MgCO₃ to MgO + CO₂. However, the literature is lacking in studies on the dehydration of magnesium oxalate dihydrate.

Such a study might elucidate the mechanism of the process and the presence of different phases under certain conditions.

The object of this investigation was to study the dehydration and simultaneous or subsequent structural transformations associated with such a treatment. Supplementary studies were carried out by DT, TG and X-ray analyses. The present paper also deals with the isothermal treatment of magnesium oxalate dihydrate in order to determine the presence of different hydrates and to explain the mechanism of dehydration.

EXPERIMENTAL

Materials

Magnesium oxalate dihydrate was prepared by using equal volumes of 0.5 M $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ and 0.55 M pure sodium oxalate. These two volumes were brought to their boiling points and the former was added rapidly to the latter [14]. The mixture was stirred occasionally until it had cooled to room temperature. The crystals of the dihydrate formed in this way are fine (12 : 16 μm) and rather uniform in appearance. The precipitate was washed thoroughly with distilled water, and left overnight in a drying oven at 85–90°C until constant weight was attained.

Procedures

Differential thermal analysis (DTA) was carried out using a Type L 160 KS (West Germany) automatic recording Linseis apparatus at a heating rate of 1°C min^{-1} .

Thermogravimetry (TG) was performed using an automatic recording thermobalance (Gebrüder Netzsch-Selb, West Germany) as described by Gordon and Campbell [15]. The weight change was recorded (on a 6-in. chart with a range of 240 mg) simultaneously with temperature (at a rate of 2.5°C min^{-1}). For DTA and TG, the technique adopted was according to the recommendations of McAdie [16].

The isothermal decomposition was followed with the above thermobalance after incorporating a device to keep the temperature constant arbitrarily throughout the experiment. The temperature of the furnace was first raised to the required degree and the specimen was then shock-heated by lowering the furnace to surround it.

X-ray diffraction patterns were obtained using X-ray diffraction Philips unit, Type PW 1010, applying CuK_α radiation. The diffraction patterns were matched with ASTM cards [17].

RESULTS AND DISCUSSION

DTA and TG

From the DTA curve shown in Fig. 1, it can be clearly shown that a sharp endothermic peak is displayed in the temperature range 165–235°C, with a

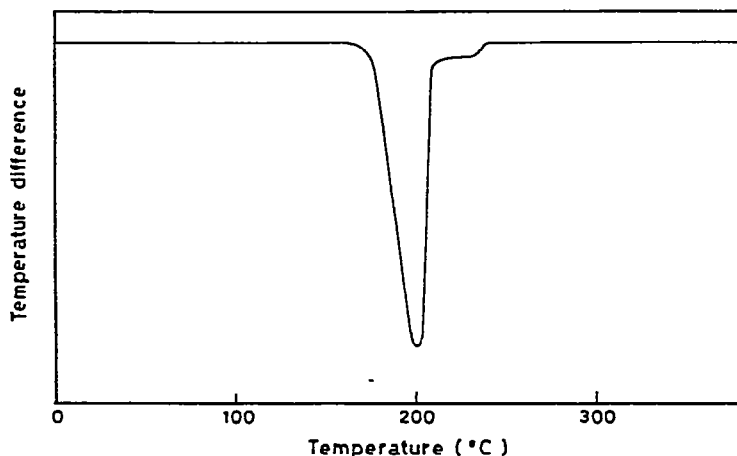


Fig. 1. DTA curve for magnesium oxalate dihydrate. Heating rate: $1^{\circ}\text{C min}^{-1}$.

maximum at 200°C , despite the fact that the analysis is performed with a markedly slow heating rate, viz. $1^{\circ}\text{C min}^{-1}$ (Fig. 1). It is also worth noting that the endothermic peak presents a shoulder above 210°C which extends to the upper temperature limit of the endothermic peak. This shoulder may be taken as an indication of the dehydration of the remaining bound water taking place with a different activation energy.

On the other hand, the TG curve shown in Fig. 2 indicates a continuous decrease in weight which starts at about 170°C and is completed at about 290°C , thus showing that dehydration of the bound water corresponding to the shoulder indicated in the DTA curve has no bearing on breaking the rate of dehydration displayed by the TG curve.

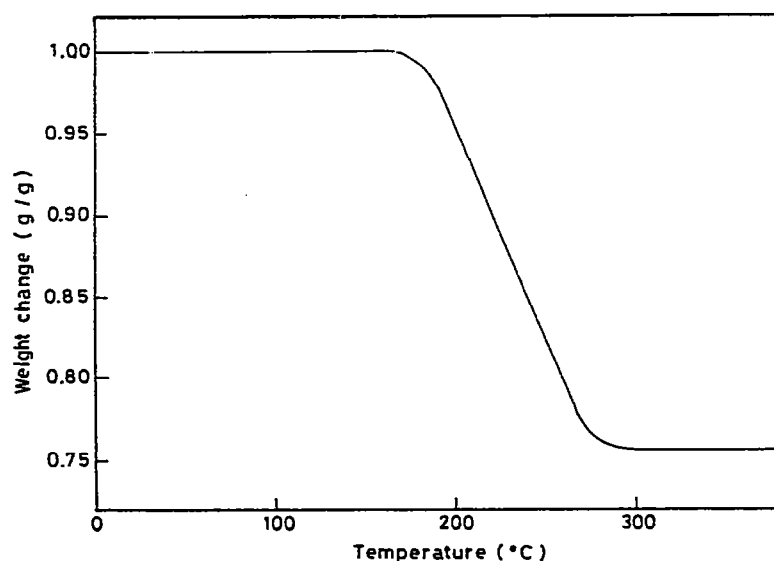


Fig. 2. TGA curve for magnesium oxalate dihydrate. Heating rate: $2.5^{\circ}\text{C min}^{-1}$.

Isothermal dehydration

The results of isothermal dehydration are shown in Fig. 3, in which the decreasing weight of a 1 g sample of the oxalate dihydrate salt is plotted vs. time at each of the dehydration temperatures. The curves show the usual sigmoidal character, indicating that the autocatalytic process of nucleation and growth commonly encountered in solids also occurs here. It is to be noted that the sigmoidal character of the isothermal curves increases with the decrease of temperature of dehydration. Moreover, an induction period is indicated which becomes markedly significant at lower temperatures, reaching about 15 min at the lowest temperature, viz. 190°C. The induction period may be correlated to the rate of nuclei formation which precedes the growth of nuclei. The rate of nuclei formation is temperature dependent, increasing with increase of temperature, and thus leads to decreasing the induction period.

The dehydration reaction performed at the different temperatures may be satisfactorily represented by Mampel's equation [18] given as

$$(W/W_0)^{1/3} = -kt + A \quad (1)$$

applied for a sphere contracting at a uniform rate, where W_0 is the starting weight, W is the corresponding weight reached after time t , k is the velocity constant and A is a constant.

Thus, plotting $(W/W_0)^{1/3}$ vs. t for each of the dehydration processes, gives straight lines, as indicated in Fig. 4. The slopes of these lines determine the velocity constants at the various temperatures. Applying the Arrhenius equation

$$d \ln k / d (1/T) = -E/R \quad (2)$$

and from the plot of $\log k$ vs. the reciprocal of the absolute temperature ($1/T$), the activation energy of the dehydration process was calculated

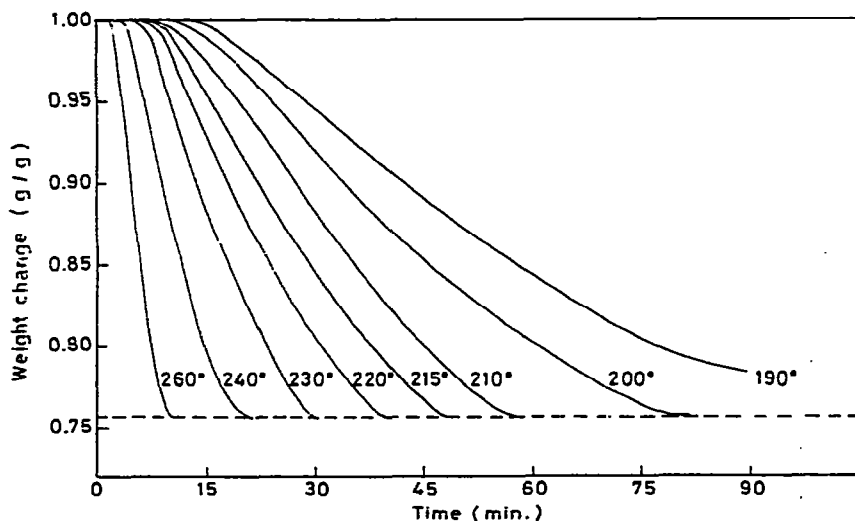


Fig. 3. Weight changes accompanying the dehydration of magnesium oxalate dihydrate.

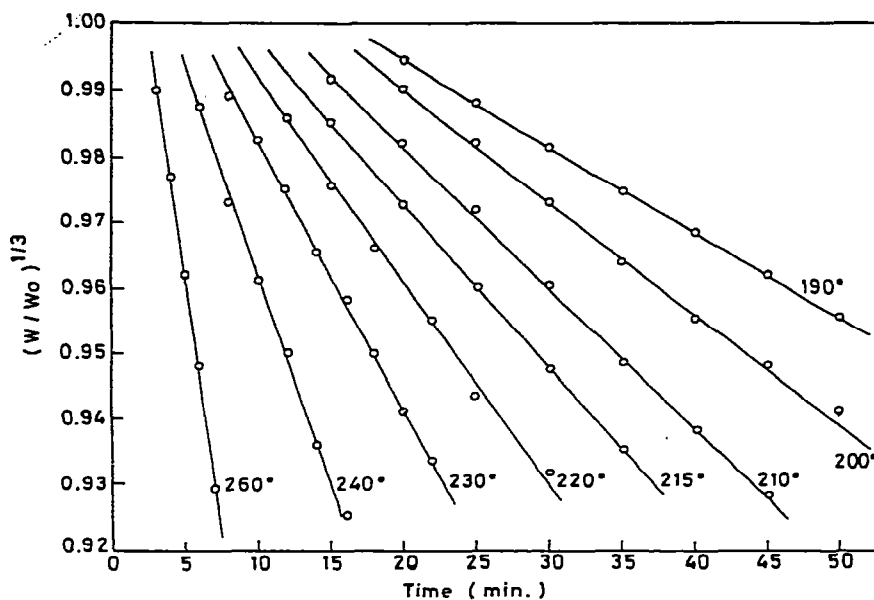


Fig. 4. Plot of $(W/W_0)^{1/3}$ vs. time.

(Fig. 5). The points in Fig. 5 can be carefully represented by two straight lines, intersecting at a value of $1/T$ corresponding to 215°C . Careful repetition of the dehydration experiments showed marked reproducibility, which confirmed the real occurrence of the break indicated in the Arrhenius plot. The slope of the low-temperature section of the plot shows an activation energy of $12.3 \text{ kcal mole}^{-1}$, which is markedly lower than that indicated by

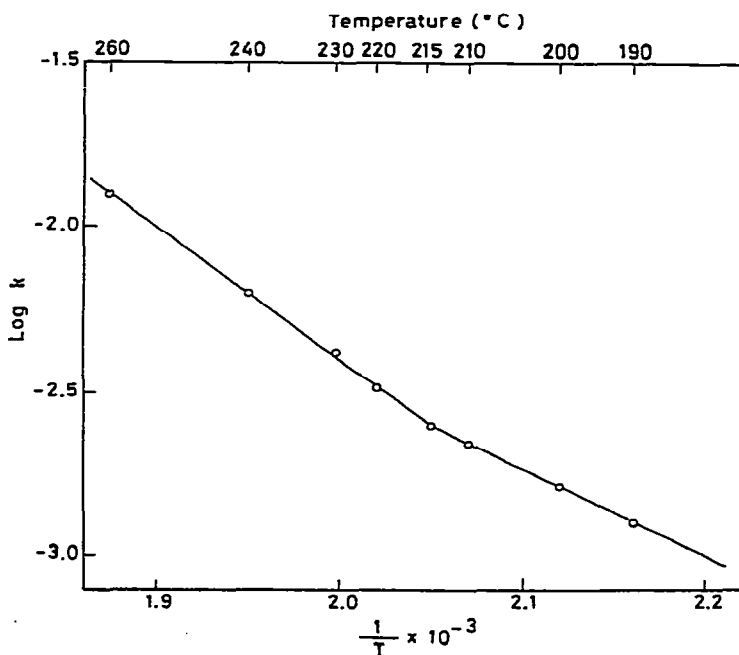


Fig. 5. Plot of $\log k$ vs. $1/T$ for dehydration of magnesium oxalate dihydrate.

the slope of the high-temperature section of the plot ($18.3 \text{ kcal mole}^{-1}$). This inconsistency of the activation energy of dehydration of magnesium oxalate over the experimental temperature range ($190\text{--}260^\circ\text{C}$) appears uncommon and may be tentatively explained in terms of a change in the dehydration mechanism beyond the limiting temperature (215°C) rather than ascribed to the formation of some phase other than the two characteristic phases of the system, namely dihydrate and anhydrous oxalate, as indicated from X-ray studies.

The effect of increase of temperature on the rate of dehydration of crystalline hydrated solids is generally attributed to an increase in the rate of nucleation of dehydration sites. The increase of temperature above a certain limit probably may result in a weakening of the oxalate–water bonding. This thermal effect on the extent of water bonding may result in the formation of augmented dehydration centres within the solid which may be considered as internal water vapour centres. This requires a higher activation energy to achieve dehydration at temperatures higher than a certain limit, despite the increase in the rate constant of isothermal dehydration.

X-Ray analysis

X-Ray analysis was performed on the oxalate dihydrate (original sample) and on samples heated for 30, 60 and 120 min at 200°C . The results are represented by the Debyograms illustrated in Fig. 6. It is noticed that when

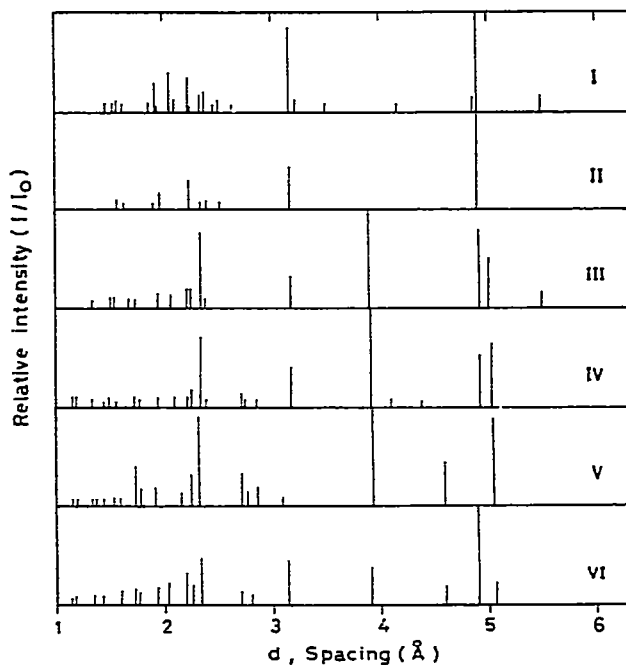


Fig. 6. X-Ray diffraction patterns of magnesium oxalate dihydrate and its dehydrated products. I, Original sample; II, $\text{MgC}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ (ASTM); III, product heated for 30 min at 200°C ; IV, product heated for 60 min at 200°C ; V, product heated for 120 min at 200°C ; VI, product heated and left for 3 weeks.

the X-ray diffraction was carried out instantaneously on the heated samples, new patterns of the anhydrous oxalate could be easily identified, especially when the dihydrate was heated for 120 min at 200°C, whereas X-ray patterns of the dihydrate are completely undetected. Thus, there is no indication of formation of any intermediate hydrate compounds, which is accordingly an improbable interpretation of the observed break in the $\log k$ vs. $1/T$ plot obtained from isothermal studies.

On the other hand, on leaving the heated samples (anhydrous oxalate) for few days at room temperature before subjecting them to X-ray analysis, patterns of the anhydrous oxalate were not easily detected. The patterns thus obtained are nearly identical to the original dihydrate, and display variations in the intensities and broadness of a few lines which can be attributed to the poor crystallinity of the hydrated samples. This behaviour may be considered as indicating the marked sensitivity of the anhydrous phase to the dihydrate phase.

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