

KINETIC ASPECTS OF THE THERMAL TREATMENT OF ACID CRYSTALLOHYDRATE, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$. PART 2. DEHYDRATION AND ACCOMPANYING EFFECTS

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ABSTRACT

Dehydration of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ takes place in the temperature interval from 120°C to 250°C. Continuous water loss in a wide temperature range results in the formation of MgHPO_4 at 250°C. Dehydration was studied under non-isothermal conditions, using differential scanning calorimetry (DSC). The reaction kinetics were followed by making a number of DSC patterns at different heating rates. Activation energy was found to be 144 kJ mol⁻¹ by the Kissinger method and 149 kJ mol⁻¹ by the Ozawa method. The order of reaction was 0.7.

Dehydration increases disorder of the system, changes the actual symmetry of PO_4 groups and causes breakdown of the crystal structure.

INTRODUCTION

Two processes can be distinguished in the thermal treatment of acid magnesium phosphate trihydrate. The first, taking place in the temperature interval from room temperature to 120°C, is proton delocalization [1] and the second, at higher temperatures, is dehydration, i.e., the loss of water of crystallization. The effect of temperature, and some thermal properties of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ are known from study of the compound as a solid electrolyte [2]. However, it has been found that the electrical conductivity of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ changes suddenly after dehydration. Since ionic conductivity is related to structural characteristics, we investigated this acid salt in the temperature range of dehydration in greater detail. Some accompanying effects are also discussed.

EXPERIMENTAL

The method used for recording infrared spectra has been described [1].

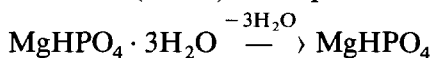
The dehydration process was followed using a Du Pont 1090 Thermal Analyzer with a DSC Cell. Heating rates were: 2, 4, 7, 10 and 15°C min⁻¹.

The peak temperature (T_m) was determined from the DSC curves using the program INTERACTIVE DSC V1.1.

X-ray powder diagrams were obtained with a Philips diffractometer PW-1051, using $\text{CuK}\alpha$ radiation and a graphite monochromator, at room temperature.

RESULTS AND DISCUSSION

A "predehydration state", characterized by delocalization of constitutional protons, was observed during thermal treatment of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ below 120°C [1]. Dehydration begins at about 120°C . Water loss is shown by the appearance of an endothermic peak on a DSC curve (Fig. 1). The mass loss (30.5%) corresponds to the phase transformation



As the process is of the type (solid \rightarrow solid + gas), the kinetic treatment was performed according to the equations and methods given for this type of process under non-isothermal conditions.

Kinetic treatment

The kinetics of reaction of the type (solid \rightarrow solid + gas) can be expressed as

$$\frac{dx}{dt} = k(1-x)^n \quad (1)$$

where dx/dt is the rate, x is the fraction of reacted material, k is the specific constant rate and n is the order of reaction. Under non-isothermal conditions the following relation can be used

$$\frac{dx}{dt} = A e^{-E/RT}(1-x)^n \quad (2)$$

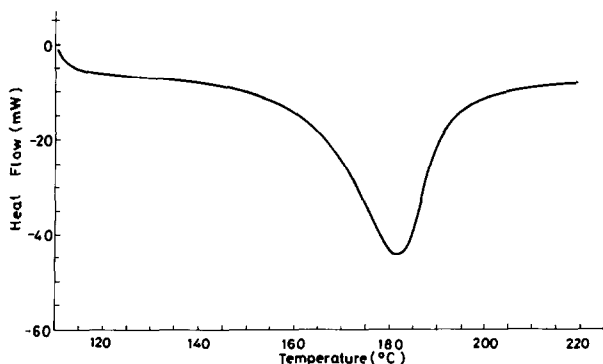


Fig. 1. DSC curve for $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$. Heating rate was $20^\circ\text{C min}^{-1}$.

E is the activation energy, T is the temperature and A is a pre-exponential factor. In most cases studied the exponent n is unity or fractional for this type of reaction. The differential dx/dt can be changed to dx/dT

$$\frac{dx}{dt} = b \frac{dx}{dT} \quad (3)$$

where b is the heating rate. Eqn. (2) now becomes

$$\frac{dx}{dT} = \frac{1}{b} A e^{-E/RT} (1-x)^n \quad (4)$$

By differentiation of eqn. (4) with respect to temperature and assuming $d^2x/dT^2 = 0$

$$\frac{E}{RT_m^2} = \frac{A}{b} e^{-E/RT} \quad (5)$$

T_m is the sample temperature at which the peak differential thermal analysis deflection occurs. This equation was derived by Murray and White [3]. Using the assumptions of these authors Kissinger [4] derived the relationship

$$\left[\frac{d\left(\ln \frac{b}{T_m^2}\right)}{d\left(\frac{1}{T}\right)} \right] = -E/R \quad (6)$$

and applied it to reactions of the type (solid \rightarrow solid + gas). Eqn. (6) makes determination of the activation energy E possible regardless of reaction order. Kissinger has also proposed a simple method for estimating the order of reaction of a particular reaction from the asymmetry of the differential thermal analysis peak, S

$$n = 1.26S^{1/2} \quad (7)$$

Ozawa [5], in his study of kinetic analysis of derivative curves in thermal analysis, has also derived an expression relating the variation of heating rate and the peak temperature T_m

$$\ln b = C - E/RT_m \quad (8)$$

C is a constant and the other symbols have the same meaning as in eqn. (6). Thus, $\ln b$ is related linearly to $1/T_m$. This method of obtaining the activation energy is equivalent to that proposed by Kissinger for DTA, but is more general and applicable to a wider variety of reactions.

In order to obtain kinetic parameters from differential thermal analysis data for dehydration of $MgHPO_4 \cdot 3H_2O$ we used the Kissinger and Ozawa methods. Figure 2 shows a number of DSC curves at different heating rates. From Fig. 3, where plots of $\log b/T_m^2$ vs. $1/T$ and $\log b$ vs. $1/T$ are given, the activation energy was determined and the values 144 kJ mol^{-1} (Kis-

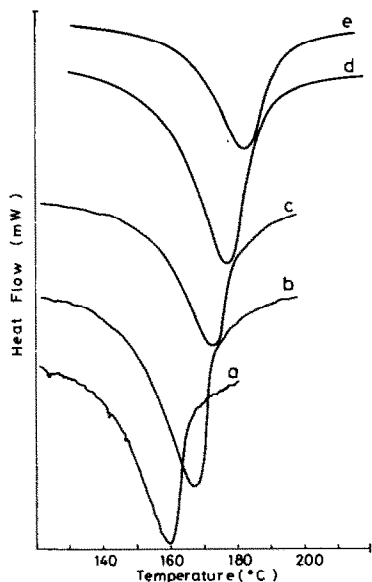


Fig. 2. DSC curves for $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ at different heating rates: (a) 2°C min^{-1} ; (b) 4°C min^{-1} ; (c) 7°C min^{-1} ; (d) $10^\circ\text{C min}^{-1}$; (e) $15^\circ\text{C min}^{-1}$.

singer method), and 149 kJ mol^{-1} (Ozawa method) were obtained. Using eqn. (7) the order of reaction is calculated from the peak asymmetry as 0.7.

The order of reaction $0 < n < 1$ is typical for reactions of decomposition when the surface is decomposed by first order kinetics and the bulk by zero order kinetics, causing the complete reaction to have a fractional order.

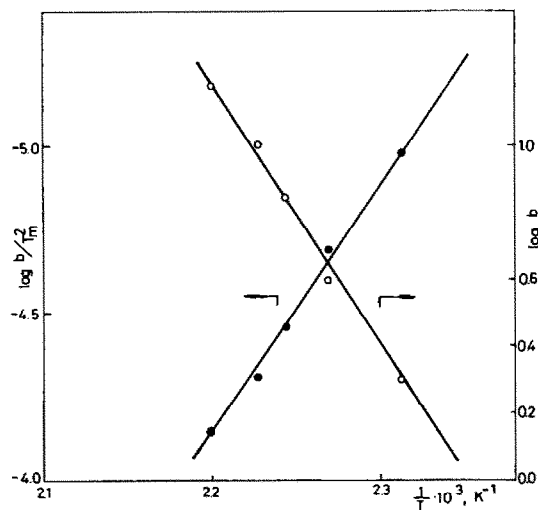


Fig. 3. Plots of $\log b/T_m^2$ vs. $1/T$ (Kissinger method) and $\log b$ vs. $1/T$ (Ozawa method).

Structure transformations

In the IR spectra the dehydration process is shown as a decrease of band intensities of both OH and H₂O stretching and bending vibrations. Some changes are also observed in the region below 1300 cm⁻¹, where bands characteristic of the PO₄ group are expected [1]. IR spectra of MgHPO₄ · 3H₂O at different temperatures are given in Fig. 4.

In the IR spectrum of a sample heated at 250 °C all bands characteristic of both OH and H₂O stretching and bending vibrations disappear, except for very weak bands at 3450 cm⁻¹ and 1650 cm⁻¹. These bands can be ascribed to water molecules additionally sorbed at the surface, since the IR spectra were recorded in an open atmosphere, at room temperature. From Fig. 4 it is seen that all the bands characteristic of the PO₄ groups at about 910(ν₁), 420(ν₂), 1065(ν₃) and 560(ν₄) cm⁻¹ become broader. This implies a change of the PO₄ group symmetry, as well as an increased disorder of the system. It is evident that water molecules affect the arrangement of the PO₄ tetrahedra in the acid crystallohydrate MgHPO₄ · 3H₂O.

Structure transformations are also evident from X-ray powder patterns of samples heated at different temperatures (Fig. 5). Magnesium phosphate trihydrate shows very good crystallinity before the beginning of the dehydration process (Fig. 5a and b). However, when water molecules leave the crystal structure the decrease in the X-ray intensity of reflections is considerable (Fig. 5c). At 250 °C the sample is completely amorphous (Fig. 5d).

Loss of constitutional water (3H₂O) during thermal treatment of MgHPO₄ · 3H₂O causes breakdown of the structure and appearance of an

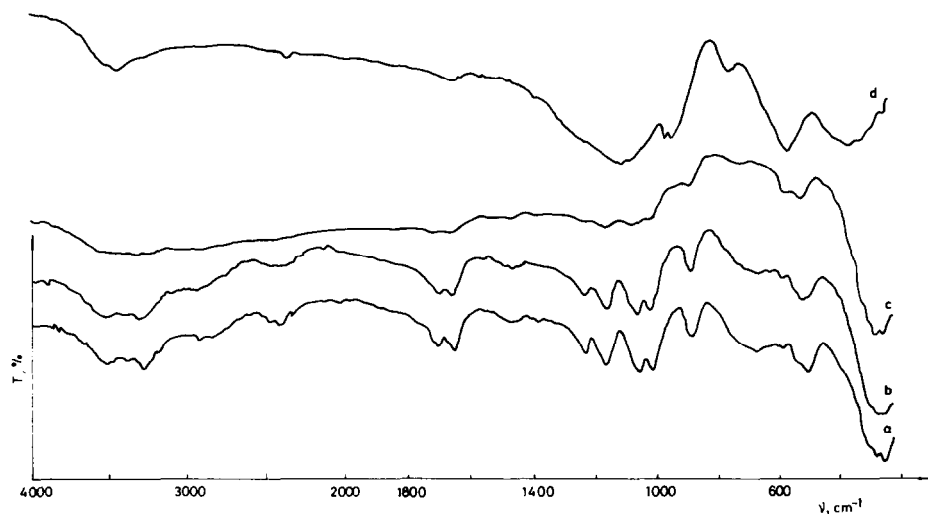


Fig. 4. IR spectra of MgHPO₄ · 3H₂O at different temperatures: (a) at room temperature; (b) at 120 °C; (c) at 160 °C; (d) at 250 °C.

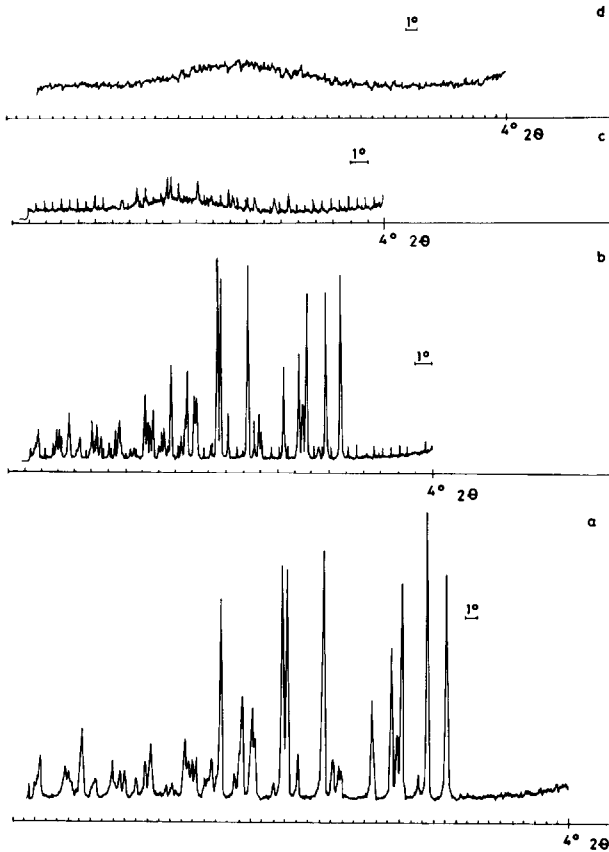


Fig. 5. X-ray powder diffraction patterns of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ at different temperatures: (a) at room temperature; (b) heated at 100°C ; (c) heated at 160°C ; (d) heated at 250°C .

amorphous phase, MgHPO_4 (Fig. 4d and Fig. 5d). From all this evidence, it may be concluded that the crystal structure of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ is supported by water molecules multiply coordinated with Mg^{2+} ions and oxygen atoms from PO_4 groups.

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