

KINETIC ASPECTS OF THE THERMAL TREATMENT OF ACID CRYSTALLOHYDRATE, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$. PART 1. CHANGES IN THE IR SPECTRA AND PROTON DELOCALIZATION

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ABSTRACT

Changes in the IR spectra of acid magnesium phosphate trihydrate heated to progressively higher temperatures point to increased proton mobility. A strong band, of complex structure, in the region of OH stretching vibrations is convoluted. Components of this band are supposed to be due to vibrations of different hydrogen bonded hydroxyl groups. From the changes of relative band intensities with temperature, using the Boltzmann equation, the activation energy is calculated and possible mechanism of proton delocalization discussed. It has been found that proton delocalization is a complex process which includes the following steps: dissociation of hydrogen bond, proton tunnelling effect and orientation of acceptor sites.

INTRODUCTION

It has been noticed, by heating some minerals to progressively higher temperatures, that dehydroxylation is preceded by increased mobility of constitutional protons. Fripiat et al. [1] defined a “predehydroxylation state” characterized by the delocalization of constitutional protons. The same effect was observed by studying intensities of IR absorption bands of OH stretching vibrations of acid magnesium phosphate trihydrate treated at high temperatures.

These investigations continue a study of a number of crystallohydrates and acid salts from the standpoint of solid electrolytes [2–4]. The presence of protons in the acid salts investigated has a very important role in the mechanism of ionic conductivity. As the structure and cross-links are dominant factors it was also interesting to examine in greater detail the behaviour of the system at high temperatures. It was observed earlier that characteristics of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ were considerably changed in the interval from room to dehydration temperature, as well as in the process of dehydration [5,6].

The subject of this paper is the behaviour of acid magnesium phosphate trihydrate from ambient temperature to that where dehydration begins. The dehydration process is reported in part two of this series [7].

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer in the $4000\text{--}250\text{ cm}^{-1}$ region. Samples prepared as Nujol and hexafluorobutadiene mulls on KBr disks, or KBr pellets, were used. Spectra at higher temperatures, from ambient to 160°C , were recorded in an adapted variable-temperature cell (model VLT-2) (RIIC, London).

In this paper special attention is paid to the spectral region of stretching OH vibrations and to the band intensity changes due to temperature increase up to the beginning of dehydration, at about 120°C .

RESULTS AND DISCUSSION

IR and Raman spectra were analysed, and the characteristics of this crystallohydrate discussed with reference to the nature and strength of hydrogen bonds at room temperature, in an earlier publication [8].

IR spectra of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ in the range from room temperature to 120°C , are shown in Fig. 1. Nine sub-bands are obtained by convolution of the complex band in the region of OH stretching vibrations: 3635, 3560, 3525, 3485, 3420, 3375, 3305, 3270 and 3200 cm^{-1} . Each band is attributed

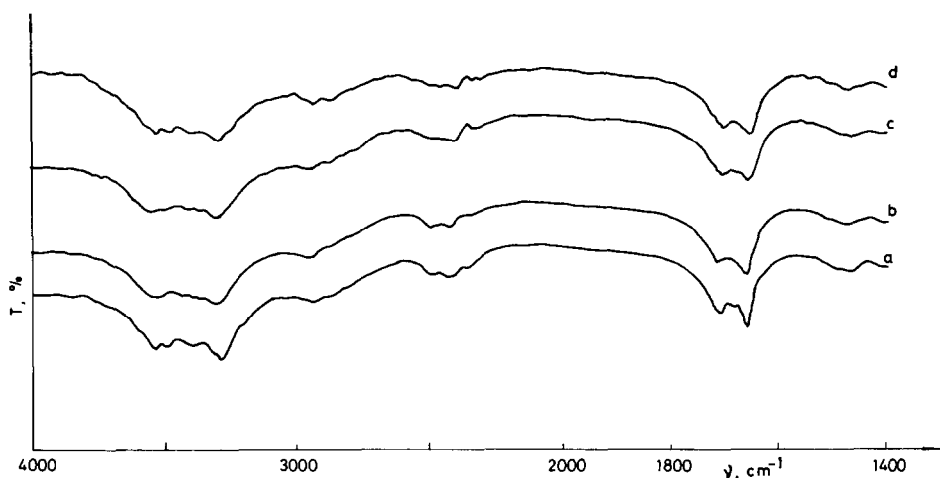


Fig. 1. IR spectra of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ at different temperatures: (a) 20°C , (b) 80°C , (c) 100°C , (d) 120°C .

to the OH group bonded to other constituents of the structure by a hydrogen bond of different strength. The shortest interatomic distance $R(O \cdots O)$ and the strongest hydrogen bond is attributed to the interaction of the acid proton with an oxygen atom from PO_4 group [8,9].

A very important phenomenon is the intensity decrease of the bands ascribed to OH stretching vibrations. This decrease is usually expressed as $P/P_{ref} = \alpha$, where P is the band intensity at the running temperature and P_{ref} the intensity of the same band at room temperature. Decreasing intensities of the bands of OH stretching vibrations with increasing temperature, if not due to dehydration, are indicative of the degree of mobility of the constitutional proton. This reversible process is described as proton delocalization [1].

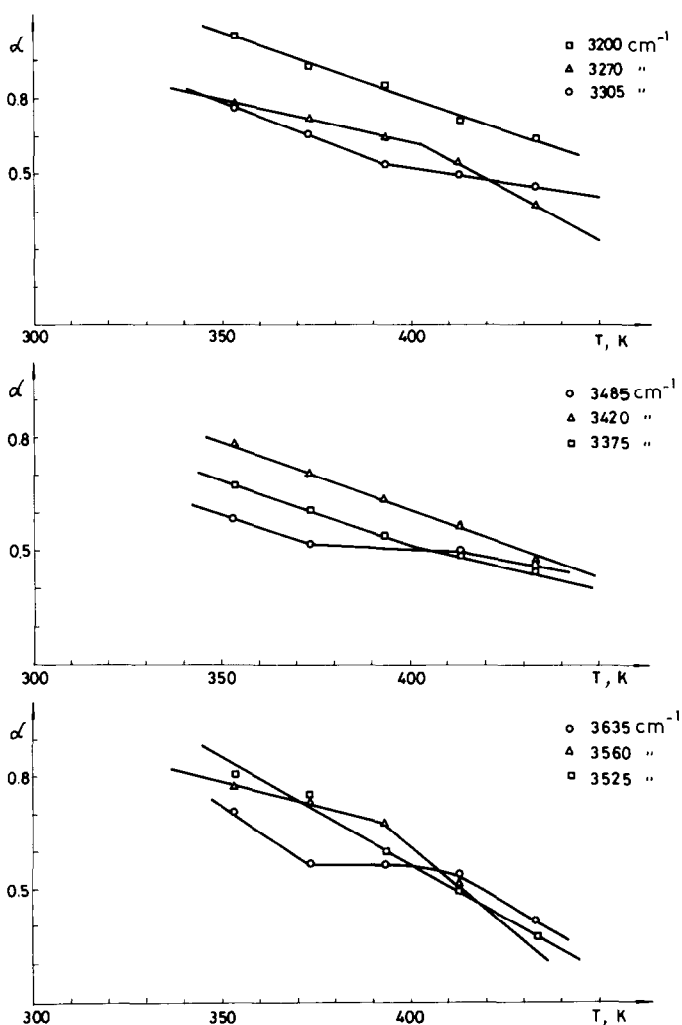


Fig. 2. Relative intensities (α) of different OH bands as a function of temperature.

More information on the process investigated can be obtained by the dependence of $\alpha = f(T)$. If there is proton delocalization only, $\alpha = f(T)$ exponentially decreases with increasing temperature. If the temperature increase is followed by dehydration, then the shape of the curve changes at the dehydration temperature. Plots of α vs. T for different OH bands of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ are given in Fig. 2. For the bands at 3525, 3420 and 3200 cm^{-1} this dependence decreases steadily, whereas for the bands at 3635, 3560, 3485, 3375 and 3305 cm^{-1} a change of the slope at about 120 °C is observed, indicating the beginning of the dehydration process.

Since delocalization is considered as a transition of the proton to an excited state, due to thermal activation, the Boltzmann equation can be used

$$1 - \alpha = B \exp(-E/RT)$$

where E is the activation energy for the delocalization. Activation energies of proton delocalization, given in Table 1, are calculated from the linear dependence $\log(1 - \alpha)$ vs. $1/T$ (Fig. 3). Different numerical values, grouped around two values (10 and 19 kJ mol^{-1}) indicate the complexity of the mechanism of the proton delocalization. The band at about 2400 cm^{-1} , present in the IR spectra of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ throughout the whole temperature region investigated, is indicative of the proton tunnelling effect (Fig. 1) and from this it can be concluded that this effect represents one of the steps in the process mechanism. This step is no doubt preceded by increased mobility of the constitutional proton due to thermal activation. The activation energies of about 10 kJ mol^{-1} obtained are close to the hydrogen bond dissociation energy value [10] suggesting that hydrogen bond dissociation may be the first step of the proton delocalization mechanism. Doubtless an orientation of the acceptor site has to exist in order to accept the incoming proton. This occurs at the same time as the step responsible for the appearance of the differing activation energies of the delocalization process

TABLE 1
Activation energies of proton delocalization

Frequencies (cm^{-1})	Assignment	Activation energy (kJ mol^{-1})
3635	H...OH	11.5
3560	H...OH	10.4
3525	H...OH	19.6
3485	H...OPO ₃	8.7
3420	H...OPO ₃	14.2
3375	H...OPO ₃	10.3
3305	H...OPO ₃	10.9
3270	H...OPO ₃	7.3
3200	H...OPO ₃	19.1

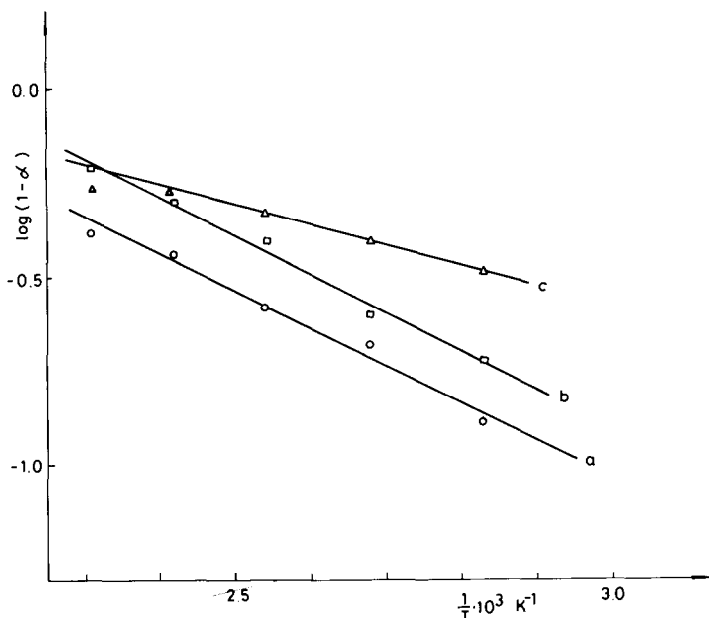


Fig. 3. Some typical plots $\log(1 - \alpha)$ vs. $1/T$ for OH stretching bands: (a) 3200, (b) 3525 and (c) 3305 cm^{-1} .

as a whole, since the acceptor sites differ. When water is the acceptor site, because of a sufficient number of properly oriented water molecules, the proton delocalization process can be represented by the hydrogen bond dissociation energy value only, corresponding in our results to 10 kJ mol^{-1} . However, the activation energy value of about 19 kJ mol^{-1} obtained indicates participation of some acceptor sites requiring corresponding orientation energy. In the system observed such acceptors are PO_4 groups, and the differences in the activation energy values required for the proton delocalization process can be ascribed to the energy spent for orientation, i.e., rotation of the PO_4 groups.

ACKNOWLEDGEMENT

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