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PSEUDO-PHASE CHANGES IN CUPRIC SULFATE PENTAHYDRATE DURING DEHYDRATION

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ABSTRACT

A study of the dehydration kinetics of a model system, cupric sulfate pentahydrate, was made using the temperature programmed desorption technique. The three decomposition steps from the pentahydrate to the anhydrous salt were clearly resolved into distinct spectral peaks even at sample heating rates in excess of 10 K min^{-1}. A linear relationship between spectral peak temperature and square root of heating rate was observed for each dehydration step. The kinetic data revealed different activation enthalpies and entropies for each dehydration sequence for heating rates above and below approximately 8 K min^{-1}. These latter findings are interpreted in terms of crystalline to amorphous pseudo-phase changes in the solid hydrate during decomposition which become apparent only at fast sample heating rates. Enthalpy and entropy changes associated with these structural alterations are evaluated. The results also help to clarify earlier work on the dehydration mechanism in calcium phosphates.

INTRODUCTION

The temperature programmed desorption (TPD) technique of Cvetanović and Amenoniya[1], originally developed for investigating desorption of gases from catalytic surfaces, has more recently been applied to chemical decomposition of solids (e.g., silver carbonate[2]). In another recent study on dehydration of poorly crystalline calcium phosphate[3] the fairly narrow single peak TPD spectrum gave some support to previous descriptions of the material as an amorphous agglomerate of hydrated calcium and phosphate ions. However, the kinetic data in that work yielded two substantially different activation energies for sample heating rates below and above about 10 K min^{-1}. The larger activation energy was found for the lower heating rates (and lower peak temperatures). Two tentative explanations were suggested for that finding. First, there may be two types of water (surface adsorbed, internal waters

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of hydration) being evolved simultaneously. Secondly, a pseudo-phase transition in the hydrated solid could account for the observed sharp change in activation energy of dehydration when the sample heating rate was higher than about 10 K min^{-1}.

It is appropriate to examine the kinetics of water loss from a model system, cupric sulfate pentahydrate, in order to clarify the nature of the dehydration processes in phosphate minerals. Characterization of the states of bound water in amorphous calcium phosphate and octacalcium phosphate is important because both materials are known to be precursors of crystalline hydroxyapatite, the major inorganic constituent of mature bone, when the latter is formed by chemical precipitation[4-6].

EXPERIMENTAL

The TPD apparatus described previously[3] was used in the present work to obtain dehydration spectra for cupric sulfate pentahydrate. In each programmed run a sample of about 60 mg of analytical reagent $CuSO_4 \cdot 5H_2O$ was heated in a dry helium carrier gas stream. The carrier gas entered through fine stainless-steel screens into the bottom of the sample holder, passed upwards through the bed of solids, and exited through another set of steel screens at the top of the sample holder. The sample particles were no larger than about 0.05 cm in their longest dimension. Ten programmed rates of heating were used which ranged from 2.54 to 33.0 K min^{-1}. The concentration of evolved water in the carrier gas stream and the sample temperature were simultaneously and continuously recorded on a two pen Hewlett-Packard recorder as functions of time. The sample temperature was determined by a chromel–alumel thermocouple with an ice reference. Water concentration in the helium stream was monitored using a rhenium–tungsten filament thermal conductivity detector maintained at 80°C by a thermostat. Pure helium was used in the reference side of the thermal detector.

RESULTS

A typical TPD spectrum is shown in Fig. 1. The three dehydration steps were readily identifiable except at the fastest heating rate ($b = 33.0$ K min^{-1}) at which only the temperature at peak III could be resolved. The temperatures, T_M, of the three spectral peaks at all heating rates are listed in Table 1.

DISCUSSION

Morphology of dehydration spectra

The existence of three distinguishable dehydration peaks is consistent with the four common forms of cupric sulfate: penta-, tri-, and monohydrates and anhydrous. Only at the fastest heating rate (33 K min^{-1}) was it not possible to resolve peaks I and II. The fast carrier gas flow-rate and good contact between sample and carrier gas ensured resolution of dehydration processes I and II even up to 27.8 K min^{-1}. The respective peaks in the spectra are associated with the following dehydration sequences:

$$\text{(I)}\quad CuSO_4\cdot 5H_2O \rightarrow CuSO_4\cdot 3H_2O + 2H_2O(g)$$

$$\text{(II)}\quad CuSO_4\cdot 3H_2O \rightarrow CuSO_4\cdot 1H_2O + 2H_2O(g)$$

$$\text{(III)}\quad CuSO_4\cdot 1H_2O \rightarrow CuSO_4\cdot 0H_2O + 1H_2O(g)$$

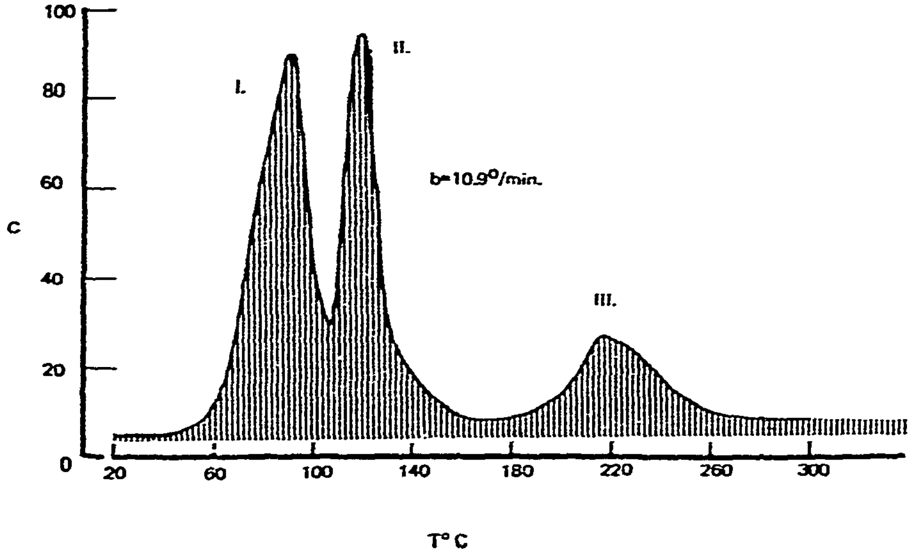

Fig. 1. Temperature programmed dehydration spectrum of $CuSO_4\cdot 5H_2O$ for a sample heating rate of 10.9 °C per minute. Ordinate: Concentration of water in carrier gas stream *in terms of* thermal detector response (mV); abscissa: sample temperature (°C).

TABLE 1

TEMPERATURES OF DEHYDRATION PEAKS IN TEMPERATURE PROGRAMMED DESORPTION SPECTRA FOR $CuSO_4\cdot 5H_2O$ AS A FUNCTION OF SAMPLE HEATING RATE

b (°*C min*$^{-1}$)	T_M (°*C*)		
	Peak I (5→3)	*Peak II (3→1)* (±*0.5 °C*)	*Peak III (1→0)*
2.54	67.7	100.7	193.5
3.23	68.5	101.2	196.2
4.33	76.7	107.0	206.2
5.45	80.0	109.7	209.0
8.14	89.0	117.0	214.5
10.9	93.2	123.7	220.7
16.5	106.8	135.0	230.5
22.1	111.6	144.5	238.0
27.8	125.2	153.7	249.7
33.0	—	—	255.5

It is important to note the capability of the TPD method in the rapid detection of several individual steps in the dehydration of a solid hydrate. In other experiments several closely spaced spectral peaks were found for $FeSO_4 \cdot xH_2O$ where x is non-integral and variable[7]. The width of a dehydration peak is a measure of the distribution of the molecules in a particular hydration state about the average energy for that state. As might be expected the dehydration peaks for crystalline cupric sulfate are much narrower than those observed for poorly crystalline calcium phosphate[3].

The results in this work can be compared with a thermogravimetry (TG) of the pentahydrate of cupric sulfate[8]. On a theoretical basis a TPD spectrum is equivalent to the first derivative of a TG curve when results for the same system and the same heating rates are being compared. Moreover, a peak maximum on a TPD spectrum corresponds to an inflection point on a TG curve. The temperature at inflection points (i.e., peak maxima) should, therefore, be more easily determined from a TPD spectrum than from a TG curve because the former is in essence a differential weight loss curve. TG curves for $CuSO_4 \cdot 5H_2O$ were reported for only two sample heating rates[8], 0.10 and 2.50 K min^{-1}. No attempt was made in that work to evaluate heats of decomposition of the pentahydrate. The peak temperatures in Table 1 for $b = 2.54$ K min^{-1} agree most closely with TG inflection points determined at the same heating rate in the presence of about 10 torr water vapor pressure. At vapor pressures less than about 6 torr the TG curves became less well-defined.

A fast flowing dry helium stream was used as the carrier gas in the present study to enhance detector response and sensitivity toward liberated water and to eliminate readsorption of water. Therefore, it was not possible to maintain a constant

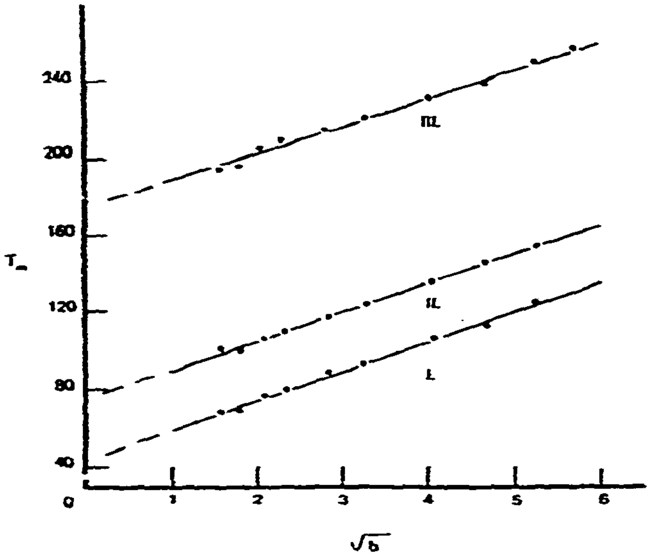

Fig. 2. Temperatures at maxima in dehydration spectra of $CuSO_4 \cdot 5H_2O$ as functions of the square root of sample heating rate. Ordinate °C; abscissa (°C/min)$^{1/2}$.

partial pressure of water in the carrier gas during a TPD heating experiment. In fact, the water content in the gas phase necessarily varies with temperature in the TPD method. An estimate can be made of the water partial pressure, P_w, in the carrier gas at the TPD spectral maxima. However, under conditions of the TPD experiment the remaining hydrated solid at any instant may not be in equilibrium with water in the vapor phase. For comparison purposes only, P_w was estimated at the peak maxima for the TPD spectrum obtained at 5.45 K min^{-1}. The area of a one minute segment under a spectral peak divided by the total area under the complete spectrum and then multiplied by the weight of water in the original sample gives the instantaneous weight loss at the peak (mg H_2O per minute). Division of the weight loss per unit time by the carrier gas flow-rate (referred to the temperature at the peak) gives the water concentration in mg H_2O per cm^3 of He. This latter quantity is easily converted to partial pressure of water using ideal gas laws. In this manner P_w was calculated to be of the order of 8–10 torr at peaks I and II and about 2–4 torr at peak III. No further use is made of these pressures. It is merely noted that they are similar to those employed in the TG studies[8].

The T_M vs. $b^{1/2}$ plots shown in Fig. 2 for the three dehydration steps are a set of essentially parallel straight lines. Linearity in this type of plot had been reported for calcium phosphate dehydration[3]. In view of this empirical finding the following equation can be written:

$$T_M = T_M^\circ + mb^{1/2} \tag{1}$$

Limiting peak temperatures, T_M°, obtained by extrapolation to $b^{1/2} = 0$ are 43, 75 and 173 °C for peaks I, II and III, respectively. In principle, T_M° represents the temperature at the peak maximum (TPD spectrum) or at the inflection point (TG spectrum) under conditions of a vanishingly small sample heating rate ($b^{1/2} \rightarrow 0$). As expected the T_M° values for the three peaks are all smaller than those obtained by TG at the respective inflection points in the presence of about 10 torr partial pressure of water at the very slow heating rate of 0.10 K min^{-1}. This observation establishes the reliability of extrapolation of TPD data at fast heating rates back to zero heating rate in the assessment of the equilibrium temperature of transformation of a particular hydrate to the next lower hydrated state.

Evidence for pseudo-phase changes during dehydration

According to theory[1] the heat of activation can be obtained from the variation in peak temperature, T_M, with sample heating rate, b, by means of eqn (2). Since the TPD spectra were taken at constant pressure the heat of activation is hereafter referred to as an enthalpy change[9], ΔH.

$$\ln (T_M^2/b) = \Delta H/RT_M + \ln (\Delta H/AR) \tag{2}$$

The term A in eqn (2) is the pre-exponential factor in the desorption rate constant, k_M, expression,

$$k_M = A \exp (-\Delta H/RT_M) \tag{3}$$

In view of absolute reaction rate theory we have written the following equation for A,

$$A = \frac{kT_M}{h} \exp(\Delta S/R) \tag{4}$$

In principle, ΔH and ΔS can be obtained from the slope and intercept, respectively, of a $\ln(T_M^2/b)$ vs. $1/T_M$ plot. When the experimental data of Table 1 were plotted according to eqn (2) each peak had two linear segments with widely different slopes. These diagrams are not reproduced here, since all data points are available in Table 1. Points for $b \leq 8.14$ K min^{-1} constituted one segment and points for $b > 8.14$ K min^{-1} comprised the other segment. ΔH and ΔS values for the two branches of the $\ln(T_M^2/b)$ vs. $10^3/T_M$ plots for each dehydration step were computed from slopes and intercepts and are listed in Table 2. Entropies were evaluated for each peak at the temperature at which the two line segments intersected. It is noted that heats of activation determined by TPD may on the average have uncertainties of the order of 10–20% (cf. ref. 10).

TABLE 2

ACTIVATION ENTHALPIES AND ENTROPIES FOR DEHYDRATION OF $CuSO_4 \cdot 5H_2O$ AND ENTHALPY AND ENTROPY CHANGES FOR THE PSEUDO-PHASE TRANSITION OCCURRING IN EACH DEHYDRATION STEP

ΔH in kcal/mole water, ΔS in cal/mole water K.

Peak	*ΔH of dehydration*		*ΔS of dehydration*		*Pseudo-phase transitions*	
	$b \leq 8.14$ K min^{-1}	*$b > 8.14$ K min^{-1}*	*$b \leq 8.14$ K min^{-1}*	*$b > 8.14$ K min^{-1}*	*ΔH_{sa}*	*ΔS_{sa}*
I(5→3)	10.8	7.0	−39	−50	+3.0	+11
II(3→1)	17.8	8.9	−23	−47	+8.9	+24
III(1→0)	20.8	14.0	−27	−42	+6.8	+15

For each dehydration step for $CuSO_4 \cdot 5H_2O$ a more positive enthalpy of activation and entropy of activation was found for the lower heating rates (and lower temperature ranges). $\Sigma\Delta H$ for the complete dehydration process,

$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 + 5H_2O(g)$$

can be estimated by means of eqn (5)

$$\Sigma\Delta H = 2(\Delta H_{I} + \Delta H_{II}) + \Delta H_{III} \tag{5}$$

The summation gave 78.0 kcal per mole $CuSO_4$ for $b \leq 8.14$ K min^{-1} and 45.8 kcal per mole $CuSO_4$ for $b > 8.14$ K per mole $CuSO_4$. $\Sigma\Delta H$ for the slower heating rates is only a few kcal in the excess of the standard thermodynamic value[11], ΔH°_{298} (which does not vary greatly with temperature). $\Sigma\Delta H$ for the faster heating rates is much smaller than ΔH°_{298}. The lower ΔH values at faster heating rates signify that under those conditions water is being evolved from a state of higher energy in the solid. At rapid rates of heating there may be a structural alteration in the solid phase before the bulk of the water for a given dehydration step appears in the carrier gas stream. The abrupt changes in ΔH do not appear to be caused by overlapping of two dehydration processes. All three dehydration steps for $CuSO_4 \cdot 5H_2O$ show a change in ΔH (and ΔS) as the heating rate is increased beyond 8 K min^{-1}; peaks I and II overlap one another some-what but peak III appears nearly 100°C above peak II. It was shown previously[3] that errors in temperature measurements at fast heating rates in the TPD method cannot explain the changes in slope of the ln (T_M^2/b) vs. $10^3/T_M$ plots.

The assumption of a pseudo-phase change in the solid during each dehydration step implies that the difference between activation enthalpies at slow and fast heating rates is equivalent to the enthalpy change of the structural alteration in the solid, ΔH_{sa}. That is, a smaller ΔH at faster heating rates means that water is being liberated from a higher energy state as compared to water evolution at slow heating rates. By a similar line of reasoning the more negative entropies of activation at the faster heating rates indicate water evolution from a state of higher entropy under those conditions. Thus, ΔS_{sa} for the structural alteration is equal to the difference between slow and fast heating rate values of ΔS. For a true phase transition ΔH and ΔS must both change in the same direction (increase or decrease) and ΔH must necessarily equal $T\Delta S$. We, therefore, conclude that under fast sample heating conditions in the TPD method a structural alteration in the solid phase occurs during each dehydration step which is characterized by an increased enthalpy and entropy. Pannetier et al.[8], on the basis of TG curves and other independent information, proposed that intermediate *amorphous* phases are formed under certain experimental conditions of heating rate and water partial pressure during the transition of one definite crystal hydrate of cupric sulfate to the next lower hydrate. The present results (positive ΔH_{sa} and positive ΔS_{sa}) not only confirm the existence of "crystal-to-amorphous intermediate" transitions in the hydrated cupric sulfate system but provide numerical values of the enthalpy and entropy changes associated with those transitions. In retrospect, our earlier results on the dehydration of calcium phosphates are indicative of a similar pseudo-transformation in the hydrate solid phase.

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