Dependence of Kinetics of Copper Sulfate Pentahydrate Dehydration on Water Vapor Pressure

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The dependence of the growth rate v_g of nuclei during $CuSO_4 \cdot 5H_2O$ dehydration upon water vapor pressure P_{H_2O} has been investigated. At small P_{H_2O} (less than 1 Torr at 50°C), v_g falls rapidly with decreasing P_{H_2O}, and simultaneously v_g anisotropy disappears. At $P_{H_2O} = 1$–9 Torr, v_g for elliptic and round nuclei is constant and independent of P_{H_2O}. The influence of initially keeping the samples in water vapor upon the kinetics of the following dehydration has been studied. Treatment by water vapor leads to slowing of dehydration and increasing its degree of transformation. On the basis of data obtained a kinetic interpretation of the Topley–Smith effect has been proposed.

Introduction

Crystallohydrates represent a convenient model system for studying the characteristics of topochemical reactions. Dehydration of copper sulfate pentahydrate is one of the reactions most frequently investigated kinetically. Recently a number of important results have been obtained for this compound, allowing a new hypothesis about the mechanism of water vapor influence on dehydration kinetics (1, 2) to be developed.

However, the clarity of the conclusions suffers considerably because, like earlier works, these works deal with the dependence of the total reaction rate on the water vapor pressure measured by the weight loss of a primary sample. Therefore in the present paper the dependence of dehydration kinetics on water vapor pressure is discussed on the basis of the investigation of the growth rate of nuclei formed during $CuSO_4 \cdot 5H_2O$ dehydration *in vacuo* and in water vapor.

Experimental

The kinetics of nuclei growth have been studied using the installation shown schematically in Fig. 1. The reaction cell allowed observation of the surface of separate monocrystals, simultaneously providing temperature constancy in a reaction zone up to ±1°C and controllable pressure of water vapor. The pressure was measured by an oil manometer. The reactor construction permitted experiments both by the static method of "cold point" and under dynamic (flow of water vapor) conditions.

$CuSO_4 \cdot 5H_2O$ monocrystals have been grown from an aqueous solution of this salt ("chemically pure") by the method of isothermal evaporation. In all cases the most commonly developed face (110) has been studied.

The kinetics of dehydration of powder samples were investigated in the flowing differential reactor in the flow of pure helium
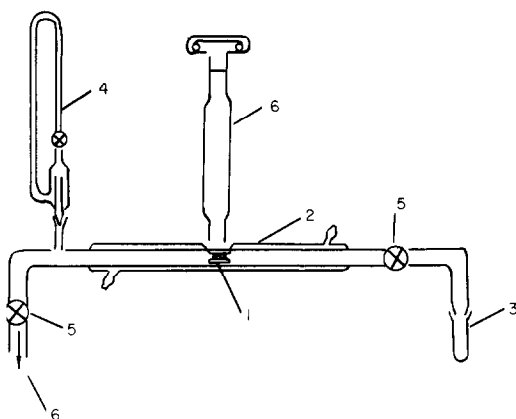
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FIG. 1. Layout of the installation for measuring the growth rate of nuclei at controllable pressures of water vapor. (1) Sample; (2) thermostating reactor; (3) reservoir for liquid water; (4) oil manometer; (5) taps for pumping out of the reactor and setting a pressure of water vapors; (6) microscope (above) and connection to a vacuum pump (below).
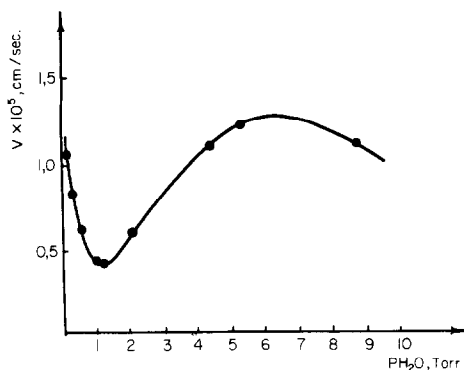

FIG. 2. Boundary propagation velocity vs pressure of water vapor, obtained from the kinetical curves by the equation of the contracting sphere. Temperature, 52°C (2).

saturated with water vapor up to the necessary partial pressure. A thin layer of the sample was placed in the transverse cross section of the reactor. The diameter of the reactor tube was 1.6 cm, the mass of the specimen was 50 mg, and the flow rate of the gas carrier was 150 cm³/min. Detection of water concentration in gas at the reactor exit was performed by the catarometer of the "Chrom-3" chromatograph. The accuracy of reactor temperature regulation is ±1°C.

Samples of $CuSO_4 \cdot 5H_2O$ powders were used with particle size 0.100–0.125 mm obtained by splitting monocrystals and by subsequent sieving of the necessary fraction.

Results

1. Influence of Water Vapors on Dehydration Kinetics

The dependence of the mass reaction rate (determined by weight loss) on water vapor pressure is described by the well-known curve of Topley and Smith (3). The most complete kinetic analysis of the curves' "degree of transformation–time" obtained at different

pressures P_{H_2O} was reported in (2). It included the treatment of experimental curves in the coordinates of the contracting sphere equation with subsequent determination of the velocity of the reagent–product boundary using a given initial particle size. The curve obtained is shown in Fig. 2.

However, this approach to kinetic description is unsatisfactory, for several reasons. First, the equation of the contracting sphere describes experimental data satisfactorily only after the velocity maximum; thus the initial sphere radius must depend on the position of the flex point on the curve α–t and at any rate is not equal to the size of the reagent particles. Second, the real distribution of powder particles with respect to the time when they begin to participate in the reaction is unknown, whereas the model of the contracting sphere assumes simultaneous initiation of the whole free surface of a sample in the initial moment.

The third and most important reason is that the propagation velocity of the boundary in $CuSO_4 \cdot 5H_2O$, as shown below, is essentially anisotropic. Thus, the value of the velocity shown in Fig. 2 is regarded as an average quantity the nature of which must be examined further.

To this end consider a micropicture of the $CuSO_4 \cdot 5H_2O$ dehydration process. Accord-

ing to Garner and Jennings (4), in the region of P_{H_2O} up to 10 Torr at 50°C formation of three types of nuclei is possible: star-shaped, round, and elliptic (on the (110) face of a monocrystal). More detailed studies showed that star-shaped nuclei are formed and grow only under vacuum, $P < 10^{-2}$ Torr. With pressure increases they lose their shape, and become round.

In the region of pressures above 1 Torr two types of nuclei form and grow simultaneously: round and elliptic. An analysis of water contents of the different types of nuclei in a solid product showed that star-shaped and round nuclei belong to the monohydrate, while the elliptic nuclei belong to the trihydrate.

Direct observation of the decomposition of separate monocrystals at 50°C and controllable pressure of water vapor showed that the growth rates of various types of nuclei differed considerably. Figure 3 presents growth rate dependence on the pressure of water vapor. Two peculiar features of these curves attract attention:

In the region of small P_{H_2O} (<1 Torr) the growth rate for monohydrate nuclei decreases rapidly with pressure. If one takes the average value of the rate this decrease is in good
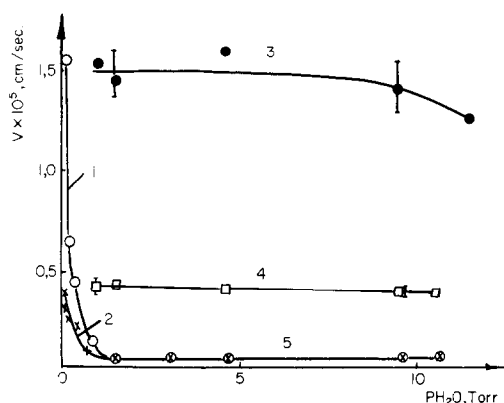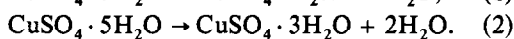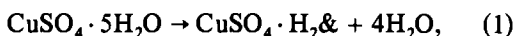

FIG. 3. Dependence of growth rates of various types of nuclei on water vapor pressure at 50°C. (1) Star-shaped nuclei parallel to the C axis of a crystal, (2) star-shaped nuclei perpendicular to the C axis; (3) elliptic nuclei parallel to the C axis, (4) elliptic nuclei perpendicular to the C axis, (5) round nuclei.
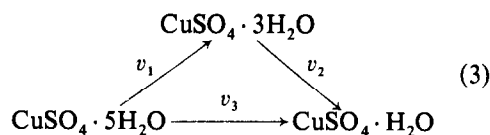
agreement with a corresponding part of the Topley–Smith curve (Fig. 2). Simultaneously, anisotropy of the growth rate disappears, so that at $P_{H_2O} > 1$ Torr (at 50°C) one can observe round and elliptic nuclei only.

In the region of the Topley–Smith curve maximum (1–7 Torr) the growth rates of both round and elliptic nuclei are independent of the chosen value of P_{H_2O}, in contrast with expectation. This result contradicts the curve of Fig. 2, obtained by the kinetic analysis described above.

To overcome this contradiction partially, one can assume that for pressures from the minimum to the maximum of the Topley–Smith curve the total reaction rate is determined by competition of two reactions. In fact, according to the microscopic observations mentioned above two reactions proceed simultaneously in this region of water vapor pressures:

$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot H_2\& + 4H_2O, \quad (1)$$
$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 \cdot 3H_2O + 2H_2O. \quad (2)$$

Note that this region corresponds to the region of existence of a stable crystal monohydrate. Hence, a trihydrate produced in a system is a metastable product under these conditions. The sequence of the corresponding chemical transformations can be presented as

$$\begin{array}{c} CuSO_4 \cdot 3H_2O \\ v_1 \nearrow \qquad \searrow v_2 \\ CuSO_4 \cdot 5H_2O \xrightarrow{\quad v_3 \quad} CuSO_4 \cdot H_2O \end{array} \quad (3)$$

If numerical values of the rates are considered, one can note that in the region of the maximum of the Topley–Smith curve v_1 is on the average an order of magnitude higher than v_3 (Fig. 3). Under these conditions v_2, the rate of trihydrate transformation into monohydrate, is negligible (5). Thus, there is a certain probability that each particle of the powder reagent will react according to (1) or (2) with essentially different rates. One can therefore consider the upward branch of the Topley–Smith curve as the result of subse-

quent replacement of a slow reaction (1) by a more rapid reaction (2). This results in a variation of the composition of the final dehydration product in good agreement with experiment: near the minimum of the Topley–Smith curve the product composition is close to $CuSO_4 \cdot H_2O$, while near the maximum it is close to $CuSO_4 \cdot 3H_2O$. In the intermediate region the product is a mixture of tri- and monohydrates (2).

2. Influence of Preliminary Treatment by Water Vapors on Dehydration Kinetics

It was reported earlier (6) that keeping samples of some crystallohydrates, including $CuSO_4 \cdot 5H_2O$, in water vapor at room temperature under conditions excluding their dehydration resulted in the accumulation in crystals of so-called "free water." It appears in PMR spectra as a narrow component in the center of a signal due to crystallized water. Subsequently it was shown that the accumulation of "free water" in samples leads to considerable slowing of a mass rate of dehydration as well as to a simultaneous increase of the degree of transformation of the reaction (7) (Fig. 4). We assume that this is due to rehydration of the nucleation centers of a trihydrate. If, in fact, one takes a sample, usually decomposing in water vapor (with P_{H_2O} corresponding to the maximum of the Topley–Smith curve) to a trihydrate, and keeps it in

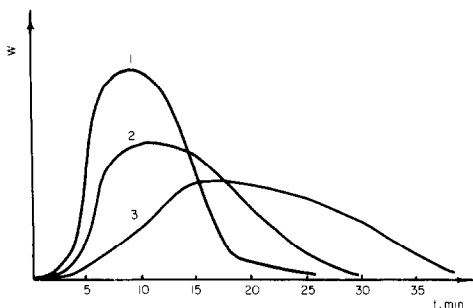FIG. 5. Variation in rate and degree of transformation of dehydration for $CuSO_4 \cdot 5H_2O$ after preliminary treatment of samples by water vapor (10 days at $P_{H_2O} = 17.5$ Torr). Temperature, 50°C: (1) Before treatment; (2) after treatment. $n =$ number of moles of water eliminated by dehydration of 1 mole of the salt. Decomposition conditions: Helium flux with $P_{H_2O} = 4.8$ Torr.

water vapor over a saturated solution of this salt for a long time (more than a week), then the reaction rate decreases by about an order of magnitude, while the degree of transformation increases almost twice, so that the final product is $CuSO_4 \cdot (1.5–1.7)H_2O$ (Fig. 5).

The curves shown in Fig. 5 best characterize the "illusiveness" of the Topley–Smith effect: Under the same conditions one is able to obtain the whole spectrum of rates from the minimum (curve 2) to the maximum (curve 1) by varying only the initial state of the reacting product.

These results are in good agreement with the conclusions of (8), where through thermogravimetric studies it was shown that a trihydrate is produced in a system only when its nuclei are present in a sample before the experiment. In the other case polythermal decomposition of $CuSO_4 \cdot 5H_2O$ to a mono-

FIG. 4. Dependence of the dehydration rate of $CuSO_4 \cdot 5H_2O$ upon preliminary treatment of samples by water vapor. Treatment time, 70 hr at pressures 12 (1), 15 (2) and 17.5 Torr (3). Temperature, 50°C. Decomposition conditions, dry helium.
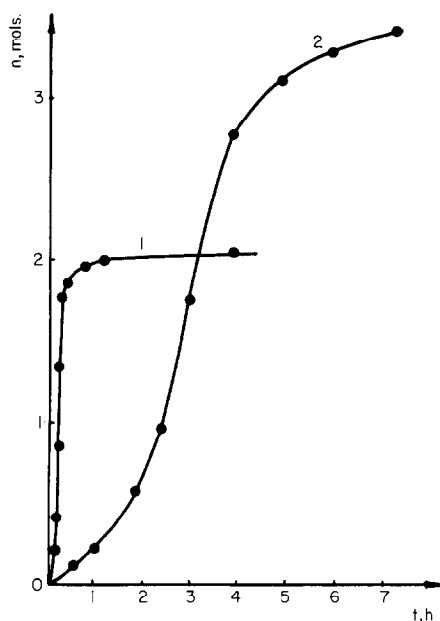
hydrate occurs in one stage both *in vacuo* and in water vapor atmosphere.

Discussion

The Topley–Smith effect is, without doubt, the most important feature of dehydration reactions, owing to which they differ from the other reactions of thermal decomposition. By reconsidering reaction scheme (3) one can conclude that if the proposed explanation is valid, then the Topley–Smith effect must hold for all the reactions in which the following sequence of transformations occurs:

$$A_{solid} \xrightarrow{B^x_{solid}} B_{solid} + (C_{gas}), \qquad (4)$$
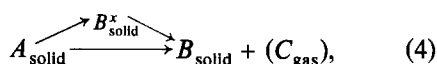
where B^x_{solid} is the intermediate metastable compound (under experimental conditions). B^x_{solid} and B_{solid} must not necessarily differ in composition: They can be different crystalline modifications of one solid compound. It is important that an intermediate metastable state can appear in the system, into which the rate of transfer is higher than that in the final state, owing to the Ostwald rule.

An interpretation of the Topley–Smith effect similar to the present one was suggested earlier by de Hartoulari and Dufour (9), also taking into account the appearance of intermediate products in a system. However, a quantitative test of their hypothesis led to disagreement with experiment because the authors used the "thermodynamic" dependence of the reaction rate on oversaturation in the system.

In considering studies of the Topley–Smith effect known today (they are analyzed in (10)), one notes that for some systems, such as $MgSO_4 \cdot 4H_2O$ and $MgCrO_4 \cdot 5H_2O$, the validity of scheme (4) can be assumed, as intermediate phases have been discovered in them (2, 11, 12). However, there are systems, e.g., $Li_2SO_4 \cdot H_2O$ and $CuSO_4 \cdot 3H_2O$, in which dehydration occurs in one stage without the formation of intermediate phases. Serious

systematic investigations are needed to test whether the mechanism (4) is common.

It should be noted that in the comparison of rates of nuclei growth (Fig. 3) with the velocity of the boundary propagation (Fig. 2), we believe that the dependence of the dehydration rate on water vapor pressure was predominantly determined by the growth of nuclei and considerably less by their formation. Evidence for this belief is provided by the Topley–Smith curves obtained by the method of stage separation (10). However, the possibility of the participation of nucleation processes during subsequent stages cannot be completely excluded, as in our experiments we observed mutual transformations of nuclei during the transfer from higher pressures to vacuum and back. For example, elliptic nuclei of a trihydrate stopped growing when the pressure became lower than 1 Torr at 50°C; somewhat later, star-shaped monohydrate nuclei appeared at the boundary.

Pressure dependence of the kinetics of nuclei growth (Fig. 3) points to the existence of considerable differences of the dehydration mechanism for reactions *in vacuo* and water vapor—differences which cannot yet be explained. One notes that, at large deviations of a system from equilibrium, the inverse reaction is not always essential, resulting in growth rate independence of the pressure of water vapor.

In conclusion we can say that the proposed approach to the interpretation of the Topley–Smith effect may appear more efficient for other systems as well, because it is based on the investigation of real kinetic characteristics of topochemical reactions.

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