Thermochimica Acta, 29 (1979) 115–119

STUDY OF THE PRODUCTS OF THE DEHYDRATION REACTION OF $CuSO_4 \cdot 5H_2O$ IN X-SHAPED AND ELLIPTIC NUCLEI

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(Received 6 March 1978)

ABSTRACT

The products of the dehydration of $CuSO_4 \cdot 5H_2O$ under different conditions have been studied by the methods of local X-ray diffraction analysis and EPR. It is shown that the dehydration in vacuo when X-shaped nuclei are formed proceeds through the formation of an intermediate product having a monohydrate composition and a crystalline lattice close to the initial lattice of the pentahydrate. Then the amorphization and crystallization of $CuSO_4 \cdot H_2O$ follows. When dehydration occurs in water vapour through ellipsoidal nuclei the structure of the trihydrate formed is oriented relative to the initial structure of $CuSO_4 \cdot 5H_2O$.

INTRODUCTION

The dehydration reactions of crystallohydrates present a convenient model for studying the kinetics and mechanism of topochemical reactions. Of all the crystallohydrates the copper sulphate pentahydrate is of special interest since it shows nearly all peculiarities that make the process of dehydration so specifically complicated: the Topley–Smith effect, formation of intermediate hydrates, as well as of amorphous and crystalline products[1].

Dehydration of $CuSO_4 \cdot 5H_2O$ proceeds through formation and growth of nuclei. When dehydration occurs in vacuo ($P_{H_2O} < 10^{-2}$ mm Hg) the nuclei have an X-like shape (star-shaped)[2]. As the water vapour pressure increases ($P_{H_2O} > 1$ mm Hg, $T = 50\,°C$), elliptic nuclei are observed to form and at the same time the X-shaped ones become rounded[2, 3]. Elliptic nuclei probably consist of crystalline trihydrate and the round ones, of crystalline monohydrate[3, 4]. Qualitative study of the product with the X-shaped nuclei have shown it to be X-ray amorphous monohydrate of copper sulphate[5]. The X-ray patterns show only faint lines of pentahydrate which were connected with undecomposed residue. When heated in vacuo to 100°C the product obtained was crystallized into normal stable monohydrate.

It should be noted that in several cases there was disagreement between the data of structural analysis and the sample composition obtained from gravimetric and gas analysis[6]. The results obtained were regarded by the authors as a desynchronisation between the chemical and the structural stage of the process. The technique of the experiment, however, shows this conclusion to be somewhat hasty[7].

EXPERIMENTAL AND RESULTS

The method of local X-ray diffraction used in the present work makes it possible to obtain more reliable data on the reaction products in different nuclei.

Use was made of the unfiltered radiation of the copper anode of a YPC-70K apparatus. A collimator was used to obtain a beam with a diameter of 250 mcm which is much smaller than the sizes of the nuclei dealt with. Monocrystals up to 0.5 mm thick were fixed, using an optical system, with the face (110) perpendicular to the beam.

X-ray patterns of elliptic nuclei taken just after the process of dehydration was stopped represented Debye rings with non-uniform intensity distribution which indicates the product orientation. To reveal this orientation a series of X-ray patterns was made with a sample placed in different positions. As a result, polar figures were constructed for three planes — (002), (110) and (111) — showing the distribution of face normals in space. They were used to determine the orientation of the axes of trihydrate cells with respect to those of the crystal lattice of initial $CuSO_4 \cdot 5H_2O$[8]. The angular disorientation amounted to 80–110°. However, the prevalent orientation

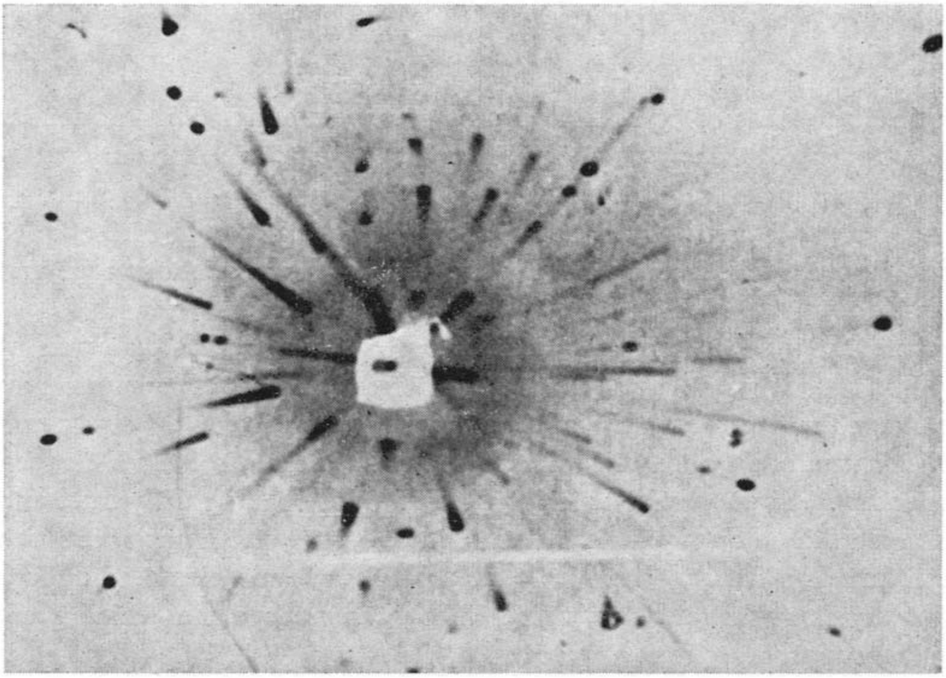

Fig. 1. X-ray pattern of the product of dehydration of $CuSO_4 \cdot 5H_2O$ in vacuo at a temperature of 50°C.

of $CuSO_4 \cdot 3H_2O$ with respect to $CuSO_4 \cdot 5H_2O$ is as follows: the *a*-axis of trihydrate is perpendicular to the direction (110) of pentahydrate, the *b*-axis of trihydrate is parallel to (110) pentahydrate and the *c*-axes are parallel to each other. The values of interplanar distances obtained coincide well with those known for trihydrate.

Thus it has been shown that in the process of dehydration oriented crystallization of the reaction product — trihydrate — occurs on the initial matrix of copper sulphate pentahydrate.

X-ray patterns of X-shaped nuclei taken immediately after a reaction stopped presented the diffraction picture in the form of long "tails" stretched towards the centre (Fig. 1). This picture can be given by an ensemble of poorly disoriented crystallites. The angles of disorientation were 5–15°. The traces of the characteristic

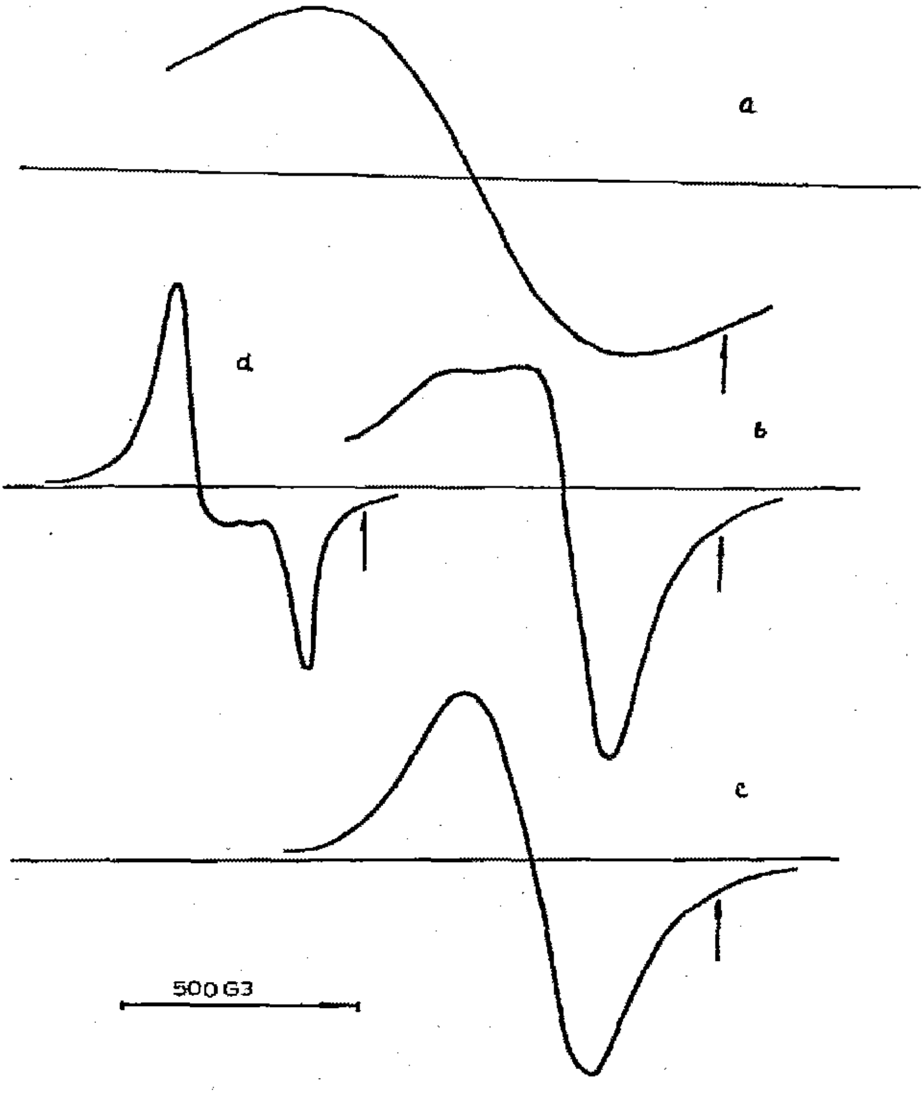

Fig. 2. EPR spectra of the products of dehydration of $CuSO_4 \cdot 5H_2O$. a, $CuSO_4 \cdot H_2O$ (pseudostructure); b, $CuSO_4 \cdot 3H_2O$; c, $CuSO_4 \cdot H_2O$ (crystalline); d, $CuSO_4 \cdot 5H_2O$ initial, for comparison. The arrow marks the position of the line of the standard substance — diphenylpicrilhydrazine.

irradiation on the "tails" were used to calculate part of interplanar distances. The obtained d_{hkl} are close to the interplanar distances in the structure of pentahydrate. A few hours later the picture observed disappears and in about 24 h there appear rings of crystalline monohydrate.

The above diffraction picture (Fig. 1) could be attributed to the X-ray beam overlapping the edge of the initial pentahydrate greatly distorted by a nucleus. Comparison of Laue X-ray photographes shows that pentahydrate gives much fewer "tails" than Laue reflexes. Besides, the "tails" do not represent an uninterrupted continuation of Laue reflexes. One can therefore assume the observed diffraction picture to be due to a "pseudostructure" — a phase with the composition of monohydrate and a crystalline lattice close to that of pentahydrate.

$CuSO_4 \cdot 5H_2O$ is known to be a chain sulphate. The water molecules from the coordination sphere of ions Cu^{2+} do not participate in the building of chains; but their hydrogen bonds, alongside those of uncoordinated molecules of water, take part in uniting the chains into one structure[9]. However, the contribution of uncoordinated water molecules to the joining of chains is far greater. It allows us to suggest that four molecules are removed from the coordination sphere of the copper ion. In this case the coordination of the ion Cu^{2+} will be performed by two couples of oxygens of the SO_4^{2-} — groups distanced at 2.4 and 2.75 Å. A direct exchange interaction must be observed in a pseudostructure with such a coordination of copper ions.

Fig. 2a shows the EPR spectrum of a sample obtained by dehydration of a pentahydrate at $P_{H_2O} = 10^{-2}$ mm Hg and $T = 50°C$. The spectrum practically does not change in the temperature range 77–300 K.

DISCUSSION

The line width recorded in the EPR spectrum of the pseudostructure cannot be explained by dipole–dipole interaction alone, since at the same distances between copper ions the width of the EPR spectrum lines in pentahydrate amounts to $\simeq$ 15 Gs and the EPR spectrum lines of crystalline trihydrate (Fig. 2b) and crystalline monohydrate (Fig. 2c) are essentially narrower than the line of the pseudostructure despite the short distances between copper ions. The main contribution to the line width appears to be made by direct exchange interaction.

Exchange-bound couples and triplets of ions play an important part in energy transfer from a spin-system to lattice vibration[10, 11]. The efficiency of this process, determining to a great extent the line width, can be expected to increase with the growing number of exchange-bound ions as is the case in the pseudostructure.

An anomalous line width can also be observed when a strong exchange interaction lifts a ban on the transitions $\Delta M = 0, \pm 2, \cdots$, which in the final analysis not only leads to widening of the line, but also shifts the g-factor[12]. There is really a shift of the g-factor in the EPR spectrum of the pseudostructure as compared with the initial pentahydrate; it amounts to 0.14.

The formation of the intermediate product $CuSO_4 \cdot H_2O$ with a structure close to that of $CuSO_4 \cdot 5H_2O$ allows us to explain a number of experimental facts. For example, the growth rate of X-shaped nuclei is known[4] to greatly depend on the water vapour pressure. It becomes understandable if one takes into account the possibility of the inverse reaction of the pseudostructure with gas phase water molecules which results in closing the channel for the removal of water from a crystal.

The formation of pseudostructures in topochemical reactions has already been observed earlier in the dehydration of $MoO_3 \cdot H_2O$[13], $Ba_2C_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$[14] and in some other instances.

Consequently, the formation of pseudostructures in this kind of process appears to be rule rather than exception. It is an intermediate stage in many reactions and it is only the instability of there kinds of structure in most cases that does not allow their unequivocal identification.

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