JOURNAL OF SOLID STATE CHEMISTRY **28**, 1-12 (1979)

Study of a Lacunary Solid Phase
II—Morphological and Kinetic Characteristics of its Formation

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Received April 5, 1978; in revised form July 5, 1978

The morphological changes which take place during the formation of the lacunary phase $\alpha H_2C_2O_4 \cdot BaC_2O_4$ by isothermal dehydration of the oxalate $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$, are characteristic for dihydrations of hydrates which, with water vapor, form a divariant system.

They show that the transformation affects the entire bulk of the solid from the very first moments of the reaction. The dihydrate crystal undergo a very regular fragmentation and the pseudomorph appears as a stacking of microcrystals whose shape and dimensions are unique and independent of the size and habit of the initial crystals.

The kinetic characteristics of the reaction show that the microcrystal dimensions do not depend on dehydration rate, they enable the precise role of crystalline faces in gas evacuation to be evaluated.

The origin of fragmentation, the microcrystal habit produced, the anisotropy of transformation of the crystalline faces and the process of water elimination are explained by means of structural considerations.

Introduction

In a preceding paper (*1*) we have described the thermodynamic and crystallographic characteristics associated with the formation of a stable lacunary phase $\alpha H_2C_2O_4 \cdot BaC_2O_4$[1] obtained by isothermal dehydration of barium acid oxalate $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$.[1]

An infinite number of nonstoichiometric hydrates (designated as $H_2C_2O_4 \cdot BaC_2O_4 \cdot \varepsilon H_2O$[1] with $0 < \varepsilon < 2$) can be prepared in particular conditions which identifies the "hydrate–vapor" system studied as divariant.

The stacking in the α anhydrous salt differs very little from that of the dihydrate.

In this paper, we will describe in detail the typical morphological changes caused by this particular dehydration as well as the kinetic characteristics of lacunary phase formation. Then, by analyzing these observations in the light of structural data on the 1/1/2 and α1/1/0 salts, we will give a description of the transformation mode for the oxalate stacking. In particular we will be concerned with the process of formation and the habit of the α anhydrous microcrystals, as well as the way in which the gas leaves the solid.

Materials and Methods

Morphological modifications of 1/1/2 oxalate monocrystals during the reaction 1/1/2 → α1/1/0 were studied along with the analysis of kinetic characteristics of this transformation such as to emphasize fundamental aspects of gas elimination and

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[1] For convenience these compounds will be written α1/1/0, 1/1/2 and 1/1/ε respectively.

0022-4596/79/040001-12$02.00/0

Printed in Great Britain

of lacunary phase formation. For this three experiments were carried out:

1. The isothermal dehydration is effected slowly using equilibrium stages; thus a succession of hydrates is obtained which contain less and less water [see part I, (*1*)]. It has been possible under these conditions to follow the progressive transformation of crystals.

2. The isothermal dehydration is performed abruptly. The dihydrate is first maintained at 50°C under 20 torr (within its stability domain), then, with the temperature fixed at the same value,[2] it is rapidly subjected to the vapor pressure of ice at −193°C. The weight loss curves are recorded and from them, the (α, time) plots and kinetic characteristics of the reaction (kinetics of the first dehydration) are deduced.

Then, assuming perfect reversibility of this reaction we have measured the rehydration rate. This is done by subjecting the α1/1/0 oxalate to 20 torr, with the temperature kept constant at 50°C. Finally, after deactivation of the sample by return to ambiant temperature over 24 hr, a second dehydration was carried out under the same conditions as the first (kinetics of second dehydration).

3. In the third experiment, the rapid isothermal dehydration is stopped at different levels of transformation so as to observe the state of the crystals.

These experiments were performed separately on two types of crystals in which the 1/1/2 monoclinic oxalate exist, namely acicular and prismatic forms. The indexation of their principal faces were determined by goniometry (Fig. 1).

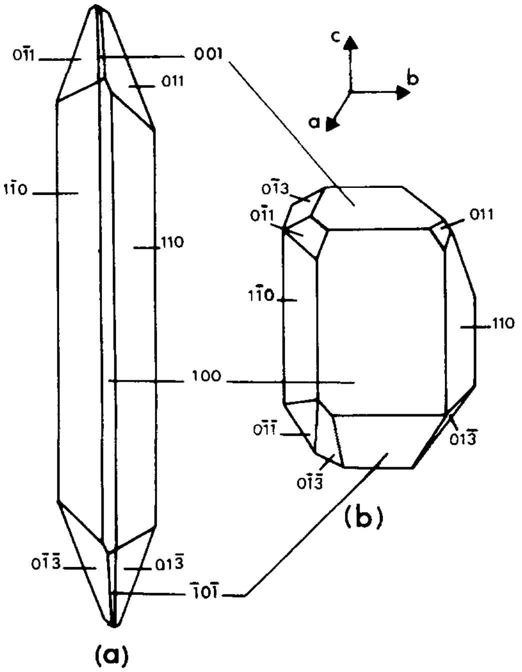

FIG. 1. Crystalline forms of the $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$ oxalate. (a) acicular crystals, (b) prismatic crystals.

A preparation of crystals of the same form was sieved (eleven sieves −1000, 750, 510, 355, 250, 180, 125, 90, 63, 45, 37.5 μm were used). Each sample analyzed for TGA was then prepared by removing from the different sieved fractions about 18 mg of well formed monocrystals not showing any water of inclusion. The distance ϕ between the 100 faces of each crystal was measured, the mean ϕ value being the sample's dimensional characteristic.

Morphological observations were made by light microscopy and scanning electron microscopy. Complementary information was obtained from X-ray diffraction (rotating crystal and Weissenberg patterns).

Results

Morphological Transformation Characteristics Observed during Slow Dehydration

Morphological transformations are seen as cleavages which affect the entire bulk of the crystal; but the sequence of their appearance depends on the crystal size. For crystals of

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[2] The temperature to which the reaction tube is subjected is kept at 50°C but we are aware (*2, 3*) that the temperature of the solid during the transformation is lower than this value because of the reaction's endothermicity.

mean diameter 250 μm the changes can be described as follows:

From the first moments of the dehydration a first type of cleavage is formed. Over the entire extent of 110 faces regularly spaced rectilinear striations appear. They make an angle of 116° with the crystal's longitudinal direction [001] (Fig. 2a) (this is the angle β of the 1/1/2 oxalate monoclinic unit-cell).

At the same time, on the 100 faces a longitudinal cleavage is observed (Fig. 2b).

As the reaction progresses these two types of stratifications become more pronounced and a third cleavage appears. This opens out on to the 110 faces and makes an angle of about 94° with the direction of the first cleavage (Fig. 2c).

During transformation the crystal looks like a pile of lamellae; this is easily visible on 100 faces (Fig. 2d).

The elimination of the last traces of water causes a better individualization of these lamellae (Fig. 2e).

These observations reveal three particular features of the transformation:

1. The entire bulk of the crystal is affected by the cleavage from the very first moments of the reaction.
2. The aspect of the two types of face is very different.
3. Water loss causes the transformation of a monocrystal into a compact assembly of well individualized "microcrystals"[3] which are perfectly oriented with respect to one another and with respect to the habitus of the parent crystal.

This last aspect is confirmed by the diffraction patterns which are made on 300 μm diameter crystals placed in Lindeman tubes and slowly dehydrated [see part I (*1*)]. The patterns obtained are the same as for the dihydrate crystal. There is only a diffuse appearance to the spots which reveals the pseudomorph's mosaic character.

We have examined microcrystal dimensions obtained from dihydrate monocrystals of different size (ϕ) and habit. We have observed:

That whatever the habit and for values of $\phi > 50$ μm the form and dimensions of the anhydrous microcrystals are unique.

Table I indicates mean values of the dimension D (Fig. 3) for microcrystals as measured from scanning electron micrographs for 110 faces of acicular crystals.

If the dihydrate crystals have a diameter $\phi < 50$ μm their complete dehydration to the α anhydrous salt alters neither their brilliance nor their transparency and the diffraction spots are not diffuse.

Kinetic and Morphological Characteristics of Lacunary Phase Formation by Rapid Dehydration

Kinetic Characteristics of the First Dehydration

Figures 4a and 4b show the α(time) plots recorded on acicular and prismatic crystal samples.

In the case of acicular crystals the curves include a linear part which shortens as the size of the 1/1/2 crystals increases. It seems to be a period of acceleration of water loss for the biggest ϕ values (curves 5, 6 and 7, Fig. 4a); the weightloss at the end of this period always corresponds to a value of α less than 0.15.

In the case of prismatic crystals the curves are sigmoïd and have an inflexion point close

TABLE I

ϕ mean (μm)	80	150	300	1000	2000
D mean·(μm)	4.3	4.9	4.7	4.4	4.3

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[3] In using the term "microcrystals" or "crystallites" here to designate the small blocks which make up the pseudomorph, we recognize that we have not been able to demonstrate that each of them is individually a coherent diffraction domain for X ray or electrons and that therefore its use is a matter of convenience.

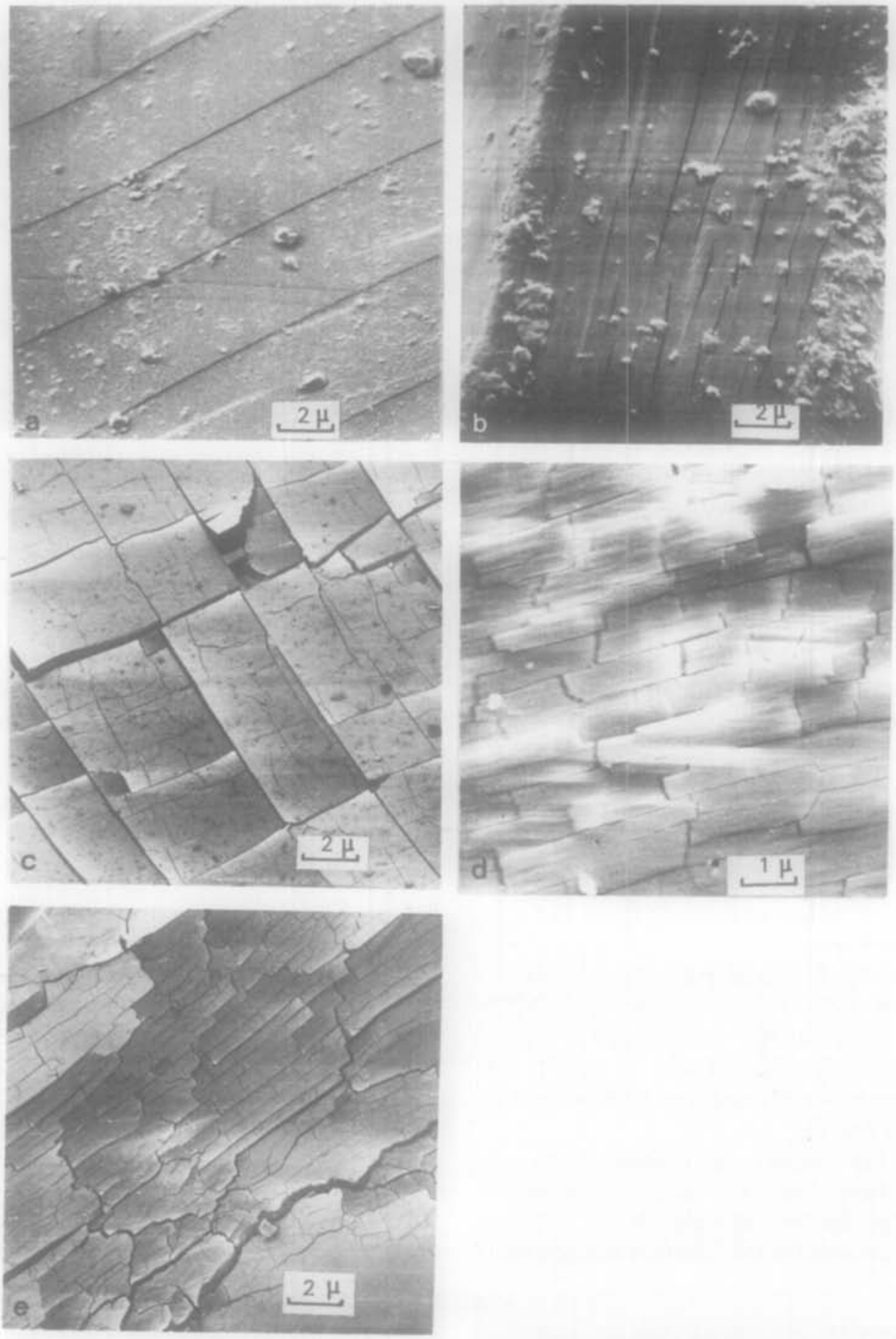

FIG. 2. Consecutive morphological changes in the slow isothermal dehydration for acicular crystals. (a) Linear striations appearing on a 110 face during the first moments of dehydration. (b) Fissuration of a 100 face ($\alpha = 0.05$). (c) Small plates of $\alpha 1/1/0$ oxalate observed on a 110 face. (d) 100 face of a totally dehydrated 1/1/2 crystal. (e) Stacking of $\alpha 1/1/0$ microcrystals seen from a section of a totally dehydrated crystal.

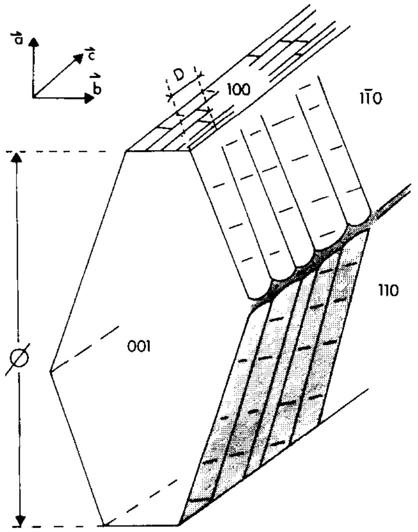

FIG. 3. Aspect of 100 and 110 faces as they appear at the end of the dehydration.

to $\alpha_i = 0.25$ whatever the value of ϕ. The dehydration rate is a decreasing fonction of ϕ and that of prismatic crystals measured at the inflexion point of $\alpha(t)$ curves $(\alpha_i \simeq 0.25)$ is generally higher than that of acicular crystals measured at a similar α value $(\alpha \simeq 0.3)$.

Moreover, the change in shape of the α(time) plots observed during the dehydration of 1/1/2 oxalate needles (Fig. 4a) is well illustrated by the function $V_M/V_{0.5} = f(\log \phi)$ (Fig. 5), where V_M is the maximum rate i.e. that corresponding to the linear part of the curves, $V_{0.5}$ being the rate measured at $\alpha = 0.5$. This representation, although arbitrary, can be justified if the following two experimental facts are taken into account:

1. If two experiments are carried out under identical conditions except the rate at which the vapor pressure is decreased from 20 torr to that of ice at −193°C, one sees that the reaction rate measured at varying α values are different but that the ratio $V_M/V_{0.5}$ stays the same.
2. The function $V_{0.5} = f(\log \phi)$ is linear for almost all ϕ values (Fig. 8).

Consecutive Morphological Changes in the First Dehydration

The observations made for different α values of kinetic plots show that:

For either crystalline form and for any initial crystal size the entire bulk of every crystal is affected from the very first moments of the reaction. Figure 6a shows the aspect of a crystal of diameter ϕ about 750 μm for $\alpha = 0.08$.

Anisotropy of transformation of the crystalline faces is evident: 110 faces are much more disturbed than the 100 type.

The microcrystals produced during the induction period have the form and dimensions (within our limits of detection) that we have found during slow dehydration. This form and these dimensions do not seem to be changed after complete dehydration (Fig. 6b).

Macroscopic changes of the habit are obtained for both crystalline forms for $\alpha < 0.20$, but they are different in that:

1. For small-sized acicular crystals ($\phi <$ 250 μm) the abrupt loss of water causes a longitudinal rent along the junction of the 110 faces; however the crystals remain whole (Fig. 6c).
2. If the acicular crystals are of greater diameter they break up into characteristically shaped pieces (Fig. 6d) their number increasing in proportion to the initial crystal size.
3. On the other hand, prismatic crystals, for all diameters, remain whole during the transformation (Fig. 6e).

Kinetic Characteristics of Rehydration and of the Second Dehydration

These characteristics are the same for both crystalline forms of the 1/1/2 oxalate before the first dehydration. They can be summarized as follows:

The rehydration rate is independent of the initial diameter ϕ (Fig. 7).

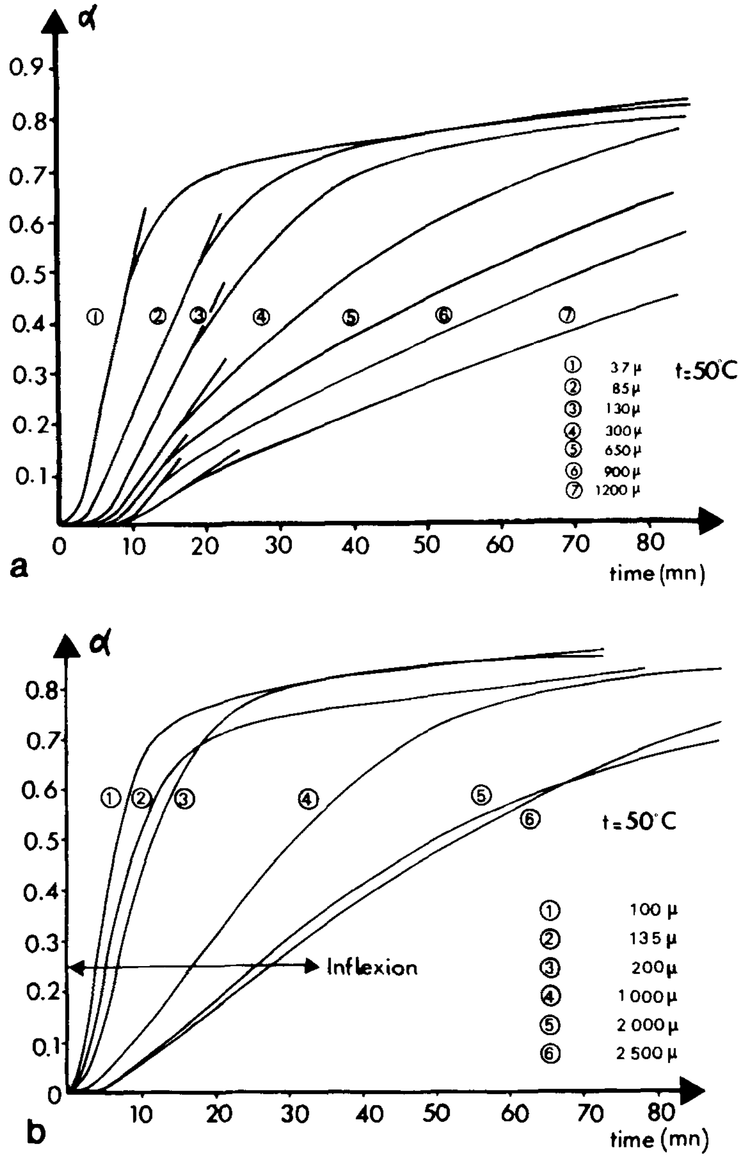

FIG. 4. Influence of diameter ϕ on the isothermal dehydration rate (temperature 50°C, vapor pressure of ice at −193°C); (a) for acicular crystals, (b) for prismatic crystals.

The α(time) plots which characterize the second dehydration are all sigmoïd and the rate evaluated at different α values depends of the initial diameter as indicated by the curve Ⓑ in Fig. 8.

A result of striking interest is provided by comparison of the $V_\alpha = f(\log \phi)$ curves for the two successive dehydrations. Figure 8 for acicular crystals, shows that for $\alpha = 0.5$, the intersection point's abscissa corresponds to $\phi_1 \simeq 3.3$ μm. Now as the values in Table II indicate, ϕ_1 depends neither on the α value nor on the crystalline form. It will be noted that the intersection point's ordinate, V_1, varies with α but does not depend on the initial habit.

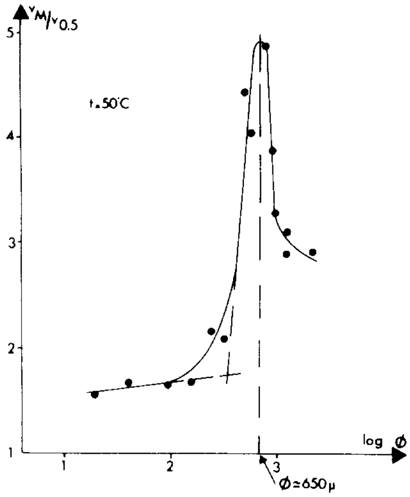

FIG. 5. $V_M/V_{0.5} = f(\log \phi)$ curve.

Discussion

The foregoing results sharply delineate the essential characteristics of the morphological changes which $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$ oxalate crystals undergo during dehydration to the α anhydrous salt:

Whatever the rate of water removal (dehydration by equilibrium stages or abrupt dehydration).

Whatever the dimensions and the habit of the dihydrate monocrystals lacunary phase formation causes a remarkably uniform fragmentation of these crystals and the pseudomorph appears like a stacking of identical microcrystals of well defined shape and size.

We shall discuss more especially the three following points:

First, the relation between the kinetic characteristics of the transformation and the state of division of the solid; second, the habit of the anhydrous microcrystals; third, the water elimination process.

TABLE II

	Acicular crystals		Prismatic crystals
α	0.5	0.3	0.25
ϕ_1 (μm)	3.3	3.2	3.3
V_1	2.8	5.9	5.8

State of Division of the Pseudomorph and Kinetic Features of Transformation

The determination of the rate of the first and second dehydrations and of the rehydration gives indirect evidence for the regularity of the solid's transformation.

Indeed, the coordinates ϕ_1 and V_1 of the $V(\phi)$ curves' intersection (Fig. 8) show that if the initial dihydrate crystals had diameter ϕ_1 the two dehydration rates would be equal (the initial morphology not being affected by the early loss of water). One can deduce that, first, ϕ_1 also represents the mean dimension of the anhydrous α oxalate microcrystals produced during the first dehydration and second, that V_1 represents the rate of the second dehydration for all the samples. Two observations favor these deductions:

The value of ϕ_1 (3–4 μm) is of the same order as the dimension measured from electron micrographs (Table I).

The rehydration rate is independent of the initial size of the 1/1/2 crystals (Fig. 7).

On the other hand, the fact that the rate of the second dehydration still depends on the initial ϕ value may appear contradictory. We do not think so, however; rather we believe that this phenomenon constitutes strong evidence for the compactness of the microcrystal assembly in the pseudomorph. The qualitative explanation of this contradiction would be as follows:

The rehydration—the vapor pressure used to bring about rehydration is necessarily higher than that between α anhydrous microcrystals and thus water molecules do not accumulate between these blocks. Each microcrystal acts as if it were separate; consequently its size alone and not the pseudomorph's is important.

The second dehydration—the phenomenon is the inverse of the preceding one. Water

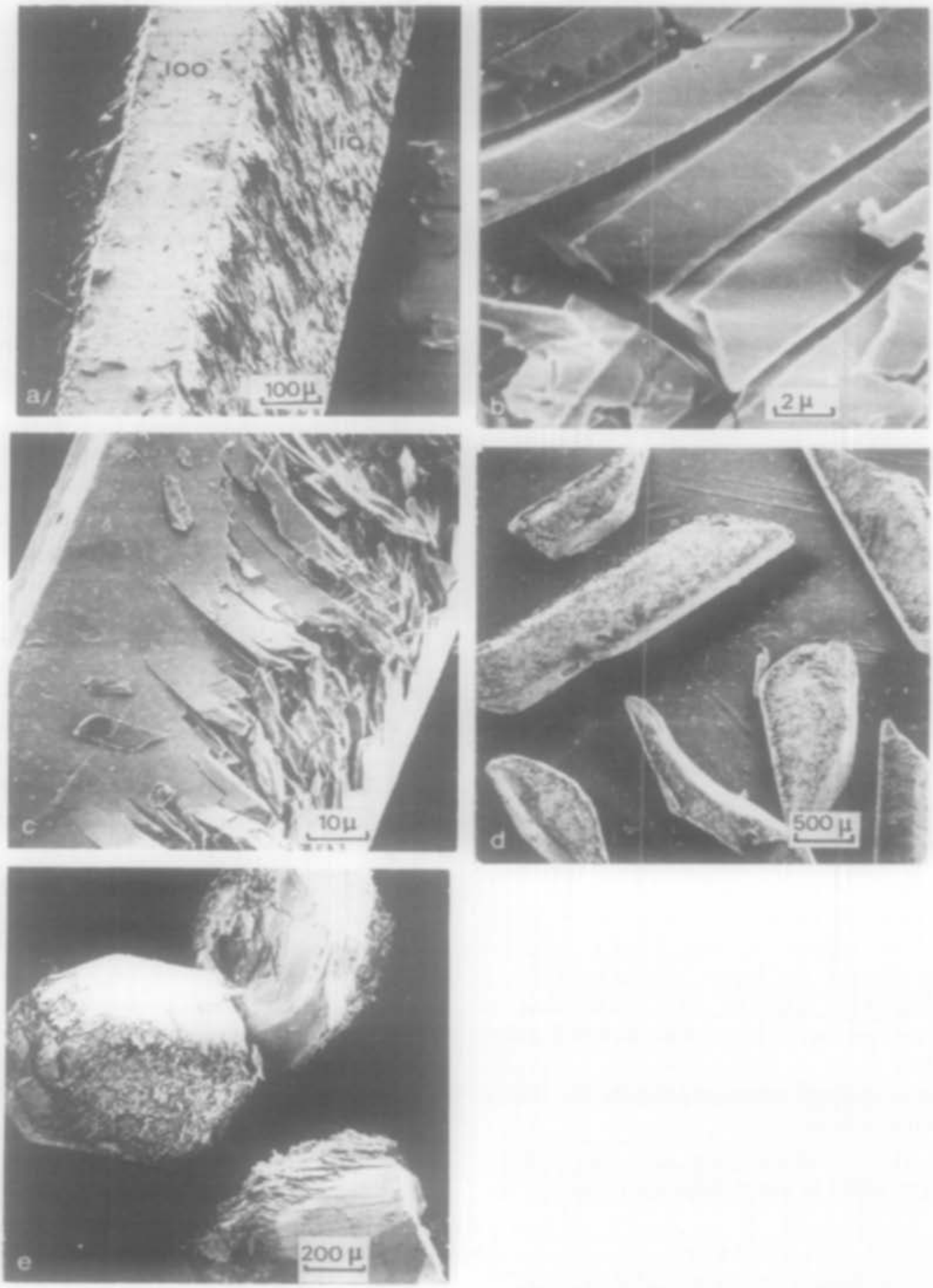

FIG. 6. Consecutive morphological changes in the first rapid isothermal dehydration for acicular crystals (a, b, c, d) and prismatic crystals (e). (a) Anisotropy of transformation of the crystalline faces (acicular crystal $\phi = 750\ \mu\mathrm{m}$). (b) Shape of α anhydrous microcrystals obtained at the end of abrupt dehydration. (c) Longitudinal rent observed after abrupt dehydration of a small-sized acicular crystal ($\phi \simeq 250\ \mu\mathrm{m}$). (d) Characteristically shaped pieces appear during abrupt dehydration of large-sized acicular crystal. (e) Prismatic crystals, for all diameters, remain whole during abrupt dehydration.

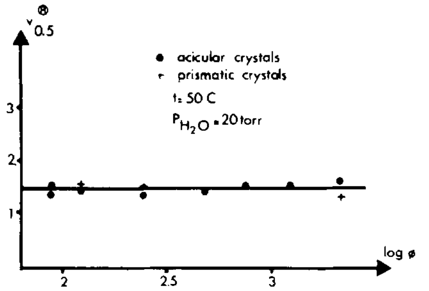

FIG. 7. Rehydration rate is independent of the initial diameter and of the 1/1/2 crystal's habit.

molecules escape from the microcrystals and accumulate in the interstices and a higher pressure than that fixed in the reaction tube develops around the microcrystals. There follows, first, a lowering of reaction rate (measured < theoretical rate, curves Ⓑ and Ⓒ Fig. 8); second, the size of the pseudomorph becomes more important (and therefore that of the original monocrystal). It is probable that the theoretical curve Ⓒ will be approached after several cycles of rehydration–dehydration.

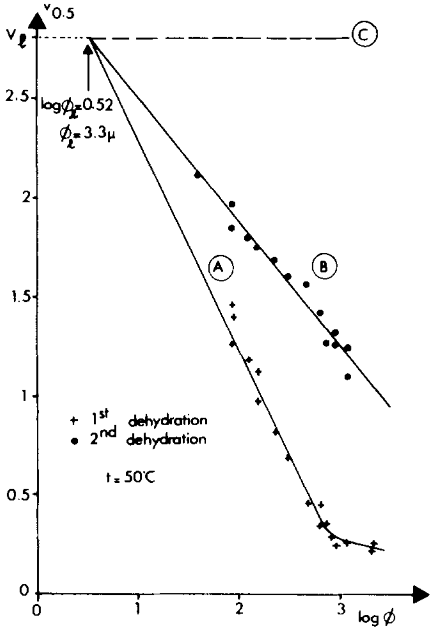

FIG. 8. Comparison of the $V_{0.5} = f(\log \phi)$ curves for two successive dehydrations for acicular crystals.

The Habit of the α Anhydrous Microcrystals

The possibility of crystal cleavage is due to the presence of atomic planes the cohesion between which is weak.

Assuming that the transformation of the dihydrate to the anhydrous lacunary structure only gives rise to small changes in unit cell parameters and to limited atomic movements [see part *I* (*1*)]; the regularity of fragmentation which accompanies this transformation must be associated with the existence of such planes in the oxalate 1/1/2 stacking.

We have analysed the orientation of the series of fissures (visible on the 110 faces) with respect to the crystal's reference-axes. This has shown that the most obvious series make an angle β of 116° with the crystal's longitudinal [001] direction. The nature of the fractures within the crystal which correspond to this series allows us to unambigously attribute it to the (001) cleavage.

The second series makes an angle of about 94° with the first. If one considers the (*xoz*) projection of 1/1/2 oxalate stacking (Fig. 9), one may state that the $(20\bar{1})$ plane which makes an angle of 98° with the (001) (i.e. first

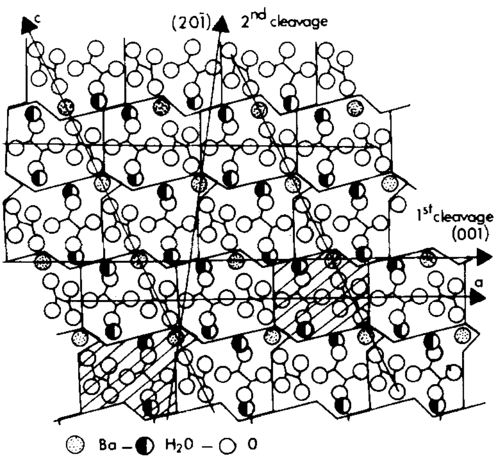

FIG. 9. The (001) and $(20\bar{1})$ cleavages coincide with planes containing Ba^{2+} ions and water molecules. Each "construction unit" (dashed area) contains the grouping formula $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$.

obvious cleavage) probably corresponds to the second cleavage.

For the third series of fissurations (visible on the 100 faces), which cannot be seen at the same time as the preceding series, examination of the structure's (*xoy*) projection (Fig. 10) leads us to consider this as corresponding to the (110) cleavage plane. This choice is justified by the longitudinal orientation (i.e. parallel to [001] direction) of these fissures, by the existence of natural faces of the same indices, and by the plate-like form of the microcrystals detaching themselves from these 110 faces.

Thus, the stacking's three planes of least resistance coincide with those containing the cations and the water molecules. They cut the stacking, without touching the ($H_2C_2O_4 \cdot BaC_2O_4$) groupings, into an infinite number of small blocks of perfectly defined form. This phenomenon recalls the well known pyroxene–amphibole transformation (*4*).

Figures 11 and 12 show the transformation of a 110 face and the habit of an α anhydrous microcrystal as it appears in the pseudomorph; we can index its faces: 001–20$\bar{1}$–110.

In order to define precisely the microcrystal size it would be necessary to evaluate the surface energy σ_{hkl} associated which each crystalline face resulting from the cleavage. Calculation of σ_{001}, $\sigma_{20\bar{1}}$, σ_{110} is possible if the strength of interaction between atoms or neighboring particles in the crystal is known. We will limit ourselves to making the qualitative remark that, the size and direction of

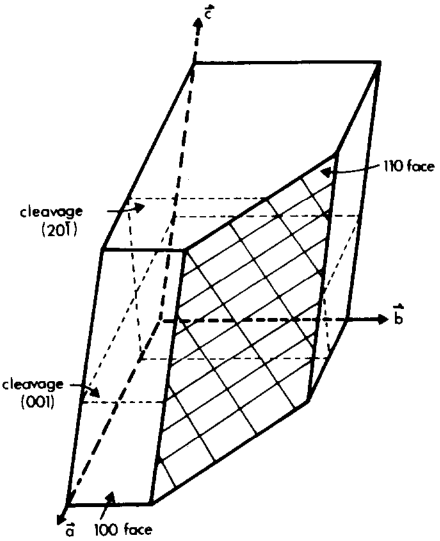

FIG. 11. The first and second cleavage planes and the transformation of the 110 natural face.

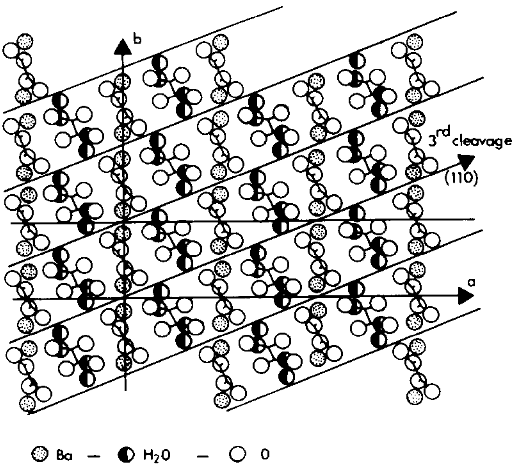

FIG. 10. The third cleavage plane is parallel to the (110) plane.

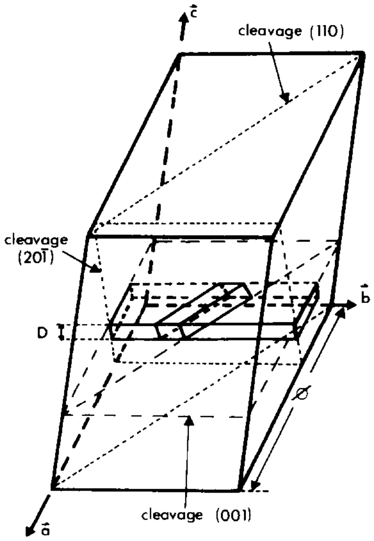

FIG. 12. The three cleavage planes and the habit of an α anhydrous oxalate microcrystal.

the strains which appear in the initial crystal are responsible for the dimension and form of the anhydrous microcrystals. The breaks which detach them are repeated for a number of "units of construction" (Fig. 9). which varies according to the three directions perpendicular to the (001), (20$\bar{1}$), (110) planes. Thus, the platelet microcrystal form is explained by the fact that the atomic movements (thus the strains) are greater for [100] and [010] directions than for the [001] direction [see part I (*1*)].

Remark. The strains resulting from water loss in crystals with $\phi < 50$ μm do not cause cleavages in the bulk but certainly introduce such defects as staking faults dislocations . . . which macroscopic observations cannot reveal and thus, the crystals seem to be unaffected by the dehydration.

The Water Elimination Process

Microscopy observations show (Fig. 8a) that the 110 faces are much more affected by water loss than the others (100 faces for acicular and 100–001–101 for prismatic crystals). This anisotropy of transformation suggests the probability that these faces do not play the same role in gas elimination. Comparison of kinetic characteristics of the first dehydration for the two crystalline forms enables us to clarify this point:

Examination of the 1/1/2 habit reveals that the ratio between the area of the two faces 100 and 110, S_{100}/S_{110}, is clearly different for the two crystalline forms. If acicular and prismatic crystals of the same diameter ϕ are compared, the 110 faces occupy about 70% of the total surface for acicular crystals, while for prismatic crystals this percentage is only about 40%. Now, it appears from the shape of the α(time) plots (Figs. 4a and 4b) and the rate in each case that the prismatic crystal dehydration is more rapid.

We have observed for the series of acicular samples that the ratio S_{100}/S_{110} was greatest for crystals whose diameter is close to 700 μm. This value corresponds approximately to the ϕ value at the maximum of the $V_M/V_{0.5} = f(\log \phi)$ curve (Fig. 5); in other words, the dehydration rate varies as the 100 face area.

It may be noted also that the part of the α(time) curve giving maximum rate (Fig. 4a) coincides with the appearance of characteristic breaks which create faces similar to 100 faces (Fig. 6d).

Consequently, the kinetic characteristics, exactly like the morphological considerations, show conclusively that gas elimination takes place mainly at 100 faces; also the observation shows very clearly that the breaking up of the entire crystal mass is already accomplished for α close to 0.20. It remains, therefore, to specify how the water leaves the microcrystal formed and how it escapes from the pseudomorph.

Of each of the microcrystal's six faces, it is probably by the 110 faces that the water molecules will leave the stacking. It is indeed upon these faces that the canals open out in which these molecules are located. By contrast, the microcrystal assembly is such that 110 faces are opposed and the funnelling of gas towards the exterior can only occur along these faces (Fig. 13). It is therefore essentially by those pseudomorph faces which make a large angle with respect to the (110) plane (100, 001, 101 faces) that water leaves the crystal. This schema explains the appearance of 110 faces under the lateral pressure of gas while this is being eliminated abruptly (Fig. 6c).

Conclusion

The system "hydrate$_{(s)}$–water$_{(g)}$" studied here is divariant and the structural transformation of the dihydrate $H_2C_2O_4 \cdot BaC_2O_4 \cdot 2H_2O$ into the anhydrous salt $\alpha H_2C_2O_4 \cdot BaC_2O_4$, only involves minor alterations of its stacking. The morphological examination of crystals during transformation demonstrates certain

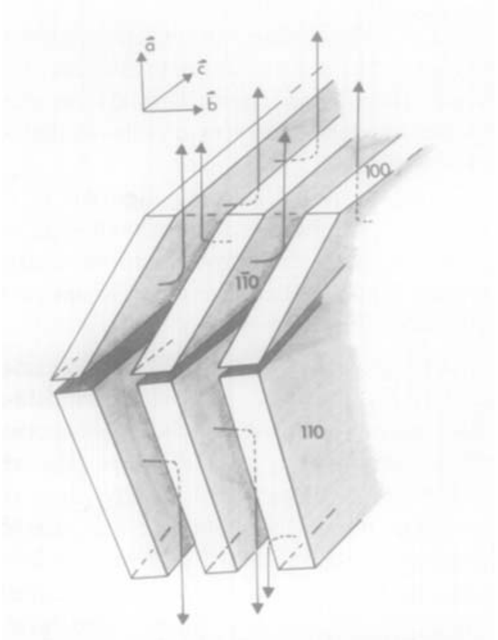

FIG. 13. It is essentially by the pseudomorph faces which make a large angle with respect to the (110) plane that water molecules leave the crystal.

modifications characteristic of this particular type of solid state reaction. It shows principally that all at once and from the very first moments of the reaction it is the entire bulk of the crystal which is affected. This phenomenon is very different from the case of compounds forming a monovariant system with the gas phase *(5–7)*.

These modifications are remarkable in that the loss of water causes a regular fragmentation of the initial solid, and that the pseudomorph appears as a compact stacking of microcrystals: the shape and dimensions of the latter are unique and independent of the size and habit of the dihydrate crystals but also independent of the percentage of transformation and of the dehydration rate.

The kinetic characteristics of the reaction corroborate the morphological observations. They show very clearly the role played by the crystalline faces in gas elimination. The comparison of reaction rates for the two successive dehydrations constitutes an indirect means of determining the microcrystal dimensions of the lacunary phase.

By analysis of the dihydrate oxalate structure the origin of the fragmentation can be described very precisely. This is associated with cleavage planes which coincide with planes containing Ba^{2+} cations and water molecules. The exact habit of the α anhydrous salt microcrystals has been determined and the anisotropy of transformation of crystalline faces explained. These considerations taken together enable a description of gas elimination to be formulated.

The study of the dehydration of barium acid oxalate constitutes an important contribution in the search for a reaction mechanism for decompositions.

The results illustrate the time-sequence of possible stages in these reactions *(1)* and give detailed thermodynamic, crystallographic and morphological characteristics associated with the formation of the intermediate lacunary phase.

Acknowledgment

The authors express their thanks and gratitude to Dr. B. Heyden for his help in translation of this paper.

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