

The Role of Dislocations in the Thermal Dehydration of Lithium Formate Monohydrate *

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The kinetics of Lithium Formate Monohydrate (LFM) dehydration (single crystal samples) has been investigated at constant temperature ($317 < T < 353$) under dynamic vacuum both optically and thermogravimetrically.

The process takes place with an induction period followed by a constant rate period. The first one is characterized by a surface nucleation which occurs mostly in connection with dislocations emerging on the (021), (110) and (010) faces and at the vertex-intersections of these planes; the second one corresponds to the advancement of a reaction interface (formed on the planes with $l \neq 0$) along the c -axis.

This topochemical model has been interpreted on the basis of the different features of the actual dislocations and of the reticular geometry of the LFM crystal.

This work, aiming at investigating the role of surface defects and reticular geometry on solid state reactions, reports the results concerning the dehydration of Lithium Formate Monohydrate (LFM), a crystal which finds application for non-linear optical devices in lasers [1].

The structure of this compound has been recently determined [2]. The lithium ion is tetrahedrally coordinated with three oxygen atoms of the formate group and one water oxygen. The water molecules, bound together by hydrogen bonds, form infinite zig-zag chains parallel to the c -axis; they are also linked to the formate group through the following links: $O(H_2O) \text{---} Li$ and $H(H_2O) \text{---} O$ (formate group).

Furthermore, Klapper has investigated the structural defects of this compound by X-ray topography [3], pointing out, besides planar defects, dislocations with Burgers vectors parallel to the [100], [010], [001] and $\langle 110 \rangle$ directions.

The present kinetic study has been carried out, employing single crystals, isothermally in the temperature range 317–353 K under dynamic vacuum [4] both by microscopic observations and by thermogravimetric measurements.

The etching technique has been employed to bring into evidence the actual dislocations, in order to investigate their influence on the nucleation.

Moreover, the heat of dehydration, the value of which was not available in the literature, has been determined.

Experimental

LFM single crystals were prepared by slowly evaporating at 303 K a solution obtained by neutralization of aqueous HCOOH (C. Erba RPE) with Li_2CO_3 (Fluka puriss.): the single crystals obtained had grown preferably along the c -axis and averaged $1 \times 2.5 \times 4$ mm. X-ray analysis and polarizing microscopy allowed us to state that the most developed faces were the following: (110), (010) and (021).

The etching tests were carried out by dipping these crystals for a few seconds into water (or a mixture water-propanol 1 : 1 by vol). Dislocation etch pits have been observed on all these faces. The etch pits on the (110) face had a rectangular basis with the longer side parallel to the [001] direction. Their centres were shifted toward the c -axis direction, thus showing [5] that the corresponding dislocation lines were not perpendicular to the plane considered (Figure 1 a, b).

On the (010) face the etch pits, again with rectangular basis and with the longer side parallel to the [001] direction, were more symmetrical and lined-up along the [100] and [001] directions (Figure 2).

The etch pits observed on the (021) face were highly asymmetrical (Figure 3).

To gain direct information on the nucleation process, a small-sized vacuum-proof reactor, adjustable on the sample holder slide of the micro-

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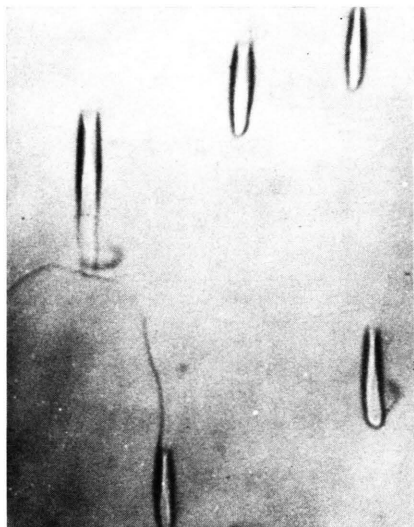


Fig. 1 a

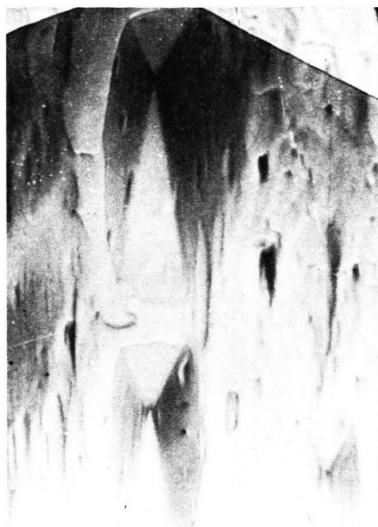


Fig. 1 b

Fig. 1. Dislocation etch pits on the (110) face. *c*-axis vertical, a) 100 \times , b) 500 \times .

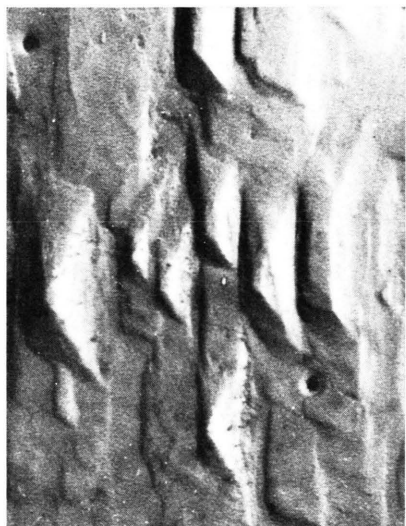


Fig. 2. Dislocation etch pits on the (010) face. *c*-axis vertical (100 \times).

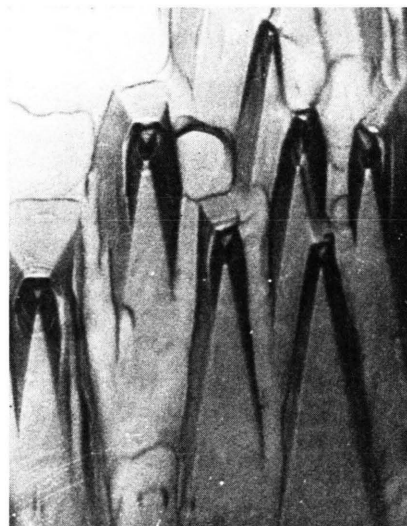


Fig. 3. Dislocation etch pits on the (021) face (100 \times). *a*-axis horizontal.

scope, was devised; the crystals were placed (at 323 K under dynamic vacuum of 10^{-4} mm Hg) at the center of the chamber, close to a thermocouple.

The thermogravimetric study of dehydration was carried out by means of a Dupont de Nemours "950 Thermogravimetric Analyzer" connected with a "900 Differential Thermal Analyzer", recording at different temperatures the weight loss vs. time; a sensitivity of 12.7 cm mg^{-1} has been used.

In order to reduce the time requested to attain the proper temperature, the original furnace was

replaced with a red light source which was controlled by a BCS "Ether" unit; this allowed to reach the working temperature in not more than 30 sec.

Furthermore the rate of interface advancement was directly measured at the optical microscope (under the same conditions as used in the thermogravimetric determinations) employing the above vacuum-proof reactor.

A large crystal was cutted along the (110), (010) and (001) planes (the former two being cleavage planes) to have samples with similar shape

and dimensions. The samples so obtained ($0.5 \times 1 \times 3.5$ mm) were used both for thermogravimetric and microscopic observations.

The enthalpy change occurring in the dehydration process was measured by means of a Perkin-Elmer DSC-2 calorimeter; with heating rates of 0.3 and 0.6 K min^{-1} a ΔH of $13.1 \text{ kcal mole}^{-1}$ has been found.

Results

Microscopic observations

The direct microscopic observation of a large number of as-grown crystals accurately selected allowed to obtain the following information:

a) The first nuclei appear on the (021) face and on the small faces with $l \neq 0$. Subsequently a few isolated nuclei form also on the (110) and (010) faces.

b) The nuclei on the (021) face did not grow significantly during this period but coalesced with the neighbouring ones to form "islets" of product uniformly scattered on the surface. The nuclei on the (110) and (010) faces were similar to one another and, unlike the preceding ones, grew considerably (Figure 4).

c) From the arrangement of the nuclei, similar to that of the etch pits, it can be thought that these nuclei form mostly in connection with the emergent dislocations.



Fig. 4. Nuclei on the (110) face. c-axial vertical ($100\times$).

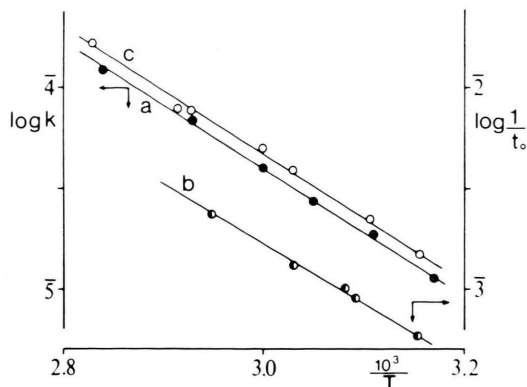


Fig. 5. Arrhenius plots: a) k_{micr} for the linear period; b) $1/t_0$ data for the induction period; c) k_{TG} for the linear period.

d) In many instances it was observed that the vertex-intersection of the (021), (110) and (010) faces is a very active nucleation site.

e) The reaction interface forms on the (021) face and on the small ones with $l \neq 0$ in all the samples considered.

On the basis of the latter information, we thought it proper to use the samples obtained by cleavage, as previously described, in order to determine the rate of interface advancement.

Such determinations were performed in the temperature range 313–349 K under dynamic vacuum (10^{-4} mm Hg). The k_{micr} values so obtained satisfy the equation

$$\log k_{\text{micr}} = 5.00 - 14,347/4.576 T$$

where k_{micr} is in cm sec^{-1} (Figure 5, curve a).

Thermogravimetric Determinations

The curves of fractional dehydration (α) vs. time (t), some of which are reported in Fig. 6, are characterized by a ($0 \leq \alpha \leq 10^{-2}$) induction period, followed by a ($0.05 \leq \alpha \leq 0.5$) linear period and finally by a decay period.

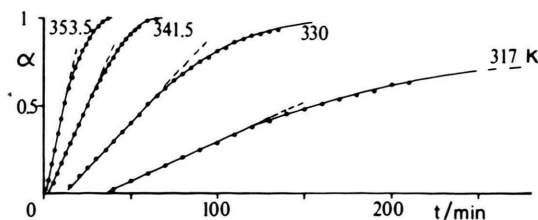


Fig. 6. Isotherms for the reaction $\text{HCOOLi} \cdot \text{H}_2\text{O} \rightarrow \text{HCOOLi} + \text{H}_2\text{O}$.

The analysis of the induction period (employing a t_0 value determined by extrapolating the linear part of the α vs. t curve) in the temperature range 317–339 K, gave an activation energy of 13.6 kcal mole⁻¹ (Figure 5, curve b).

The Arrhenius equation may be written as:

$$\log t_0 = 6.13 + 13,600/4.576 T.$$

Concerning the linear period, the kinetic constants, k_{TG} , directly obtained from the slope of the straight-lines, were expressed in cm sec⁻¹ (taking into account the shape and the size of the crystals) in order to compare them with those determined optically (k_{micr}). The pertinent values are shown in Fig. 5, curve c, as a function of $1/T$. It can be seen that the k_{micr} data are on the average some 15% lower than the k_{TG} values; such a difference is probably due to the fact that a contribution to the value of k_{TG} is given also by the process which at the same time takes place, though partially, on the external (110) and (010) planes.

The k_{TG} data satisfy the equation

$$\log k_{TG} = 5.03 - 14,282/4.576 T.$$

As for the decay period, owing to the poor reproducibility of the results obtained, a rigorous analysis of the data was not possible; anyway, the kinetic equation fitting them best is the "contracting volume" equation.

Discussion

The LFM dehydration reaction may be interpreted according to a topochemical model in which three periods are included.

a) Induction period

The results of the microscopic observations show that the dislocations emerging on the surfaces parallel to the (110), (010) and (021) faces are active nucleation sites and that the reaction interface always develops on the surfaces which intersect the c -axis. The nuclei which form on the (021) face are then autolocalizing, i. e., they cause the reaction to extend to the neighbouring parts of the crystal.

This effect can, according to Boldyrev [6], be ascribed, for the dehydration reactions, to the influence of three factors: crystallochemical properties of the starting material, autocatalysis by the solid product and autocatalysis by the gaseous product.

The experimental features of this kinetic study (dynamic vacuum) and the shape of the α vs. t curves allow to deduce that only the first of the above factors is responsible for the autolocalization.

A possible explanation of the results obtained can be found in the features of the dislocations emerging on the (021) face. Klapper observed, by X-ray topography, that different types of dislocations emerge on the (021) face, most of them having a direction almost perpendicular to the face, while others have lines parallel to the [001] direction. The symmetry of the etch pits obtained allows to conclude that they originate from this latter type of dislocations.

If we take into account that all the experimental observations individuate the [001] direction as the preferential one for the reaction advancement, it seems possible to think that this type of dislocations exerts on the reactivity a greater influence than the others do.

The enhanced reactivity at the vertex-intersection of the (021), (110) and (010) faces can also be explained on the basis of the proposed kinetic interpretation; in fact the advancement of the reaction from this vertex produces a surface which intersects the c -axis and shows, as a consequence, an enhanced reactivity.

b) Constant rate period

The topochemical mechanism of the reaction is consistent with the linear trend of the obtained isotherms. The preferred direction of interface penetration along the c -axis into the LFM bulk may be explained with regard to the LFM structure, since the interface proceeds in the same direction as the chains of water molecules.

It is worth noting that the enthalpy of dehydration (13.1 kcal mole⁻¹) and the activation energy both of the induction period (13.6 kcal mole⁻¹) and of the advancement of the reaction interface (14.3 kcal mole⁻¹ both from k_{TG} and from k_{micr}) are close to one another; the present dehydration, therefore, can be considered as a "normal" one [7].

We have also calculated the k values by an application of the Polanyi-Wigner equation in the form [8]

$$k (\text{molecules sec}^{-1}) = C A \nu \exp(-E/RT)$$

where C is the number of water molecules per cm² of interface, A is the interface area and ν is the vibration frequency of the bond involved in the

decomposition. On the basis of the structure, a value of $5.9 \cdot 10^{14}$ molecules cm^{-2} has been estimated for C ; the A and ν values were evaluated taking into account the linear dimensions of our crystals and the mean temperature at which the isothermal measurements were performed. The values so obtained were: $A = 5.0 \cdot 10^{-3} \text{ cm}^2$ and $\nu = 5 \cdot 10^{12} \text{ sec}^{-1}$.

For the constant rate period, the experimental values, k_{exp} (molecules sec^{-1}), can be satisfactorily

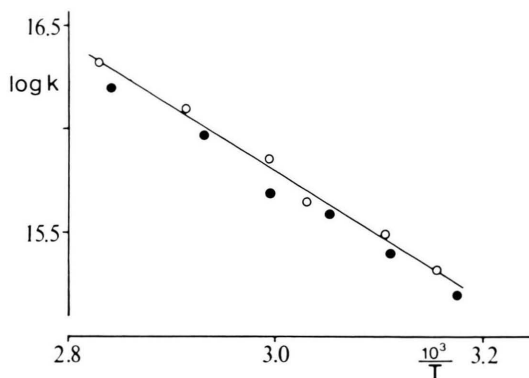


Fig. 7. Comparison between calculated (full line) and experimental (filled circles: optical data; open circles: TG data) rate constants for the linear period.

compared (see Fig. 7) with those calculated from the above equation using, for the activation energy the value $14.3 \text{ kcal mole}^{-1}$.

c) Decay period

The explanation of the TG measurements according to the "contracting volume" law is not at all reliable. In fact, the data obtained from this work follow the expected trend only in an approximate way and, in the case of a few isotherms, only for limited ranges.

This is due, among other reasons, to the different rates of interface penetration along the space coordinates.

Measurements of the interface advancements in this period, unfortunately, could not be performed by microscopic observation; therefore it has not been possible to give a kinetic equation more consistent with the experimental trend.

Acknowledgement

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