SOLID STATE REACTIONS

KINETICS AND MECHANISM OF ISOTHERMAL DEHYDRATION OF LiKC$_4$H$_4$O$_6$·H$_2$O SINGLE-CRYSTALS

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The kinetics of isothermal dehydration of LiKC$_4$H$_4$O$_6$.H$_2$O single-crystals was investigated in the [001] crystallographic direction under a dynamic vacuum of 6.7×10^{-5} Pa with a quartz crystal microbalance. The removal of H$_2$O molecules may be described by a diffusion equation for a semi-infinite medium. The diffusion coefficients vary from 2.13×10^{-11} cm^2 s^{-1} at 391.7 K to 9.9×10^{-9} cm^2 s^{-1} at 453.2 K. The scanning electron microscope data provide some evidence that the dehydration is not a topochemical reaction. From the experimental data it is concluded that the anhydrous product is in the state of "premelting". This explains the anomalous diffusion energy $E_D = 37 \pm 1$ kcal mol^{-1} and preexponential factor $D_0 = 5 \times 10^9$ cm^2 s^{-1}.

Lithium potassium tartrate monohydrate is isomorphous and iso structural with lithium ammonium tartrate monohydrate [1]. All the water molecules in these substances are crystallographically equivalent [2], and the lone-pair coordination of the water molecules is of the A type [3]. According to the SPR and NMR data, LiKC$_4$H$_4$O$_6$·H$_2$O does not undergo a structure phase transition within the temperature range 77–453 K [1, 4], whereas LiNH$_4$C$_4$H$_4$O$_6$·H$_2$O displays a ferroelectric-paraelectric phase transition [3]. It has been shown [4] that LiKC$_4$H$_4$O$_6$·H$_2$O has a usually high thermal stability for a crystalline hydrate being stabile in air up to 453 K. This interesting phenomenon is studied in the present work.

Experimental

LiKC$_4$H$_4$O$_6$·H$_2$O single-crystals were grown during the slow evaporation of a saturated aqueous solution at ambient temperature. The crystals obtained were

colourless hexagonal prisms extended in the [001] direction. Combustion analysis showed the composition of the salt to be 22.45% C, 2.82% H (theoretical composition: 22.63% C, 2.84% H). The thermal analysis data obtained with a derivatograph (5 deg min^{-1}, helium, single-crystal fragment 116.7 mg, quartz crucible) revealed that the maximum rate of dehydration occurs at 468 K and the final weight loss is close to that required according to the equation

$$LiKC_4H_4O_6 \cdot H_2O \rightarrow LiKC_4H_4O_6 + H_2O \qquad (1)$$

For isothermal experiments, the crystals were cut to give 0.1 cm thick discs, 0.6 cm in diameter, with a plane parallel to the (001) face. Their dehydration kinetics was measured with a quartz crystal microbalance [5] with a mass accuracy of $\pm 10^{-8}$ g, under conditions of a dynamic vacuum of 6.7×10^{-5} Pa. Reaction on the opposite and lateral faces of the sample was eliminated by covering these faces with an indium-gallium eutectic. The temperature control of the sample was accurate to ± 0.1 deg.

Results and discussion

Kinetic curves of the isothermal dehydration of $LiKC_4H_4O_6 \cdot H_2O$ single-crystals in the [001] crystallographic direction are depicted in Figs 1a, 1b. It is clear

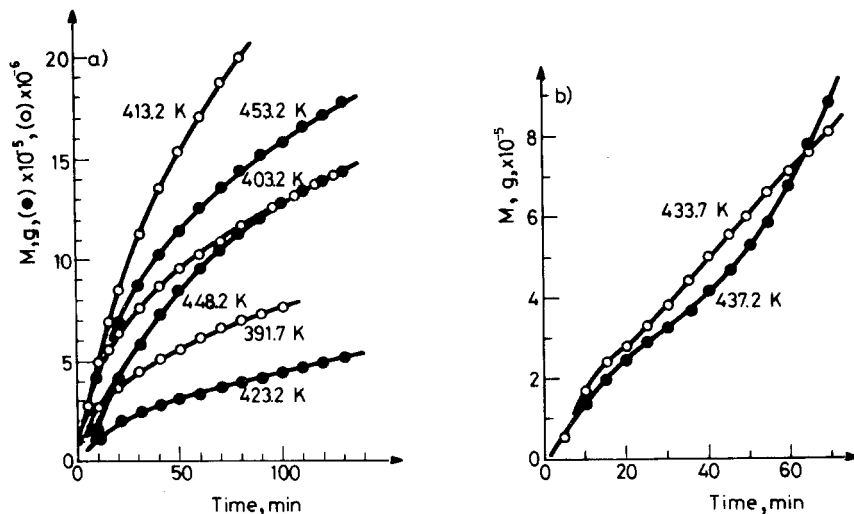Fig. 1 Mass loss vs. time plots for the isothermal dehydration of $LiKC_4H_4O_6 \cdot H_2O$ single-crystals in the [001] crystallographic direction at the indicated temperatures.
The thermal analysis data suggest a weak endothermic effect within the temperature range in Fig. 1b (433.7 − 437.2 K)

that these kinetic curves have the characteristic shape for diffusion-controlled reactions. Optical microscope investigations of partially decomposed samples showed that they are transparent. Scanning electron microscopy studies of the solid product on the (001) face demonstrated that the surface was extensively recrystallized (Fig. 2). It may be suggested that a "vacancy structure" [6] is formed
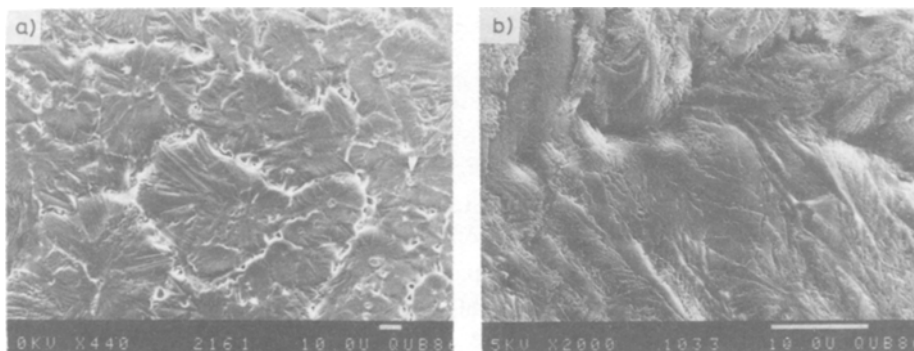

Fig. 2 Scanning electron micrographs of the morphology of the solid product formed on the (001) face after heating in vacuum at 461 K (A) and 438 K (B) (in both cases $\alpha = 0.2$). There is strong evidence that the surface is extensively recrystallized
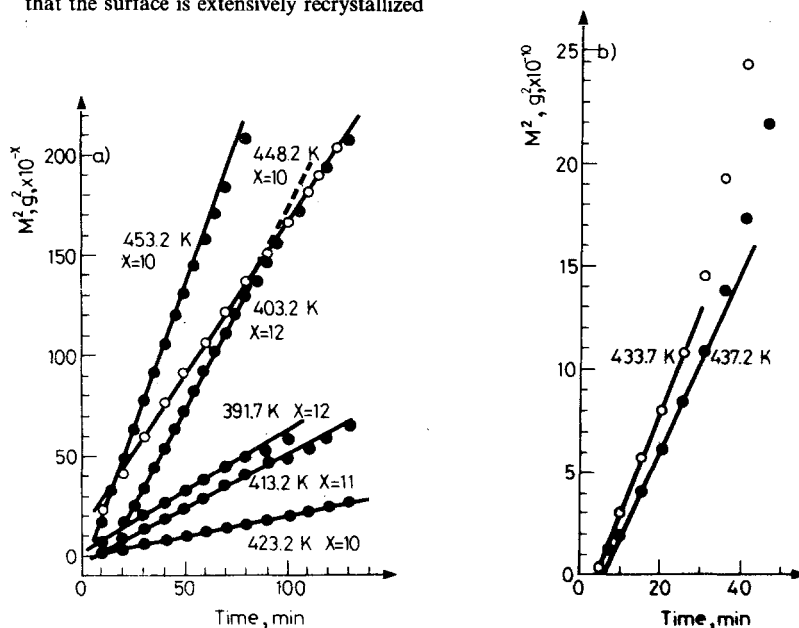

Fig. 3 Plots of (weight loss)^2 vs. reaction time. The linearity confirms kinetic control by the diffusion equation. (Initial deviations occur during sample heating to the isothermal reaction temperature.) At 433.7 and 437.2 K, the experimental points (Fig. 3b) are described by a one-dimensional equation only during the initial stages

in the course of dehydration and removal of H_2O molecules from the initial reactant is achieved by diffusion through the "vacancy structure". This process may be regarded as one-dimensional diffusion from a semi-infinite medium [7]:

$$m^2 = \frac{(\varrho S)^2}{\pi} \cdot Dt \tag{2}$$

where $\varrho = 0.137$ g·cm^{-3} is the H_2O density in the initial reactant, $S = 0.28$ cm^2 is the surface area of the sample, and D is the diffusion coefficient. Kinetic curves plotted in the m^2 vs.t coordinates are shown in Figs 3a and 3b. It is clear from the straight line that diffusion control is operating. There is a kinetic peculiarity in the temperature range 434–437 K. It is difficult to explain these phenomena on the basis of the experimental results. At least, no phase transition occurs in the initial reactant within this temperature range [4]. The values of D were calculated by the least-squares method from the linear parts of the curves (Figs 3a, b) and are presented in Table 1. The values of the diffusion coefficients plotted in the ln D vs.

Table 1 Measured diffusion coefficients for water loss during isothermal reactions at various temperatures

T, K	$D \times 10^{10}$, cm^2 s^{-1}
453.2	99.0 ± 0.4
448.2	70.1 ± 0.4
437.2	15.3 ± 0.1
433.7	17.9 ± 0.2
423.2	6.68 ± 0.04
413.2	1.928 ± 0.004
403.2	0.532 ± 0.006
391.7	0.213 ± 0.001

T^{-1} coordinates are shown in Fig. 4. The corresponding refinement by the least-squares method gives the diffusion parameters: $E_D = 37 \pm 1$ kcal mol^{-1}, and $D_0 = 5 \times 10^9$ cm^2·s^{-1}.

The "vacancy structure" formed in the reaction, as suggested above, reorganizes into the thermodynamically stable state through melting. Strong evidence of extensive surface recrystallization is presented in Fig. 2. The "anomalous" diffusion parameters E_D and D_0 obtained during the investigation are probably due to the "premelting" phenomena usually observed for mass-transfer processes in solids [8].
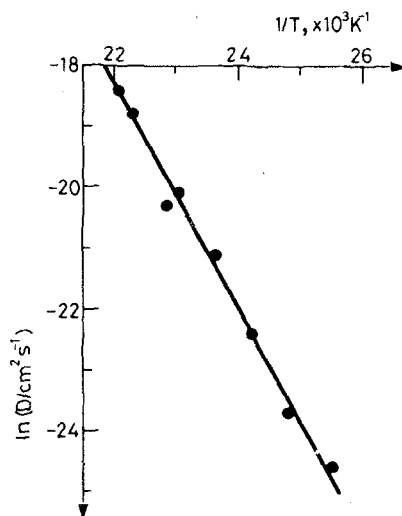
Fig. 4 Dependence of the diffusion coefficients on temperature. The anomalous point corresponds to the kinetic pecularity mentioned in Figs 1 and 3

Conclusions

1. The thermal dehydration of $LiKC_4H_4O_6 \cdot H_2O$ is not a topochemical reaction.

2. The high thermal stability of $LiKC_4H_4O_6 \cdot H_2O$ is due to the dehydration occurring via a diffusion mechanism.

References

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Zusammenfassung — Die Kinetik der Entwässerung von $LiKC_4H_4O_6 \cdot H_2O$ in [001] – Richtung unter dynamischem Vakuum wurde mit einer Quarzkristall-Mikrowaage verfolgt. Die Abgabe von Wasser kann mit einer Diffusionsgleichung für ein halb-unendliches Medium beschrieben werden, die Diffusionskoeffizienten variieren von $2,13 \cdot 10^{-11}$ cm^2 s^{-1} bei 391,7 K bis $9,9 \cdot 10^{-9}$ cm^2 s^{-1} bei 453,2 K.

Rasterelektronenmikroskopische Aufnahmen zeigen, daß die Entwässerung nicht topochemisch abläuft. Nach dem experimentellen Ergebnis befindet sich das entwässerte Produkt in einem „Vorschmelz"-Stadium. Daraus erklären sich die anomalen Werte für die Diffusionsenergie $E_D = (37 \pm 1)$ kcal mol^{-1} und den präexponentiellen Faktor $D_0 = 5 \cdot 10^9$ cm^2 s^{-1}.

Резюме — С помощью кварцевых микровесов в условиях динамического вакуума $6,7 \cdot 10$. Па исследована кинетика изотермической дегидратации монокристаллов LiKC$_4$H$_4$O$_6$.H$_2$O в кристаллографическом направлении [001]. Реакция дегидратации может быть описана уравнением диффузии из полубесконечной среды. Коэффициенты диффузии изменяются от $2,13 \cdot 10^{-11}$ см^2 сек$^{-1}$ при 391,7 К до $9,9 \cdot 10^{-9}$ см^2 сек$^{-1}$ при 453,2 К. Результаты сканирующей электронной микроскопии дают некоторое доказательство, что процесс дегидратации не является топохимической реакцией. На основе экспериментальных данных сделано заключение, что безводный продукт находится в состоянии «предплавления», чем объясняется аномальное значение энергии диффузии $E_Д = 37 \pm 1$ ккал $\cdot$ моль$^{-1}$ и предэкспоненциального множителя $Д_0 = 5 \cdot 10^9$ см$^2 \cdot$ сек$^{-1}$.