

COMPARATIVE STUDY OF SINGLE-CRYSTAL DEHYDRATION OF $\text{LiCOOH} \cdot \text{H}_2\text{O}$ AND $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$

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The kinetics of isothermal dehydration of two crystal hydrates with equivalent water molecule sublattices ($\text{LiCOOH} \cdot \text{H}_2\text{O}$ and $\text{LiSO}_4 \cdot \text{H}_2\text{O}$) was investigated in vacuum with a quartz crystal microbalance, and the dynamics of structural reorganization of the substances was studied by the synchrotron radiation method. Differences were found both in the nucleation stage and in the stage of reaction interface advance. The results indicate that the kinetic behaviour of isothermal decomposition of solids is determined by the structural reorganization of a metastable intermediate.

For a quantitative description of the kinetics of the thermal decomposition

$$AB_s = A_s + B_g \quad (1)$$

it has been postulated that the removal of the B molecules from the crystal lattice of the reactant is responsible for the kinetic behaviour [1]. On the other hand, recent experimental data concerning the organization of elastic strains and the formation of metastable intermediates allow the supposition that the kinetic behaviour depends on more complicated processes connected with the formation of the solid product. In order to verify this supposition, we have chosen for our investigations two substances with equivalent sublattices of water molecules: $\text{LiCOOH} \cdot \text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (neutron-diffraction data [2, 3]). In spite of this equivalence, their dehydration kinetics were found to be significantly different.

The difference appears in the initial stage: treatment of the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystal surface with a fine abrasive leads to instantaneous nucleation and to reaction boundary formation. In contrast, this treatment has no result in the case of $\text{LiCOOH} \cdot \text{H}_2\text{O}$. Only rubbing of the single-crystal surface with anhydrous LiCOOH product powder leads to reaction boundary formation.

The isothermal dehydration kinetics was studied under a dynamic vacuum of 6.7×10^{-5} Pa by means of a quartz crystal microbalance [4]. During the kinetic

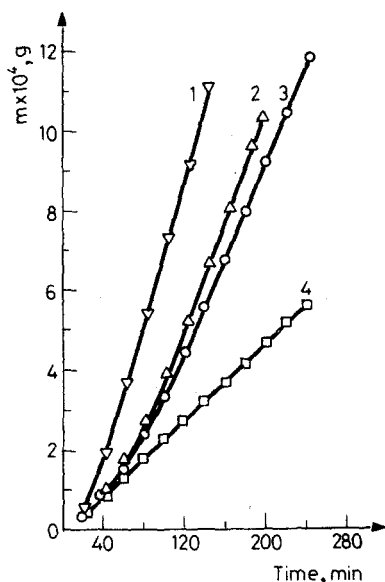


Fig. 1 Water mass loss vs. time of isothermal dehydration: $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (4) in the crystallographic direction [010] at $T = 343 \text{ K}$, $P = 6.7 \times 10^{-5} \text{ Pa}$; $\text{LiCOOH} \cdot \text{H}_2\text{O}$ in the crystallographic directions [001] (1), [010] (2) and [110] (3) at $T = 308 \text{ K}$, $P = 6.7 \times 10^{-5} \text{ Pa}$

studies, significant differences were again found: The dehydration of $\text{LiCOOH} \cdot \text{H}_2\text{O}$ begins with a prolonged induction period, with a subsequent acceleration. For instance, at a reaction temperature of about 208 K, the induction period is approximately 2 h (Fig. 1). For $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, instantaneous nucleation takes place.

In spite of the above statement, we could not find any similarity between the reaction rates (shift of reaction interface versus temperature) (Fig. 2). From a presentation in the coordinates $\ln dm/dt$ vs. T^{-1} , we calculated the kinetic parameters

$$1) \quad \text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O} - E = 20.8 \pm 0.2 \text{ kcal/mol} \quad [5], \text{ and}$$

$$2) \quad \text{LiCOOH} \cdot \text{H}_2\text{O} - E = 35 \pm 3 \text{ kcal/mol},$$

$$A = 42.6.$$

It is noteworthy that the dehydration of $\text{LiCOOH} \cdot \text{H}_2\text{O}$ under the applied experimental conditions ($T = 298.2\text{--}321.2 \text{ K}$) proceeds far from equilibrium (Fig. 3), and therefore the influence of rehydration is excluded.

The main cause of the differences in the kinetic behaviour is believed to be connected with the reorganization of the crystal lattice during the reaction. This

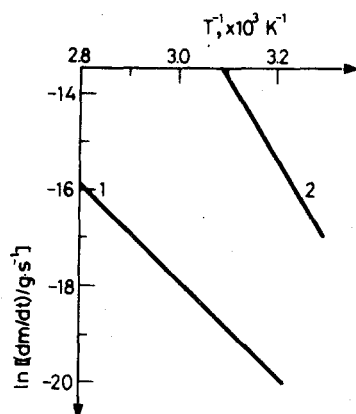


Fig. 2 Rate of mass loss vs. temperature of decomposition. 1 – $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$; 2 – $\text{LiHCOO} \cdot \text{H}_2\text{O}$

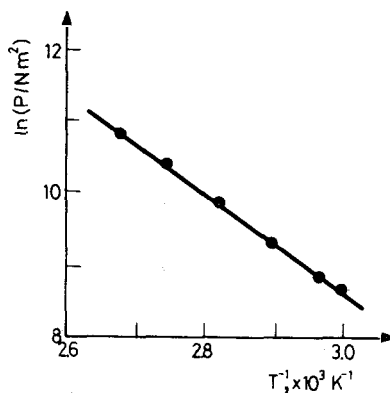


Fig. 3 Tensometric data of water-vapour equilibrium pressure in the system $\text{LiHCOO} \cdot \text{H}_2\text{O}$ — LiCOOH

supposition had been examined by means of synchrotron radiation. For this purpose, samples of $\text{LiCOOH} \cdot \text{H}_2\text{O}$ were analysed: 1) initial reactant; 2) substance under reaction; 3) final product. The results of the studies were compared with those for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ obtained earlier [6].

It was found that in both cases the dehydration occurs via a metastable intermediate, but the metastable intermediates are very different ones:

(i) For $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, the differences between the metastable intermediate and the initial reactant are very small according to the synchrotron data (small displacement of peaks, Fig. 4). In contrast, in the case of $\text{LiCOOH} \cdot \text{H}_2\text{O}$ the differences between reactant, metastable intermediate and final product are significant (Fig. 5).

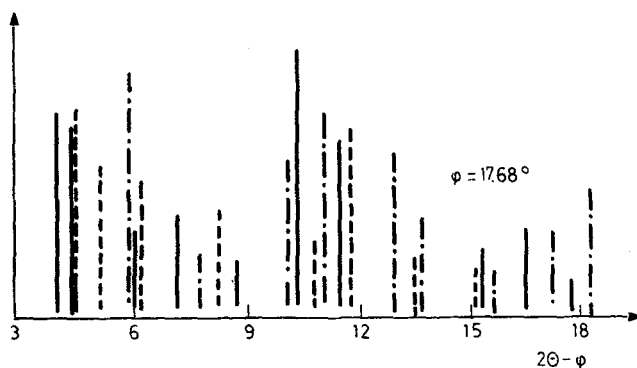


Fig. 4 Synchrotron X-ray diffractogram for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$: (—) reactant, (---) metastable intermediate, (-·-) final product

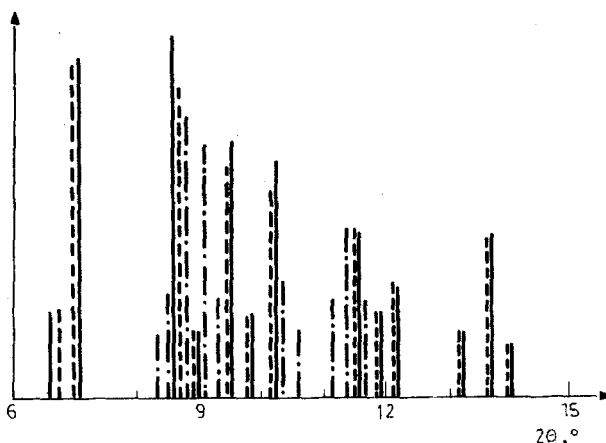


Fig. 5 Synchrotron X-ray diffractogram for $\text{LiCOOH} \cdot \text{H}_2\text{O}$: (—) reactant, (---) metastable intermediate, (-·-) final product

(ii) The metastable intermediate of $\text{LiCOOH} \cdot \text{H}_2\text{O}$ dehydration is transformed into the final product more slowly.

The above differences, existing both in the nucleation stage and during the advance of the reaction interface into the crystal bulk, indicate that the kinetic behaviour of thermal decomposition of solids is not generally determined by the rupture of the *B* molecule bonds (1) in the crystal lattice. The kinetic behaviour depends significantly on the processes of structural reorganization connected with solid product formation.

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References

- 1 M. E. Brown, D. Dollimore and A. K. Galwey, *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam, 1980, 22 Chap. 1.
- 2 H. Smith, S. Peterson and H. Levy, *J. Chem. Phys.*, 48 (1968) 5561.
- 3 R. Tellgren, P. Ramanujam and R. Liminga, *Ferroelectrics* 6 (1974) 191.
- 4 V. Okhotnikov and N. Lyakhov, *J. Solid State Chem.*, 53 (1984) 161.
- 5 V. Okhotnikov, B. Yakobson and N. Lyakhov, *React. Kinet. Catal. Lett.*, 23 (1983) 125.
- 6 Yu. Gaponov and N. Lyakhov, *Ist International Conference on the Progress in X-ray Studies by Synchrotron Radiation*, 1-4 April, Strasbourg, France, 5 (B) 2, 1985.

Zusammenfassung — Die Kinetik der isothermen Entwässerung zweier Kristallhydrate mit gleichartigen Teilgittern der Wassermoleküle wurde untersucht mittels isothermer TG im Vakuum und Synchrotron-Röntgenbeugung. Unterschiede zwischen beiden Materialien werden sowohl in der Keimbildungs- wie in der Ausbreitungsphase gefunden. Die Ergebnisse zeigen, dass die Kinetik der isothermen Zersetzung fester Stoffe durch die strukturelle Reorganisation eines metastabilen Zwischenprodukts bestimmt wird.

Резюме — Исследована кинетика изотермической дегидратации двух кристаллогидратов $\text{HCOOLi} \cdot \text{H}_2\text{O}$ и $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ с одинаковой подрешеточной молекулой воды. Дегидратация изучалась в вакууме с помощью кварцевых микровесов, а динамика структурного преобразования этих соединений — методом синхротронного излучения. Установлены различия как на стадии образования центров кристаллизации, так и на стадии продвижения реакционной поверхности раздела. Результаты показали, что кинетическое поведение изотермического разложения твердых тел определяется структурным преобразованием метастабильного промежуточно продукта.