Journal of Thermal Analysis, Vol. 34 (1988) 11–18

DEHYDRATION OF LITHIUM TRIPHOSPHATE PENTAHYDRATE, $Li_5P_3O_{10} \cdot 5H_2O$

V. M. Galogaža, E. A. Prodan**, H. V. Peslyak**, V. A. Sotnikova-Yuzhik*** and *S. A. Prodan***

*FACULTY OF TECHNOLOGY AND METALLURGY, UNIVERSITY OF BELGRADE, BELGRADE, YUGOSLAVIA
**INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY OF THE ACADEMY OF SCIENCES OF THE BSSR, MINSK, U.S.S.R.

(Received January 15, 1985: in revised form May 13, 1987)

The kinetics of isothermal-isobaric dehydration of $Li_5P_3O_{10} \cdot 5H_2O$ in vacuum ($p = 10^{-1}$ hPa) and in water vapour atmosphere ($p_{H_2O} = 23$ hPa) was investigated by TG in the temperature range 40–140°. It was shown that the initial non-degradation removal of 1/10 of the crystal water, the rate of which is sensitive to p_{H_2O}, proceeds according to the laws of reversible topochemical reactions. In the next, irreversible degradation stage, where the bulk of the crystal water is removed, the kinetic characteristics of the process and the DSC effects exhibit a low sensitivity to the water vapour pressure. The peculiarities of $Li_5P_3O_{10} \cdot 5H_2O$ dehydration were considered in comparison with the thermal behaviour of $Na_5P_3O_{10} \cdot 6H_2O$ and $K_5P_3O_{10} \cdot 4H_2O$.

In contrast to $Na_5P_3O_{10} \cdot 6H_2O$ and $K_5P_3O_{10} \cdot 4H_2O$, on thermal treatment in vacuum, water vapour atmosphere or air, $Li_5P_3O_{10} \cdot 5H_2O$ does not pass into anhydrous lithium triphosphate by either a direct or a degradation mechanism. Therefore, it could be suggested that this compound may also differ from $Na_5P_3O_{10} \cdot 6H_2O$ and $K_5P_3O_{10} \cdot 4H_2O$ in the kinetic characteristics of its thermal transformations and in particular in the characteristics of the isothermal-isobaric dehydration in the atmosphere of the gaseous reaction product.

Experimental

The kinetics of isothermal-isobaric dehydration was studied by the TG method on high-vacuum equipment with a quartz microbalance (sensitivity 0.83 mg/mm). The powdered sample (m = 25–30 mg) was arranged on the bottom of a glass sample pan suspended on a spiral microbalance, and the air was then evacuated

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

from the apparatus to the residual pressure $p = 10^{-4}$ hPa, after which the pan was drawn down into the thermostated part of the reactor, thereby starting the kinetics experiment. The experiments in water vapour atmosphere were carried out in the same manner, except that on evacuation of air, the apparatus was filled with vapour of predegassed water till the necessary pressure $p_{H_2O} = 23$ hPa was reached. During the kinetic experiments, the temperature was maintained at a constant level within ± 0.3 deg and the pressure was maintained within $p = (1 \pm 0.5) \cdot 10^{-4}$ hPa and $p_{H_2O} = (23 \pm 0.5)$ hPa.

The DSC-2 block (Scan. Auto Zero) of the Perkin-Elmer Thermal Analysis Lab 1 was used in the DSC studies (heating rate HR = 20 deg/min; sample mass $m = 10$–12 mg). Prepurified nitrogen containing up to 20–30 ppm of H_2O, 7 ppm of O_2 and 2–3 ppm of Ar was fed in at a rate of 37 ml/min. The sample was placed in a standard Perkin-Elmer gold pan (temperature range $t = 67$–$726°$) or was encapsulated in aluminium pan (temperature range 67–477°).

The powder-like sample of $Li_5P_3O_{10} \cdot 5H_2O$ (particle size 0.02–0.07 mm) was obtained by passing a 12% aqueous solution of chromatographically pure sodium triphosphate through a cation-exchanger in Li^+ form, with subsequent precipitation by acetone. A fine crystalline white precipitate separated from the solution; it was washed with acetone and dried at a relative humidity of $r = 50$–70%. The results of the determination of lithium by the colorimetric method with thoron I indicator (9.1% Li), of phosphorus by the gravimetric quinoline-molybdate method (24.2% P) and of water by calcination at 400–500° (23.3% H_2O) correspond to the values of 9.2% Li, 24.6% P and 23.8% H_2O calculated for the formula $Li_5P_3O_{10} \cdot 5H_2O$. According to the TLC data, the sample contains 0.5% P in the orthophosphate form (P_1), 3.7% P in the pyrophosphate form (P_2) and 95.8% P in the triphosphate form (P_3). The X-ray pattern of the sample coincides with the X-ray pattern of previously synthesized $Li_5P_3O_{10} \cdot 5H_2O$ [1].

Results and discussion

The Zawadski-Bretsznajder law [2] is characteristic for the initial reversible stages of the thermal dehydrations

$$Na_5P_3O_{10} \cdot 6H_2O(\text{cryst.}) \rightleftharpoons Na_5P_3O_{10} \cdot 4H_2O(\text{cryst.}) + 2\,H_2O(\text{gas})$$

$$K_5P_3O_{10} \cdot 4H_2O(\text{cryst.}) \rightleftharpoons K_5P_3O_{10} \cdot 2H_2O(\text{cryst.}) + 2\,H_2O(\text{gas})$$

Under the conditions of isothermal-isobaric dehydration, as the pressure increases the rate constant (*K*) decreases and the effective activation energy (*E*) increases; as a rule, the preexponential factor (*A*) also increases and the isokinetic effect is observed [3].

In the case of $Li_5P_3O_{10}.5H_2O$ as shown by experiments, in which the sample was kept for 200–400 days at regulated air humidity, the crystal hydrate reversibly loses up to 1/5 of the crystal water, without anion destruction and without lattice rearrangement. Practically in a kinetic experiment (time of isothermal treatment $\tau = 4$–6 hours or $\tau = 15$–25 hours), the amount of reversibly removed water is even less; it corresponds to a mass loss of $\Delta m = 0.5$–0.6 mol H_2O (Fig. 1). This is explained by the fact that in this stage dehydration proceeds in the diffusion region, where the kinetic parameter n in the equation $\alpha = 1 - \exp(-k\tau^n)$ (α = dehydration degree, τ = time, k = constant, connected with the rate constant K through the equation $K = nk^{1/n}$) is close to $n = 0.5$ and higher values of τ are required for completion of the process [4].

The results of calculations of the kinetic parameters of the reversible (n_1, interval

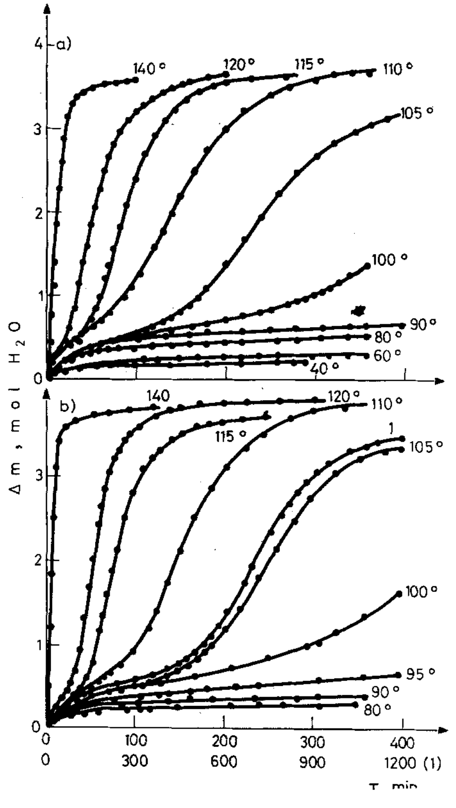

Fig. 1 Kinetics of isothermal-isobaric dehydration of $Li_5P_3O_{10} \cdot 5H_2O$ in vacuum at $p = 10^{-4}$ hPa (a) and in water vapour atmosphere at $p_{H_2O} = 23$ hPa (b); the time scala 1 is given for the curve 1 **at** $t = 95$

between $\Delta m = 0$ and $\Delta m = 0.5$–0.6 mol H_2O) and irreversible (n_2, interval between $\Delta m = 0.5$–0.6 mol H_2O and $\Delta m = 3.5$–4.0 mol H_2O) stages of dehydration of $Li_5P_3O_{10} \cdot 5H_2O$ are given in Table 1. The remaining water in the interval between $\Delta m = 4$ mol H_2O and $\Delta m = 5$ mol H_2O accounted for by hydrolysis and bound in the substance in the form of POH groups, is removed at higher temperatures. A mass loss of $\Delta m = 4$ mol H_2O was assumed as $\alpha = 1$ for calculation of the dehydration degree.

Table 1 Kinetic parameter of reversible (n_1) and irreversible (n_2) dehydration stages of $Li_5P_3O_{10} \cdot 5H_2O$

t, °C	n_1	n_2
Vacuum, $p = 10^{-4}$ hPa		
140	—	2.9
120	0.6	2.0
115	0.5	1.6
110	0.5	1.8
105	0.5	1.6
100	0.4	1.4
90	0.6	—
80	0.3	—
60	0.4	—
40	0.3	—
Water vapour atmosphere, $p_{H_2O} = 23$ hPa		
140	—	2.3
120	0.6	2.9
115	0.5	2.4
110	0.4	2.0
105	0.5	2.4
100	0.4	1.6
95	0.4	2.3
90	0.3	—
80	0.3	—

In the reversible stage at $t < 95°$, dehydration proceeds without deep anion degradation; in the irreversible stage at $t \geqslant 95°$, degradation proceeds with disintegration of the anion into ortho- and pyrophosphate fragments and with the formation of more condensed phosphate forms ($P > 3$) as compared with the initial triphosphate (Table 2). A high content of pyrophosphate in the products of irreversible dehydration, especially in water vapour atmosphere, is explained by simultaneous processes of degradation and anion condensation:

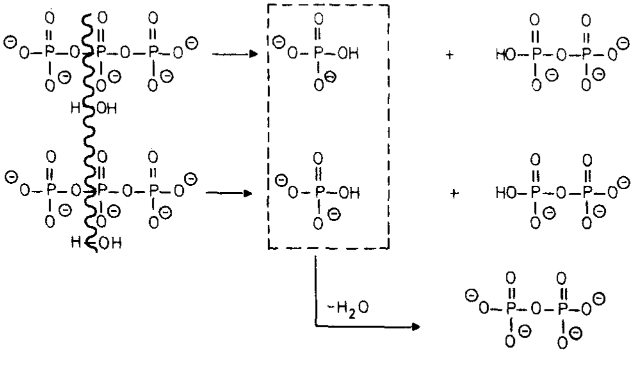

Table 2 Results of TLC analysis of $Li_5P_3O_{10} \cdot 5H_2O$ dehydration products

t, °C	Δm, mol H_2O	τ, min	Phosphorus content, mass per cent			
			P_1	P_2	P_3	$P_{>3}$
Vacuum, $p = 10^{-4}$ hPa						
40	0.27	280	2.6	3.1	94.3	0
60	0.34	360	3.6	10.0	86.4	0
80	0.72	340	1.1	6.5	92.4	0
90	1.04	965	5.9	11.8	82.3	0
100	1.45	360	12.0	26.2	61.8	0
105	3.24	400	13.0	59.6	30.4	0
110	3.95	360	13.3	71.5	15.2	0
115	3.64	265	13.5	72.8	10.6	3.1
120	3.61	350	11.6	70.3	12.7	5.4
140	3.65	300	1.8	65.9	16.8	10.3*
Water vapour atmosphere, p_{H_2O} = 23 hPa						
80	0.30	350	1.9	8.9	89.2	0
90	0.39	360	2.4	10.1	87.5	0
95	3.61	1480	16.2	83.8	0	0
100	1.62	400	9.0	91.0	0	0
105	3.20	385	2.9	97.1	0	0
110	3.84	360	1.6	98.4	0	0
115	3.74	380	7.8	92.2	0	0
120	3.94	330	10.5	89.5	0	0
140	3.79	210	10.2	89.8	0	0

* 5.2% of phosphorus remains at the start. .

Accumulation of acid phosphates leads to self-acceleration of the process. The kinetics curves in the degradation stage of dehydration have a well-defined S-form (Fig. 1) and the kinetic parameter assumes the values $n_2 = 1.4$–2.9, which are characteristics of self-acceleration processes. In water vapour atmosphere the effect of self-acceleration is manifested more strongly than in vacuum.

Two values of the kinetic parameter, n_1 and n_2, correspond to two values of the rate constant, K_1 and K_2, the temperature-dependence of which is represented in Fig. 2.

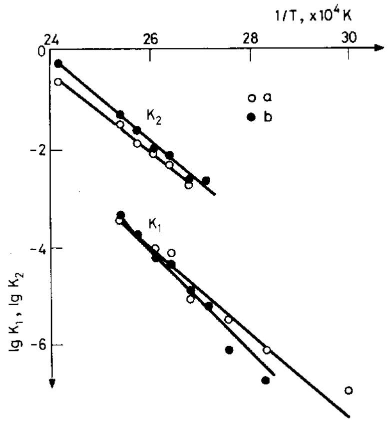

Fig. 2 Arrhenius dependence of $Li_5P_3O_{10} \cdot 5H_2O$ dehydration rate constant in vacuum at $p = 10^{-4}$ hPa (a) and in water vapour atmosphere at $p_{H_2O} = 23$ hPa (b)

During dehydration in water vapour atmosphere, the straight line for K_2 lies somewhat higher than during dehydration in vacuum, but within the error range the corresponding E_2 values are practically equal (37.4 ± 1.5 and 39.9 ± 1.5 kcal/mol, respectively). In the case of K_1, this difference between the E_1 values (38.6 ± 2 and 45.7 ± 2 kcal/mol) exceeds the above-mentioned range, though not so significantly as compared with the analogous differences for $Na_5P_3O_{10} \cdot 6H_2O$ and $K_5P_3O_{10} \cdot 4H_2O$ dehydration [3]. The increase in E_1, as p rises from 10^{-4} to 23 hPa, is compensated by the increase in the preexponential factor from $A_1 = 10^{(17.8 \pm 0.3)}$ min^{-1} to $A_1 = 10^{(21.9 \pm 0.3)}$ min^{-1}. It should be noted that the Zawadski–Bretsznajder law holds on the removal from $Li_5P_3O_{10} \cdot 5H_2O$ of only 1/10 of the crystal water. In our case the water vapour influences K_1, E_1 and A_1 substantially less than in the dehydrations of $Na_5P_3O_{10}.6H_2O$ and $K_5P_3O_{10}.4H_2O$. It also produces a weaker effect on the characteristics K_2, E_2 and A_2 of irreversible removal of the bulk of the crystal water, which is explained by the different composition of the crystalline products formed: in the dehydration of $Na_5P_3O_{10} \cdot 6H_2O$ and $K_5P_3O_{10} \cdot 4H_2O$, water vapour accelerates the crystallization of $Na_5P_3O_{10}$ (form II) and of $K_5P_3O_{10}$, while in the dehydration of $Li_5P_3O_{10} \cdot 5H_2O$ it accelerates crystallization of the low-temperature pyrophosphate form $Li_4P_2O_7$(l) (l = low).

The considered peculiarities of the dehydration kinetics of $Li_5P_3O_{10} \cdot 5H_2O$ are taken into account in the interpretation of the various sensitivities of the DSC data to the experimental conditions. Substitution of an open gold pan by a non-pierced aluminium capsule within which water vapour can accumulate, leads to shift of the endoeffect of the removal of the bulk of the crystal water from $Na_5P_3O_{10} \cdot 6H_2O$ toward higher temperature. It does not, however, affect the position of the analogous dehydration effect for $Li_5P_3O_{10} \cdot 5H_2O$ (Fig. 3): under the dynamic conditions of the DSC experiments, the reversible dehydration stage is practically not manifested. The high partial pressure of water vapour within the capsule is manifested in the stage following the first endoeffect, for instance, by splitting of the endoeffect connected with the formation of $Li_2H_2P_2O_7$ at 248°. If the sample heated to 726° is cooled and the DSC experiment is repeated, the above-mentioned effect disappears. However, the effect at 656° corresponding to the melting of insoluble crystalline polyphosphate $(LiPO_3)_x \cdot H_2O$ (656–665° according to [5–7]) remains unaffected. The effects of melting of eutectic $Li_4P_2O_7(l) + (LiPO_3)_x \cdot H_2O$ at 609° (603–608° according to [6–7]) and of the phase transition $Li_4P_2O_7(l) \rightarrow Li_4P_2O_7(h)$ at 615° merge into a single effect.

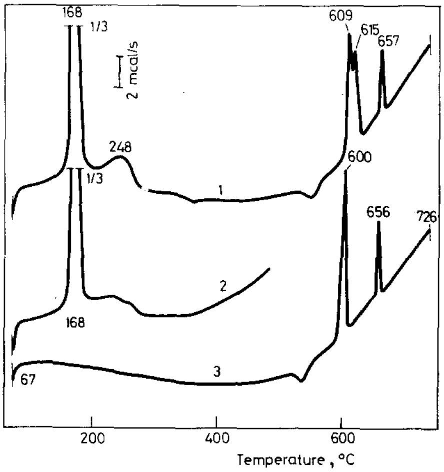

Fig. 3 DSC curves for $Li_5P_3O_{10} \cdot 5H_2O$ and its dehydration product: 1 – $Li_5P_3O_{10} \cdot 5H_2O$, open gold pan; 2 – $Li_5P_3O_{10} \cdot 5H_2O$ encapsuled in aluminium pan; 3 – product, obtained by heating $Li_5P_3O_{10} \cdot 5H_2O$ to 726° (HR = 20 deg/min) with subsequent cooling to 67° (HR = 320 deg/min), open gold pan

Conclusions

Thus, only in the comparatively short initial stage of non-degradative removal of 1/10 of the crystal water from $Li_5P_3O_{10} \cdot 5H_2O$, when the reaction rate is sensitive to p_{H_2O}, does the dehydration proceed according to the laws of reversible topochemical reactions. These laws do not extend to the removal of the bulk of the crystal water; here the process proceeds irreversibly according to the degradation mechanism; the kinetic characteristics of the process, as well as the DSC effects, exhibit low sensitivity to the water vapour pressure.

References

1 E. A. Prodan and H. V. Peslyak, Zh. Neorg. Khim., 29 (1984) 2195 (in Russian).

2 J. Zawadski and S. Bretsznajder, Z. Elektrochem., 41 (1935) 215.

3 E. A. Prodan, M. M. Pavlyuchenko and S. A. Prodan, Zakonomernosti Topokhimicheskikh Reaktsij (Principles of Topochemical Reactions), Publ. "Nauka i Tekhnika", Minsk, BSSR, 1976, p. 261 (in Russian).

4 E. A. Prodan and M. M. Pavlyuchenko, Collection: Geterogennye Khimicheskije Reaktsii (Heterogeneous Chemical Reactions), Publ. "Nauka i Tekhnika", Minsk, BSSR, 1965, p. 20 (in Russian).

5 T. Y. Tien and F. A. Hummel, J. Amer. Ceram. Soc., 44 (1961) 206.

6 M. M. Markovits, R. T. Harris and W. N. Hawley, J. Inorg. Nucl. Chem., 22 (1961) 293.

7 R. K. Osterheld, J. Inorg. Nucl. Chem., 30 (1968) 3173.

Zusammenfassung — Die Kinetik der isotherm-isobaren Dehydratisierung von $Li_5P_3O_{10} \cdot 5H_2O$ in Vakuum ($p = 10^{-4}$ hPa) und in Wasserdampfatmosphäre ($p_{H_2O} = 23$ hPa) wurde durch TG im Temperaturbereich von 40–140° untersucht. Es wurde gezeigt, daß die anfängliche, noch keine Zersetzung zur Folge habende Eliminierung von 1/10 des Kristallwassers, deren Geschwindigkeit von p_{H_2O} abhängt, nach den Gesetzen der reversiblen topochemischen Reaktionen abläuft. Im nächsten irreversiblen Zersetzungsschritt, in dem die Hauptmenge des Kristallwassers austritt, sind die kinetischen Kennwerte des Prozesses und die DSC-Effekte nur wenig vom Wasserdampfdruck abhängig. Die Besonderheiten der Dehydratisierung von $Li_5P_3O_{10} \cdot 5H_2O$ werden im Vergleich mit dem thermischen Verhalten von $Na_5P_3O_{10} \cdot 6H_2O$ und $K_5P_3O_{10} \cdot 4H_2O$ erörtert.

Резюме — Методами гравиметрии в интервале температур 40–140° исследована кинетика изотермически-изобарической дегидратации кристаллогидрата $Li_5P_3O_{10} \cdot 5H_2O$ в вакууме ($p = 10^{-4}$ гПа) и в атмосфере паров воды ($p = 23$ гПа). Показано, что начальная бездеградационная стадия удаления 1/10 части кристаллизационной воды, скорость которой чувствительна к p_{H_2O}, протекает по законам обратимых топохимических реакций. На последующей деградационной стадии необратимого удаления основной части кристаллизационной воды, кинетические характеристики процесса и ДСК-эффекты малочувствительны к давлению паров воды. Рассмотрены особенности дегидратации $Li_5P_3O_{10} \cdot 5H_2O$ в сравнении с дегидратацией $Na_5P_3O_{10} \cdot 6H_2O$ и $K_5P_3O_{10} \cdot 4H_2O$.