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THERMAL TRANSFORMATIONS OF LITHIUM PHOSPHATES

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The iso- and non-isothermal transformations taking place on the heating of LiH_2PO_4, Li_2HPO_4, $Li_5P_3O_{10}\cdot 5H_2O$, mixtures of $LiH_2PO_4 + 2Li_2HPO_4$ and $LiH_2PO_4 + Li_4P_2O_7(l)$ in vacuum, air and water vapour atmospheres at 20–1050° were studied using TG, DTG, DSC, DTA, IR spectroscopy, XRD and TLC analyses. It was shown that solid-phase interaction of the mixture components with the general ratio Li : P ≈ 5 : 3, in contrast to the interaction of analogous sodium (potassium) phosphate mixture components, does not lead to the quantitative formation of anhydrous triphosphate. This is explained by the high crystallization rate of lithium pyrophosphate, which, due to its low reactivity, does not participate in further anion condensation. The increase of triphosphate yield is promoted by the liquid phase formed on disproportionation of acid salts, on melting of reaction components or as a result of introduction of urea additive.

Crystalline form of anhydrous sodium and potassium triphosphates used as components of solid and liquid detergents are obtained by thermal treatment of phosphate mixtures with the general ratio Na : P ≈ 5 : 3 or K : P ≈ 5 : 3 [1]. There is no published evidence that anhydrous lithium triphosphate can be obtained in the same manner.

The results of studies of phase diagrams [2, 3] indicate the formation of crystalline phosphates with different condensation degrees in the Li_2O—P_2O_5 system: Li_3PO_4, $Li_4P_2O_7(l)$ (l = low), $Li_4P_2O_7(h)$ (h = high), $(LiPO_3)_x$ or $(LiPO_3)_x\cdot H_2O$. The latter is formed as a final product of the thermal transformation of LiH_2PO_4, which proceeds in air atmosphere according to the scheme [4, 5]:

$$[\mathrm{LiH_2PO_4}]\text{cryst.} \xrightarrow{>145^\circ} \begin{matrix}[\mathrm{Li_2H_2P_2O_7}]\text{cryst.}\\ [\mathrm{LiH_2P}_n\mathrm{O}_{3n+1}]\text{amorph.}\end{matrix} \xrightarrow{>210^\circ}$$

$$\begin{matrix}[(\mathrm{LiPO_3})_x\cdot \mathrm{H_2O}(l)]\text{cryst.}\\ [\mathrm{LiH_2P}_n\mathrm{O}_{3n+1}]\text{amorph.}\end{matrix} \xrightarrow{>250^\circ} [(\mathrm{LiPO_3})_x\cdot \mathrm{H_2O}(h)]\text{cryst.}$$

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The intermediates contain small amounts of amorphous lithium triphosphate. Crystalline lithium triphosphate was not detected on the thermal treatment of Li_2HPO_4 or $LiH_2PO_4 \cdot Li_3PO_4$ [6], nor in the systems $Li_4P_2O_7$–$(LiPO_3)_x$ [7] and Li_3PO_4–$(LiPO_3)_x$ [8, 9]. A vitreous phosphate with overall composition $Li_5P_3O_{10}$ was obtained by cooling a melt [10].

Experimental

In order to investigate the possibility of obtaining lithium triphosphate by thermal treatment of phosphate mixtures with the general ratio Li : P ≈ 5 : 3, we studied the thermal transformation taking place when individual phosphates and mixtures thereof were heated in different gas media in the temperature range 20–1050°. The materials investigated were crystalline orthophosphates LiH_2PO_4 and Li_2HPO_4 of reagent purity, crystalline lithium pyrophosphate $Li_4P_2O_7(l)$ obtained by the solid-phase synthesis method [2], and crystalline $Li_5P_3O_{10} \cdot 5H_2O$, obtained by passing a solution of chromatographically pure sodium triphosphate through a KU–2 cation-exchanger in Li form, with subsequent precipitation with acetone. The anion composition of the samples was determined by thin-layer chromatography (TLC). Low-soluble lithium salts were pretransferred into soluble ammonium salts according to methods used for the TLC analysis of low-soluble phosphates of multivalent metals [11]. The contents of phosphorus in the samples were determined by the gravimetric quinoline-molybdate method; the contents of lithium were determined by colorimetry with thoron *I* indicator; and the contents of water were determined via the mass loss during calcination. The TLC analysis data showed that LiH_2PO_4 and Li_2HPO_4 were chromatographically pure salts, while $Li_4P_2O_7(l)$ contained 96.9% P_2 and 3.1% P_1, and $Li_5P_3O_{10} \cdot 5H_2O$ contained 95.8% P_3, 3.7% P_2 and 0.5% P_1; P_1, P_2 and P_3 being the contents of phosphorus (mass percent) in the form of ortho-, pyro- and triphosphate, respectively.

The phase compositions of the samples were determined with a DRF–2 X-ray diffractometer (CuK_α radiation). IR spectroscopy was performed with a UR–20 spectrometer (KBr disk method). The X-ray diffraction characteristics of $Li_4P_2O_7(l)$ corresponded to the published data for $Li_4P_2O_7(l)$ [2], and the characteristics of $Li_5P_3O_{10} \cdot 5H_2O$ also corresponded to the previously obtained data [12].

The thermal transformations of the samples in air were studied with a Hungarian MOM OD–102–T derivatograph (mass of sample m = 300 mg, heating rate HR = 5 deg/min, ceramic open pan); in a flow of predried nitrogen (content of moisture additive up to 20–30 ppm, oxygen 7 ppm, argon 2–3 ppm), the thermal transformations were studied with a Perkin–Elmer Thermal Analysis Lab 1 (m = 6–12 mg, HR = 20 deg/min, standard Perkin–Elmer gold pan; nitrogen feed rate 37 ml/min in DSC–2, Scan. Auto Zero, and 14 ml/min in TGS–2 Model FDC–1). In a series of experiments, the samples ($m \approx 1$ g) were kept in air (p = 990 hPa), in vacuum ($p = 10^{-3}$ hPa) and in a flow of water vapour (p_{H_2O} = 990 hPa) in the isothermal mode, and the samples were then cooled and their anion compositions were determined.

Results and discussion

The results of TLC and XRD analyses indicate that the mixtures $LiH_2PO_4 + 2Li_2HPO_4$ and $LiH_2PO_4 + Li_4P_2O_7(l)$ subjected to isothermal treatment in air at 150–500° for 30–300 min did not contain crystalline lithium triphosphate (Table 1, Fig. 1). Triphosphate was not formed even when the treatment time was increased. Only in a mixture of $LiH_2PO_4 + Li_4P_2O_7(l)$ heated to 200° was a small amount of amorphous triphosphate (7–8% P_3) formed; its content decreased with the increase of temperature and time. The new crystalline phases during temperature increase were fixed in the following order: $Li_2H_2P_2O_7$, $Li_4P_2O_7(l)$ and $(LiPO_3)_x \cdot H_2O$. The main anion component in the reaction products was pyrophosphate, the content of which reached 87–89% P_2. The formation of its crystalline forms was reflected in the IR spectra, for instance, in the form of an absorption band at 1245 cm^{-1}, which is characteristic of the $H_2P_2O_7^{2-}$ ion [6]. The other anion components were polyphosphates ($P_{>3}$). In the products heated at 400° and higher temperatures, part of the phosphorus remained at the start (P_{start}) during chromatography. In these cases phosphorus was not fully transferred into solution with the KU–2 cation-exchanger. Polymeric crystalline phosphate $(LiPO_3)_x \cdot H_2O$ with $x > 8$–10 was not transferred into solution.

The XRD and TLC analysis data correlated with the results of DSC and TG studied (Fig. 2): the components of the $LiH_2PO_4 + 2Li_2HPO_4$ mixture were dehydrated without the formation of a triphosphate. The main effects of the thermal conversions of $LiH_2PO_4 + 2Li_2HPO_4$ corresponded to the thermal effects of the main mixture component, Li_2HPO_4 (Table 2). Specifically, there were close correlations between the temperatures of the formation $Li_2H_2P_2O_7$ (233–235° for $LiH_2PO_4 + 2Li_2HPO_4$ and 232–233° for Li_2HPO_4), of the formation of $Li_4P_2O_7(l)$ (382–385° and 375–379°), of the phase transition $Li_4P_2O_7(l) \rightarrow Li_4P_2O_7(h)$ (617° and 615°), of the melting of $(LiPO_3)_x \cdot H_2O$ (656° and 661°), of the crystallization of $(LiPO_3)_x \cdot H_2O$ during cooling (650° and 647°), and of the phase transition $Li_4P_2O_7(h) \rightarrow Li_4P_2O_7(l)$ during cooling (526° and 523°). The melting temperature found for $(LiPO_3)_x \cdot H_2O$ coincided with those reported: 656–665° [2, 7, 8]. The

Table 1 Anion and phase composition of the products of isothermal treatment of lithium phosphate mixtures in air (p = 990 hPa)

t, °C	τ, min	Phosphorus content, mass. %				Crystalline phases*
		P_1	P_2	P_3	$P_{>3}+P_{start}$	
		Mixture $LiH_2PO_4+2Li_2HPO_4$				
150	30	91.5	8.5	0	0	—
150	300	93.3	6.7	0	0	I, II
180	30	79.3	16.6	traces	4.1	—
180	300	12.7	75.9	traces	11.4	I, II, III, IV
200	30	13.9	70.3	traces	15.8	—
200	300	13.3	79.2	traces	7.5	I, II, III, IV
220	30	11.2	73.2	traces	15.5	—
220	300	9.9	74.8	traces	15.3	I, II, III, IV
300	30	6.1	78.0	traces	15.9	—
300	300	5.2	69.5	traces	25.3	III, IV, V
400	30	10.7	79.1	traces	10.2	—
400	300	7.7	87.2	traces	5.1	III, IV, V
500	30	8.3	78.5	0	13.2**	—
500	300	3.6	89.3	0	7.1**	IV, V
		Mixture $LiH_2PO_4+Li_4P_2O_7$				
20	0	37.0	63.0	0	0	I, IV
200	30	3.2	71.8	7.1	17.9	—
200	120	2.0	74.0	7.7	16.3	—
200	300	6.4	82.3	3.6	7.7	III, IV
300	30	0	70.5	0	29.5	—
300	120	0.8	65.4	0	33.8	—
300	300	1.2	73.0	0	25.8	IV, V
400	30	1.8	79.0	0	19.2	—
400	120	4.3	83.9	0	11.8	—
400	300	0.9	82.7	0	16.4	IV, V
500	30	3.1	73.7	traces	23.2	—
500	120	1.7	77.9	0	20.4**	—
500	300	1.7	71.8	0	26.5**	IV, V

* I—LiH_2PO_4, II—Li_2HPO_4, III—$Li_2H_2P_2O_7$, IV—$Li_4P_2O_7(l)$, V—$(LiPO_3)_x \cdot H_2O$

** phosphorus is not fully transferred into solution

temperatures for the transition $Li_4P_2O_7(l) \rightarrow Li_4P_2O_7(h)$ were somewhat lower than those known in the literature: 630–640° [2, 7, 8]. LiH_2PO_4 behaved quite differently during heating. First, at around 240°, in contrast to the other compounds studied, it passed into the liquid state (this phenomenon, studied microscopically, was reported in [5]), apparently due to the formation of free acid in a disproportionation reaction of the type $2\,LiH_2PO_4 \rightarrow Li_2HPO_4+H_3PO_4$. When

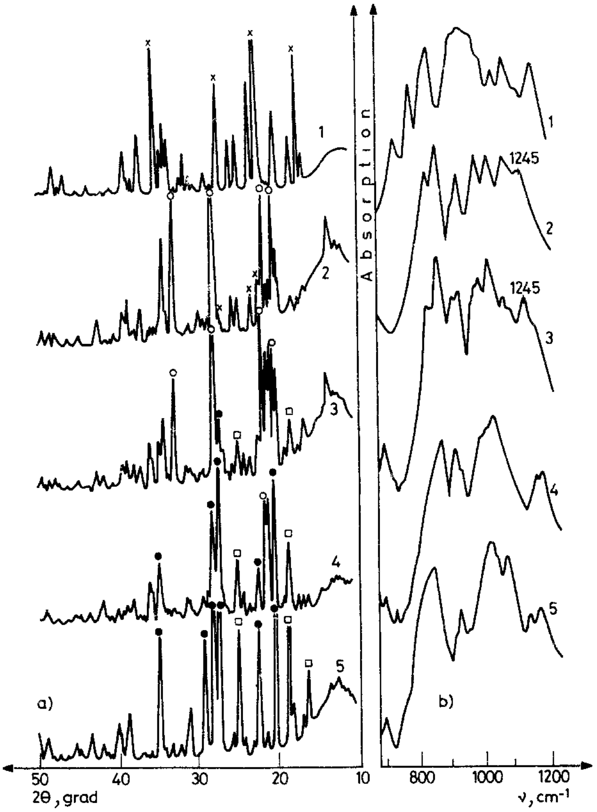

Fig. 1 X-ray patterns (a) and IR-spectra (b) of the products of isothermal treatment of the phosphate mixture $LiH_2PO_4 + 2Li_2HPO_4$ in air (p = 990 hPa, τ = 300 min): 1 – initial mixture, 2 – t = 180°, 3 – t = 300°, 4 – t = 400°, 5 – t = 500°; I – LiH_2PO_4 *, II – Li_2HPO_4 *, III – $Li_2H_2P_2O_7$ ○, IV – $Li_4P_2O_7(l)$ ●, V – $(LiPO_3)_x \cdot H_2O$ □

the temperature rose to 400–420°, the liquid boiled away (here the DSC curve had a characteristic dent-like form). Second, on cooling, the sample set to a vitreous mass without the crystallization of $(LiPO_3)_x \cdot H_2O$ or $Li_4P_2O_7(l)$ (see DSC curve 1',Fig. 2). These phases crystallized when the heating-cooling cycle was repeated several times.

Table 2 shows DTA data obtained from derivatographic experiments (Fig. 3). On the whole they correspond to the DSC data, notwithstanding the differences in the conditions of the DTA and DSC experiments. The DTG data are limited by the results obtained with the Thermal Analysis Lab 1.

The above-mentioned results and their comparison with the literature data show that, on the therml treatment below the melting temperatures, mixtures of sodium or potassium phosphates quantitatively transform into the corresponding

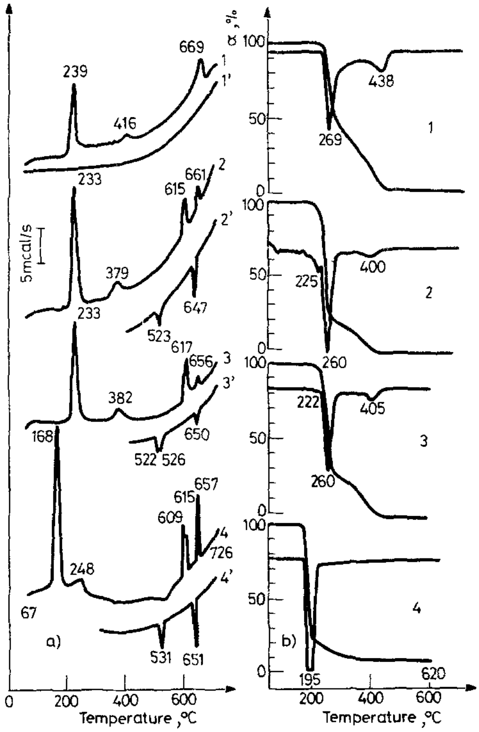

Fig. 2 DSC – (a), TG – and DTG – curves (b) of heating individual lithium phosphates and mixtures thereof in the flow of nitrogen (p = 990 hPa): 1 – LiH_2PO_4, 2 – Li_2HPO_4, 3 – LiH_2PO_4 + $2Li_2HPO_4$, 4 – $Li_5P_3O_{10} \cdot 5H_2O$; 1′, 2′, 3′, 4′ – curves of cooling (20 K/min)

crystalline triphosphates. Analogous mixtures of lithium phosphates contain either no triphosphate at all or only a small amount of it. Such a difference is explained by the specific properties of lithium ions, which, for instance, differ from sodium and potassium ions in polarization degree, their lower mobility and a higher degree of metal-phosphate bond covalency [13].

Due to their low mobility, Li^+ ions cannot migrate from regions abundant in lithium to lithium-lacking regions, as takes place with Na^+ ions during the formation of sodium triphosphate [14]. However, this is not the main reason hindering the formation of lithium triphosphate, because shortening of the migration path due to the better contact between the particles of the reacting components does not solve the problem in principle. When $Li_5P_3O_{10} \cdot 5H_2O$ is heated, the triphosphate chain ruptures into ortho- and pyrophosphate fragments, which are in close contact with each other, but further increase of temperature does not lead to recombination of the fragments into anhydrous triphosphate, as occurs with the sodium and potassium salts. On removal of the bulk of the water from the

Table 2 Temperatures of effects (*t*, °C) of thermal transformation of individual phosphates of lithium and mixtures thereof (for DSC and DTA (derivatograph)—maximum of effects, for DTG—beginning of the effects);

A—formation of $Li_2H_2P_2O_7$,
B—formation of $Li_4P_2O_7(l)$, C—transition $Li_4P_2O_7(l) \rightarrow Li_4P_2O_7(h)$,
D—melting of $(LiPO_3)_x \cdot H_2O$, E—crystallization of $(LiPO_3)_x \cdot H_2O$ during cooling,
F—transition $Li_4P_2O_7(h) \rightarrow Li_4P_2O_7(l)$ during cooling

Sample	A			B			C			D			E	F
	DSC	DTA	DTG	DSC	DTA	DTG	DSC	DTA	Published data	DSC	DTA	Published data	DSC	DSC
LiH_2PO_4	239	—	240	416	—	400	—	—	630 [2]	669	—	665 [2]	—	—
Li_2HPO_4	233	—	232	379	—	375	615	—	646 [7]	661	—	658 [7]	647	523
$LiH_2PO_4 + 2Li_2HPO_4$	233	220	235	382	370	385	617	605	645 [8]	656	650	656 [8]	650	526
$Li_5P_3O_{10} \cdot 5H_2O$*	248	270	—	—	—	—	615	595		657	640		651	531

* Effect A is preceded by the $Li_5P_3O_{10} \cdot 5H_2O$ dehydration effect at 168° (DSC), 165° (DTA), 175° (DTG)

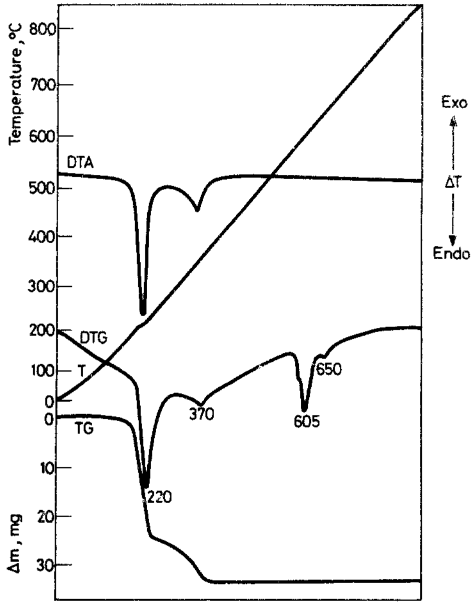

Fig. 3 Derivatogram of phosphate mixture $LiH_2PO_4 + 2Li_2HPO_4$ in air

samples, the DTA and DSC curves of $Li_5P_3O_{10} \cdot 5H_2O$ practically repeat the analogous curves for $LiH_2PO_4 + 2Li_2HPO_4$ (Fig. 2), except for an additional effect at 609°, which could be explained, taking into account the close contact between the components, by melting of the eutectic of $Li_4P_2O_7(l) - (LiPO_3)_x \cdot H_2O$ (603–604° according to [7, 8]).

The main reason for the low yield of lithium triphosphate resides in the high crystallization rate of $Li_4P_2O_7(l)$, which due to its low reactivity, practically does not participate in the recombination reaction. Such cases of reactivity loss because of the crystallization of the reacting components are also known for sodium phosphates [1].

In accordance with this, the factors that cause mineralizing action and accelerate sodium triphosphate crystallization are ineffective in our case; they increase the yield of crystalline pyrophosphate, leaving the lithium triphosphate yield unaffected. The contents of pyrophosphate in the products of thermal treatment of $LiH_2PO_4 + 2Li_2HPO_4$ and $LiH_2PO_4 + Li_4P_2O_7(l)$ in a flow of water vapour, which provides mineralizing action, increase to 96–98% P_2, while in vacuum the content does not exceed 74–77% P_2 (Table 3). The additive NH_4NO_3 ($\approx$ 1 mass per cent), which increases the yield of $Na_5P_3O_{10}$ (form II), also proved ineffective. In our case this additive, similar to the action of water vapour, increased the yield of crystalline lithium pyrophosphate.

Table 3 Anion composition of products of isothermal treatment of lithium phosphate mixtures in vacuum ($p = 10^{-3}$ hPa) and in flow of water vapour ($p_{H_2O} = 990$ hPa)

t, °C	τ, min.	Phosphorus content, mass. %			
		P_1	$_2$	$_3$	$_{>3}+P_{start}$
		Mixture $LiH_2PO_4+2Li_2HPO_4$, $p = 10^{-3}$ hPa			
218	30	46.9	53.1	0	0
218	300	7.9	73.6	traces	18.5
256	30	21.3	57.4	traces	21.3
256	300	6.5	69.6	traces	23.9
300	300	10.8	65.8	traces	23.4
400	300	3.1	76.6	traces	20.3**
500	300	9.4	66.7	traces	23.9**
		Mixture $LiH_2PO_4+2Li_2HPO_4$, $p_{H_2O} = 990$ hPa			
150	30	100.0	0	0	0
150	300	92.8	7.2	0	0
200	30	74.1	25.9	0	0
200	410	8.3	89.6	0	2.1
250	30	5.9	91.9	0	2.2
250	120	2.0	96.0	0	2.0
300	30	5.9	88.1	traces	6.0
300	300	2.8	94.7	0	2.5**
400	30	6.8	81.6	0	11.6**
400	360	5.4	86.0	0	8.6**
500	30	6.1	84.6	0	9.3**
500	300	2.5	95.5	0	2.0**
		Mixture $LiH_2PO_4+Li_4P_2O_7(l)$, $p_{H_2O} = 990$ hPa			
200	30	1.0	97.8	0	1.2
200	300	1.2	97.5	0	1.3
300	30	1.1	76.5	traces	22.4
300	120	0	81.8	traces	18.2
400	120	5.1	81.6	0	13.3**
400	300	3.8	81.7	0	14.5**
500	30	2.0	96.0	0	2.0**
500	120	1.1	97.9	0	1.0**

** phosphorus is not fully transferred into solution

The above facts do not mean that lithium triphosphate can definitely not be obtained by the thermal treatment of phosphate mixtures with the general ratio Li : P ≈ 5 : 3. Experiments with the addition of urea, which possesses condensing properties with respect to alkali metal phosphates [15], indicated that in the mixtures $LiH_2PO_4+2Li_2HPO_4+(NH_2)_2CO$ and $LiH_2PO_4+2Li_2HPO_4+2(NH_2)_2CO$ a certain amount of triphosphate was formed even at 150° (Table 4).

Table 4 Anion composition of products of isothermal treatment of mixtures of lithium phosphates with urea in air (p = 990 hPa; P_4, P_5, P_6, P_7—content of phosphorus in the form of tetra-, penta-, hexa- and heptapolyphosphate respectively)

t, °C	τ, min	Phosphorus content, mass. %				
		P_1	P_2	P_3	$P_4+P_5+P_6+P_7$	P_{start}
		Mixture $LiH_2PO_4+2Li_2HPO_4+(NH_2)_2CO$				
100	30	87.9	12.1	0	0	0
100	120	84.6	15.4	0	0	0
128	10	63.1	30.8	0	6.1	0
128	300	44.7	35.6	2.0	17.7	0
150	10	48.0	24.0	15.0	13.0	0
150	120	43.0	30.7	14.5	11.8	0
150	300	32.6	41.7	14.4	11.3	0
200	10	39.2	23.6	17.1	15.1	5.0
200	30	31.6	36.5	11.9	15.2	4.8
200	300	8.1	47.1	4.1	30.6	10.1
300	10	13.4	43.9	12.3	22.9	7.5
300	30	16.5	42.7	6.8	25.8	8.2
300	300	3.0	69.3	0	20.4	7.3
400	30	8.8	69.6	0	10.9	10.7
400	300	6.7	74.6	0	9.3	9.4
500	30	4.4	79.5	0	11.9	4.2**
500	300	6.8	68.0	0	19.0	6.2**
		Mixture $LiH_2PO_4+2Li_2HPO_4+2(NH_2)_2CO$				
100	30	97.2	2.8	0	0	0
100	300	44.6	31.9	12.7	10.8 (P_4)	0
200	30	45.0	6.0	12.1	34.9	2.0
200	300	29.3	26.8	5.6	31.1	7.2
300	10	32.9	19.9	2.0	37.3	7.9
300	300	11.1	49.0	traces	30.7	9.2
400	10	8.0	66.2	traces	20.7	5.1
400	300	2.1	95.5	0	0	2.4
500	10	20.1	75.0	0	0	4.9
500	300	5.0	89.9	0	0	5.1

** phosphorus is not fully transferred into solution

However, the formation of triphosphate is connected with the partial substitution of lithium ions by ammonium ions, as proved by the appearance of the 1400 cm^{-1} absorption band corresponding to NH_4^+ group oscillations in neutral and double ammonium phosphates (Fig. 4). With the increase of temperature and time, as the formed ammonium phosphates decompose, the intensity of the 1400 cm^{-1} absorption band diminishes and the content of P_3 simultaneously decreases. At

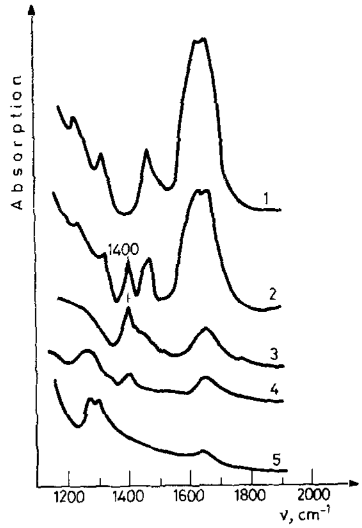

Fig. 4 IR-spectra of the products of isothermal treatment of $LiH_2PO_4+2Li_2HPO_4+(NH_2)_2CO$ mixture in air (p = 990 hPa, τ = 300 min): 1 – initial mixture, 2 – 100°, 3 – 150°, 4 – 200°, 5 – 300°

$t \geq 400°$, the anion and phase compositions of the products of thermal treatment of the mixtures $LiH_2PO_4+2Li_2HPO_4$ and $LiH_2PO_4+2Li_2HPO_4+(1-2)(NH_2)_2CO$ are identical.

Lowering of the temperature of anion condensation of the mixtures $LiH_2PO_4+2Li_2HPO_4+(1-2)(NH_2)_2CO$, as compared with $LiH_2PO_4+2Li_2HPO_4$, is connected with the formation of a liquid phase, caused by the melting of urea. The samples with urea additives at 100–300° present a sticky or viscous mass. It seems obvious that in the liquid phase the rates of formation of individual oligomers are equalized and triphosphate is formed together with pyrophosphate in the reacting mixture, but triphosphate is not accumulated in large amounts.

Other cases where triphosphate could be detected are also connected with the liquid phase. It is known that in phosphate glass with the overall composition $Li_5P_3O_{10}$, the function of the anion size distribution corresponds to the contents 34% P_2, 38% P_3, 18% P_4, 6% P_5, 3% P_6 and 1% P_7 [1]. The amount of triphosphate depends on the temperature of the melt, the duration of its isothermal treatment and the cooling rate. Vitreous samples obtained by heating $LiH_2PO_4+2Li_2HPO_4$ mixtures at temperatures above and below the melting temperature of $Li_4P_2O_7(h)$ (876–885° [2, 7, 8]) contain 7–17% P_3 (Table 5).

Table 5 Anion and phase composition of vitreous samples, obtained by isothermal treatment of the $LiH_2PO_4 + 2Li_2HPO_4$ mixture in air (p = 990 hPa, ν—rate of melt cooling)

t, °C	τ, min	ν, K/min	Phosphorus content, mass. %					Crystalline phases*
			P_1	P_2	P_3	$P_4+P_5+P_6+P_7$	P_{start}	
700	120	30–35	7.9	46.6	11.8	33.7	0	IV, VI
700	120	2–3	6.5	35.6	17.3	32.5	8.1	IV, V
850	90	30–35	2.2	59.3	6.6	25.4	6.4	IV, V, VII
850	90	2–3	0.5	59.2	7.1	26.6	6.9	IV, VII
1050	45	30–35	4.5	56.5	6.9	26.2	6.1	IV, VII

* IV—$Li_4P_2O_7(l)$, V—$(LiPO_3)_x \cdot H_2O$, VI—Li_3PO_4, VII—non-identified phase

Conclusions

In contrast to the solid-state interaction of analogous mixtures of sodium or potassium phosphates, the solid-state interaction of the components of lithium phosphate mixtures with the general ratio Li : P $\approx$ 5 : 3, does not lead to the quantitative formation of anhydrous triphosphate. This fact is explained by the high rate of crystallization of neutral lithium pyrophosphate, which due to its low reactivity, does not participate in further anion condensation. A contribution is made to the increase of triphosphate yield by the liquid phase formed on acid salt disproportionation, on the melting of reaction mixture components, or as a result of the introduction of urea additives.

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Zusammenfassung — Die während der Erwärmung von LiH_2PO_4, Li_2HPO_4 und $Li_5P_3O_{10}\cdot 5H_2O$ sowie von Gemischen von $LiH_2PO_4-2Li_2HPO_4$ und $LiH_2PO_4-Li_4P_2O_7(l)$ in Vakuum, Luft und Wasserdampfatmosphäre bei 20–1050 °C verlaufenden Umwandlungen wurden isotherm und nichtisotherm mittels TG, DTG, DTA, DSC, IR-Spektroskopie, XRD und TLC untersucht. Es wird gezeigt, daß die Festkörperreaktion der Komponenten von Gemischen mit dem allgemeinen Verhältnis Li : P ≈ 5 : 3 — im Gegensatz zur Reaktion der Komponenten der entsprechenden, Natrium- bzw. Kaliumphosphat enthaltenden Gemische — nicht zur quantitativen Bildung von Lithiumtriphosphat führt. Das wird der hohen Kristallisationsgeschwindigkeit von Lithiumpyrophosphat zugeschrieben, das wegen seiner geringen Reaktionsfähigkeit keiner weiteren Anionenkondensation unterliegt. Die Triphosphat-Ausbeute ist in flüssiger Phase, die durch Disproportionierung sauer Salze, durch Schmelzen der Reaktionskomponenten oder bei Zugabe von harnstoff gebildet wird, größer.

Резюме — Методами ТГ, ДТГ, ДСК, ДТА, рентгенофазового и ТСХ-анализов, ИК спектроскопии исследованы изо- и неизотермические превращения, происходящие при нагревании LiH_2PO_4, Li_2HPO_4, $Li_5P_3O_{10}\cdot 5H_2O$, смесей $LiH_2PO_4+2Li_2HPO_4$ и $LiH_2PO_4+Li_4P_2O_7$ (н) в вакууме, атмосфере воздуха и паров воды при 20–1050°. Показано, что твердофазное взаимодействие компонентов смесей с общим отношением Li : P ≈ 5 : 3, в отличие от твердофазного взаимодействия аналогичных смесей фосфатов натрия (калия), не приводит к количественному образованию безводного триполифосфата. Это объясняется высокой скоростью кристаллизации среднего пирофосфата лития, который, вследствие своей низкой реакционной способности, не участвует в дальнейшей анионной конденсации. Увеличению выхода триполифосфата способствует жидкая фаза, образующаяся в результате диспропорционирования кислых солей, введения добавок мочевины или плавления компонентов реакционной смеси.