THE THERMAL BEHAVIOR OF THE BINARY SYSTEMS OF LITHIUM-POTASSIUM PHOSPHATES

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Abstract The thermal behavior of some phosphates, lithium hydrogen phosphates represented by $\text{Li}_x\text{H}_{3-x}\text{PO}_4$ ($x=1, 1.5, 2$) mixed with potassium dihydrogen phosphate, were investigated using DTA-TG, XRD and HPLC-FIA. These results showed a formation region, and the reason for the formation of cyclic phosphates was discussed.

The formation region in LiH_2PO_4 - KH_2PO_4 system, LiH_2PO_4 and KH_2PO_4 influenced. The samples of R (indicated that the molar ratio of LiH_2PO_4 to KH_2PO_4) $\cong 1:1$ therefore showed original thermal behaviors in which cyclic phosphates were produced slightly above 450°C . In the $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ - KH_2PO_4 system, the addition of KH_2PO_4 to $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ greatly influenced the thermal behavior of $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ and suppressed the change of $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ to $\text{Li}_3\text{HP}_2\text{O}_7$, while the addition of $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ to KH_2PO_4 influenced slightly the thermal behavior of KH_2PO_4 . In the Li_2HPO_4 - KH_2PO_4 system, the addition of KH_2PO_4 to Li_2HPO_4 influenced slightly the thermal behavior of Li_2HPO_4 , while the addition of Li_2HPO_4 to KH_2PO_4 influenced that of KH_2PO_4 .

Although the thermal behavior of $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ due to heating was the disproportionation reaction which was composed of the main-reaction (the formation of linear poly-phosphate) and a side-reaction (that of cyclic-phosphate), the addition of KH_2PO_4 to $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ restricted the side-reaction to some extent. This seems to be due to the suppression of the formation of $\text{Li}_3\text{HP}_2\text{O}_7$ produced at first step of the side-reaction.

INTRODUCTION

It is well-known that the hydrogen ortho-phosphates changes easily to linear or cyclic condensed phosphates by heating. The linear or cyclic structure is influenced by the kind of the cation, the cation-phosphorus ratio, heating temperature, etc. For example, on heating, NaH_2PO_4 and LiH_2PO_4

changes to cyclic and/or linear condensed phosphates, and KH_2PO_4 changes to linear ones. The complex behavior of lithium salt is caused by the disproportionation shown in the Scheme. The main-reaction produced only linear condensed phosphates and the side-reaction produced cyclic condensed phosphates. It is interesting to investigate the thermal behavior of the binary system of alkali metal phosphates which have such different properties.

In this work, we mainly studied the lithium phosphate which showed a unique reaction on the process of thermal change and we investigated the thermal behavior of the binary system of lithium and potassium phosphates using DTA-TG, XRD and HPLC-FIA.

SCHEME Thermal Dehydration of LiH_2PO_4 ²⁾

EXPERIMENTAL

Preparation of samples for heating

The lithium phosphates ($\text{Li}_x\text{H}_3-x\text{PO}_4$) were prepared by mixing Li_2CO_3 and H_3PO_4 (85%) and then heating the mixture at 50°C . The phosphates obtained were analysed using HPLC-FIA, XRD, DTA-TG and ICP. From analytical results, lithium phosphates represented by $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ and Li_2HPO_4 were composed of $3\text{LiH}_2\text{PO}_4 + \text{Li}_3\text{PO}_4$ and $\text{LiH}_2\text{PO}_4 + \text{Li}_3\text{PO}_4$, respectively. The samples for heating were prepared by mixing $\text{Li}_x\text{H}_3-x\text{PO}_4$ with KH_2PO_4 at several molar ratios R ($\text{Li}_x\text{H}_3-x\text{PO}_4 / \text{KH}_2\text{PO}_4$) = 10/1 ~ 1/10.

Heating and Analysis

DTA-TG equipment was used to investigate the thermal behavior. The mixed samples were heated around the temperature shown by the DTA peaks; the heated products were cooled immediately and analysed using HPLC-FIA and XRD.

RESULTS AND DISCUSSION

LiH₂PO₄-KH₂PO₄ system

Figure 1 shows the DTA-TG curves of the sample of R (LiH₂PO₄/KH₂PO₄) = 10/1. The large endothermic peaks around 220°C, some exothermic peaks around 320°C, small peaks around 390°C and an endothermic peak around 610°C were observed. The products heated at each temperature shown by arrows in Fig. 1 were analysed. Table 1 and Fig. 2 show the results

FIGURE 1 DTA-TG Curves of R(LiH₂PO₄/KH₂PO₄)=10/1 Sample.

FIGURE 2 X-Ray Diffraction Patterns of Products Heated at Several Temperatures in LiH₂PO₄/KH₂PO₄=10/1(R) System.

○; Li₃HP₂O₇ △; (LiPO₃)_n; (1) 225°C (2) 320°C (3) 490°C (4) 700°C

of HPLC-FIA and XRD, respectively. From Table 1, the two peaks at 220°C are the condensation reaction from ortho- to pyro-phosphate, and the change from 220 to 390°C is the condensation from low-polymer to high-polymer.

The peak at 660°C was due to melting of poly-phosphate. The X-ray diffraction patterns (Fig.2) of products at 225 and 320°C showed those of Li₃HP₂O₇ which had low-crystallinity. Those at 490°C and 700°C showed

TABLE 1 Changes in the Amounts of Phosphate Compounds of the Samples Heated at Several Temperatures in $\text{LiH}_2\text{PO}_4/\text{KH}_2\text{PO}_4=10/1(\text{R})$ System

Compound ^{a)}	P1	P2	P3	Polig.	P6m	P4m	P3m	Ppoly.	Pinsol.
225(°C)	17.1	45.1	5.5	6.5	0.0	0.0	0.0	0.0	25.8
320(°C)	6.7	27.4	10.5	26.2	0.0	0.0	0.0	0.0	29.2
490(°C)	0.0	0.0	0.5	2.6	0.0	0.0	0.0	3.3	93.6
700(°C)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	11.8	88.2

a) P1, P2, P3, Polig., P6m, P4m, P3m, Ppoly. and Pinsol. represent ortho-, pyro-, tri-, olig.-(chain length, $n=5-9$), cyclo-hexa-, cyclo-tetra-, cyclo-tri-, poly.-(chain length, $n=9-20$) and insoluble phosphate, respectively.

lithium poly-phosphate and amorphous phase, respectively. These results of XRD supported those of HPLC-FIA.

The same experiments were carried out for several samples with different molar ratios and the diagrams of the formation region were designed.

Figure 3 shows the formation region in the $\text{LiH}_2\text{PO}_4\text{-KH}_2\text{PO}_4$ system. In this figure, the abbreviation (amo.) indicates an amorphous phase, as seen from XRD results.

In the region of $1/2 < R < 2$, cyclic-phosphates, i.e., cyclotri-(P3m) in the yield of 1%, cyclotetra-(P4m) in 1% and cyclohexa-(P6m) phosphate in 1%, were produced at higher temperature, except for the absence of P4m and P6m above 600°C. These cyclic-phosphates in this region do not produce through the side-reaction of the disproportionation reaction, but produce by the convenient cleavage of the P-O-P linkages of spiral structure of high polymer.

FIGURE 3 Formation Region in $\text{LiH}_2\text{PO}_4\text{-KH}_2\text{PO}_4$ System.

$\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4\text{-KH}_2\text{PO}_4$ system

Figure 4 shows the formation region in the $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4\text{-KH}_2\text{PO}_4$ system. A little addition of KH_2PO_4 to $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ influenced the thermal behavior

FIGURE 5 X-Ray Diffraction Patterns of Products Heated at Relative Low Temperature. ○; Li₃HP₂O₇ △; Li₄P₂O₇(III)

(1) Li_{1.5}H_{1.5}PO₄, 315°C (2) R=20/1, 288°C
(3) R=10/1, 285°C (4) R=5/1, 315°C

- (i) Li₄P₄O₁₂, Li₃HP₂O₇, Li₄P₂O₇(III), (Li,K)PO₃(amo.), LiPO₃
(ii) Li₄P₄O₁₂, Li₄P₂O₇(III), (Li,K)PO₃(amo.), LiPO₃
(iii) Li₄P₂O₇(III), (Li,K)PO₃(amo.), LiPO₃
(iv) Li₄P₂O₇(II), (Li,K)PO₃(amo.), LiPO₃
(v) Li₄P₄O₁₂, Li₆P₆O₁₈, Li₄P₂O₇(II), (Li,K)PO₃(amo.), LiPO₃
(vi) Li₆P₆O₁₈(amo.), Li₄P₂O₇(II), (Li,K)PO₃(amo.), LiPO₃(amo.)
(vii) KH₂PO₄, KPO₃(amo.), (Li,K)PO₃(amo.)
(viii) KPO₃(amo.), (Li,K)PO₃(amo.)
(ix) KPO₃, (Li,K)PO₃(amo.)

FIGURE 4 Formation Region in Li_{1.5}H_{1.5}PO₄-KH₂PO₄ System.

- (i) Li₄P₂O₇(III), Li₃HP₂O₇, Li₃PO₄, (Li,K)PO₃(amo.)
(ii) KH₂PO₄, (Li,K)PO₃(amo.)
(iii) KPO₃(amo.), (Li,K)PO₃(amo.)
(iv) Li₄P₂O₇(III), (Li,K)PO₃(amo.)
(v) Li₃PO₄, Li₄P₂O₇(III), Li₃HP₂O₇, Li₄P₄O₁₂
(vi) Li₃PO₄, Li₄P₂O₇(III), Li₆P₆O₁₈
(vii) Li₄P₂O₇(III), Li₄P₂O₇(II), Li₃PO₄

FIGURE 6 Formation Region in Li₂HPO₄-KH₂PO₄ System.

of $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$. P4m in the yield of about 20% and P6m in about 35% were produced when $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ alone was heated at 500 and 700°C, respectively. However, cyclic-phosphates (P4m and P6m) in 9% were produced by heating of the sample of $R=10/1$, and no cyclic-phosphates was produced from the samples of $R \leq 5/1$ at any temperature. Figure 5 shows X-ray diffraction patterns of products heated at relatively low temperature. The heated product of $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ had the strong peaks of $\text{Li}_3\text{HP}_2\text{O}_7$. As R value decreased, the intensity of the peaks of $\text{Li}_3\text{HP}_2\text{O}_7$ became weaker. This indicates that the addition of KH_2PO_4 suppressed the change of $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ to $\text{Li}_3\text{HP}_2\text{O}_7$.

Thus, in the region of $R > 5$, the disproportionation reaction occurred, though it was affected to some extent by the addition of KH_2PO_4 . On the other hand, in the region of $R \leq 5$, the addition of $\text{Li}_{1.5}\text{H}_{1.5}\text{PO}_4$ to KH_2PO_4 influenced slightly the thermal behavior of KH_2PO_4 .

$\text{Li}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ system

Figure 6 shows the formation region in the $\text{Li}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ system. The addition of KH_2PO_4 to Li_2HPO_4 did not greatly influence the thermal behavior of Li_2HPO_4 because $\text{Li}_4\text{P}_2\text{O}_7(\text{III})$ is stable. However, cyclic-phosphate was suppressed to product, e.g., 1% of P4m was produced at 400°C. At the sample of $R=10/1$, however, no cyclic-phosphate was produced at any temperature.

The addition of Li_2HPO_4 to KH_2PO_4 influenced the thermal behavior of KH_2PO_4 . The product of $R=1/2$ sample heated at about 500°C showed the X-ray diffraction patterns of $\text{Li}_4\text{P}_2\text{O}_7(\text{III})$ and $\text{Li}_4\text{P}_2\text{O}_7(\text{II})$. One reason for these results may be that many lithium cations are present in this region, and thus the molar ratio of cation to phosphorus was high.

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