NOTES *Bull. Chem. Soc. Jpn.*, **60**, 3050—3052 (1987) [Vol. 60, No. 8

The Thermal Decomposition of Lithium Hydrogenphosphoramidate Trihydrate

Choichiro Shimasaki,* Hiroki Suzuki, and Hiroshi Toda
Department of Industrial Chemistry, Faculty of Engineering, Toyama University, Gofuku, Toyama 930
(Received December 17, 1986)

Synopsis. The thermal decomposition of lithium hydrogenphosphoramidate trihydrate $LiHPO_3NH_2 \cdot 3H_2O$ was investigated by means of DTA-TG, X-ray diffraction analysis, IR, ^{31}P NMR, and compositional analysis. The decomposition proceeds via an anhydrous phase, a newly found intermediate phase, and polyphosphates to lithium metaphosphate. The activation energies of the dehydration of the water of crystallization and of the polymerization reaction for the thermal decomposition were estimated to be 96.2 and 105.4 kJ mol^{-1} respectively.

The reaction products[1,2] between urea (or its nitrogen derivatives) and phosphoric acid have been used as a flameproofing and fire-retardant (glow-retardent) agent. The derivatives of phosphoramidates have been investigated systematically for these purposes: The thermal decomposition of ammonium, sodium, and potassium hydrogenphosphoramidate (anhydrous salts) was previously reported by the present authors.[3,4] The decomposition study was been extended to lithium hydrogenphosphoramidate trihydrate $LiHPO_3NH_2 \cdot 3H_2O$ in the present work.

Experimental

Preparation Methods. No anhydrous salt was synthetically obtained. The sample (trihydrated salt, yield; 65—70%) was prepared as follows: Ammonium hydrogenphosphoramidate[5] (4.6 g 0.04 mol) was dissolved in 40 ml of a 2.0 M (1M=1 mol dm^{-3}) lithium hydroxide solution. This solution was then cooled (to 5—10 °C), neutralized (to pH 6) with glacial acetic acid, and precipitated with 300 ml of ethanol. The salt filtered out with suction was recrystallized repeatedly from a water-ethanol solution, washed with ethanol and ether, and air-dreid.

Measurements. The chemical analysis was made by the method reported by Watanabe et al.[6] The DTA-TG (Rigakudenki Co., Ltd., Japan) was performed in air. The dehydrated samples were hygroscopic, so that the X-ray diffraction was measured at high temperatures with nickel-filtered Cu*Kα* radiation with a X-ray diffractometer XD-3A (Shimazu Co., Ltd., Japan). The IR spectra (KBr disc method) of a sample (quenched and preserved in a desiccator) were measured with an IR-810 spectrometer (JASCO, Japan). The ^{31}P NMR spectra of the solutions were measured with a JNM-FX-900FT-NMR spectrometer (JEOL, Japan); the quenched sample (50 mg) was dropped into a 6% EDTA deuterated-water solution and stirred for several minutes.

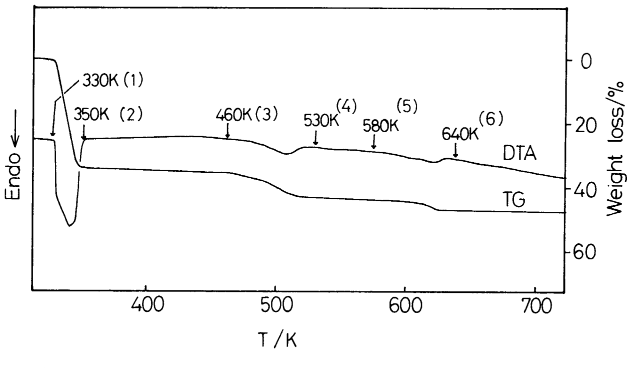


Fig. 1. DTA and TG curves of $LiHPO_3NH_2 \cdot 3H_2O$. Heating rate: 1 K min^{-1}.

Results and Discussion

A typical DTA-TG curve of $LiHPO_3NH_2 \cdot 3H_2O$ is shown in Fig. 1. In this figure, the temperatures for analyzing the samples are indicated; the results of the compositional analysis, the IR spectra, the ^{31}P NMR spectra, and the X-ray diffraction are shown in Table 1, and Figs. 2, 3, and 4 respectively. In Fig. 1, three endothermic peaks and the corresponding weight losses are shown: the first stage (330—350 K), the second stage (slight change, 460—530 K), and the third stage (slight change, 580—640 K).

The first stage of the decomposition is assumed to be the dehydration of the crystalline water as follows:

$$LiHPO_3NH_2 \cdot 3H_2O \rightarrow LiHPO_3NH_2 + 3H_2O. \qquad (1)$$

The results of the compositional analysis and the weight loss (Sample No. 2 in Table 1) support this hypothesis. The X-ray diffraction in Fig. 4 has changed from that of $LiHPO_3NH_2 \cdot 3H_2O$ (Sample No. 1) to a new pattern (Sample No. 2) which should be assigned to the anhydrous phase. A splitting of the

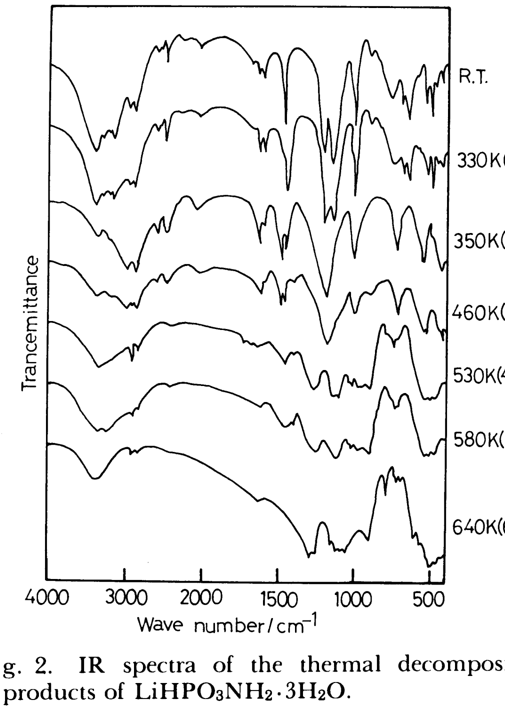
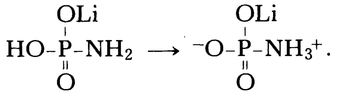


Fig. 2. IR spectra of the thermal decomposition products of $LiHPO_3NH_2 \cdot 3H_2O$.

DTA peak was observed when it was heated rapidly (e.g., 9 or 11 K min^{-1}).

The anhydrous hydrogen phosphoramidate is considered to become zwitterion as follows at 330—350 K, since the IR absorption due to the zwitterion reported by Corbrige et al.[7] were observed at 1460 and 1595 cm^{-1} in Sample Nos. 2 and 3 in Fig. 2. In Fig. 4 (the X-ray diffraction pattern of Sample Nos. 2 and 3), a decrease in the peak intensity of the anhydrous phase and a very weak trace of a different diffraction pattern (detailed analysis impossible) was apparently observed.

Therefore, lithium hydrogen phosphoramidate is considered to become zwitterion when transformed as follows:



$$\mathrm{HO{-}\overset{OLi}{\underset{O}{\overset{|}{\underset{\|}{P}}}}{-}NH_2 \longrightarrow {}^{-}O{-}\overset{OLi}{\underset{O}{\overset{|}{\underset{\|}{P}}}}{-}NH_3^{+}}. \qquad (2)$$

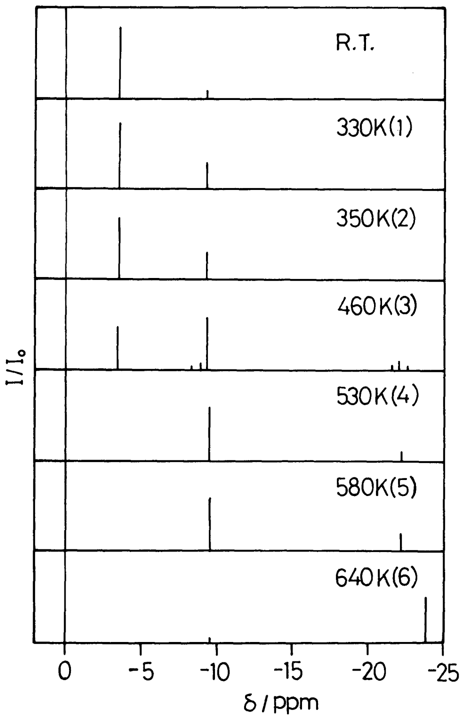
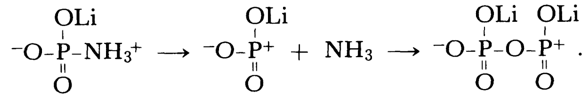


Fig. 3. ^{31}P NMR spectra and of the thermal decomposition products of $LiHPO_3NH_2 \cdot 3H_2O$.

The second stage of the decomposition is assumed to be the following reaction:



$$\mathrm{{}^{-}O{-}\overset{OLi}{\underset{O}{\overset{|}{\underset{\|}{P}}}}{-}NH_3^{+} \longrightarrow {}^{-}O{-}\overset{OLi}{\underset{O}{\overset{|}{\underset{\|}{P}}}}{}^{+} + NH_3 \longrightarrow {}^{-}O{-}\overset{OLi}{\underset{O}{\overset{|}{\underset{\|}{P}}}}{-}O{-}\overset{OLi}{\underset{O}{\overset{|}{\underset{\|}{P}}}}{}^{+}} \cdot \qquad (3)$$

The results of the compositional analysis (Sample No. 4 in Table 1), show the apparent disappearance of the IR absorption, and the X-ray diffraction pattern due to the zwitterion mentioned above (Sample No. 4 in Figs. 2 and 4), and a pungent odor of ammonia.

Concomitantly, the water in Eq. 1 is held by adsorption on the surface of the sample; therefore, the following (dimerization) reaction is assumed to occur simul-

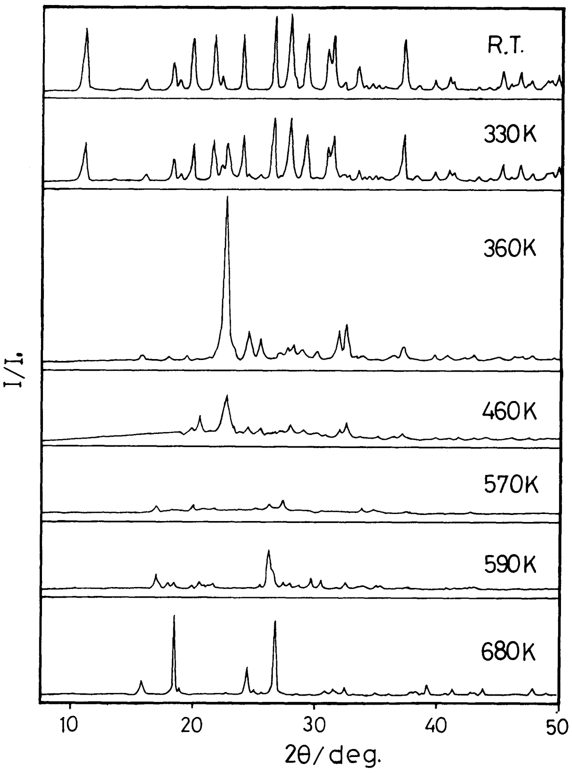


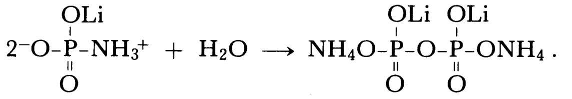
Fig. 4. X-Ray diffraction diagrams of the thermal decomposition products of $LiHPO_3NH_2 \cdot 3H_2O$. Heating rate: 2 K min^{-1}.

Table 1. Weight Loss and Composition of the Thermal Products of $LiHPO_3NH_2 \cdot 3H_2O$

Sample	Wt. loss %	P %	Li %	P/Li[a)]	Total N/%	N/% as NH_4^+	H %
R.T.	0.0	20.8	4.8	0.97	9.0	0.0	5.8
		(19.7)[b)]	(4.4)[b)]		(8.9)[b)]		(5.8)[b)]
1	2.8	20.9	4.5	1.04	9.8	0.0	5.3
2	31.4	30.0	6.4	1.05	13.0	0.0	3.3
3	33.8	30.0	6.5	1.03	12.5	2.9	3.3
	(34.4)[c)]	(30.1)[c)]	(6.7)[c)]		(13.6)[c)]		(2.9)[c)]
4	41.3	33.4	7.2	1.04	3.2	2.5	1.0
5	40.2	33.4	7.4	1.01	4.0	3.0	1.4
6	46.2	36.7	8.2	0.99	0.0	0.0	0.0
	(44.6)[d)]	(36.0)[d)]	(8.1)[d)]				

a) Mole ratios normalized by Li content. b) Calcd value of $LiHPO_3NH_2 \cdot 3H_2O$. c) Calcd value of $LiHPO_3NH_2$. d) Calcd value of $LiPO_3$.

taneously with the second stage of the decomposition:

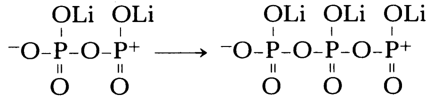


$$2\,{}^{-}O-\underset{\underset{O}{\|}}{\overset{\overset{OLi}{|}}{P}}-NH_3^{+} + H_2O \longrightarrow NH_4O-\underset{\underset{O}{\|}}{\overset{\overset{OLi}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{OLi}{|}}{P}}-ONH_4\,. \qquad (4)$$

The ^{31}P NMR spectrum of Sample No. 3 indicated small peaks of middle-PO_4 groups and small peaks of an end-PO_4 group. The product was metastable at room temperature, therefore, the ^{31}P NMR spectrum of the product indicated peaks due to phosphoramidate and an end-PO_4 group, and hardly changed in comparison with Sample No. 2. The IR absorption of a NH_4^+ was observed for Sample No. 3. It may be estimated that any indications of the polymerization reaction could be recognized by means of these results.

The ^{31}P NMR spectrum of Sample No. 6 indicated a small peak of an end-PO_4 group and a peak of a middle-PO_4 group. Sample No. 6 contained no nitrogen and hydrogen. The X-ray diffractions of the resultant thermal product at a given isothermal temperature are shown in Fig. 3. The three strongest lines of $LiPO_3NH_2 \cdot 3H_2O$ disappeared at 360 K, and the three new lines which appeared from 330 K became strong at 360 K. The diffraction lines at 360 K are considered to be those of the anhydrous product. The thermal product at 570 K was found to be amorphous by the use of an X-ray diffractor, while the product at 590 K showed weak, unknown X-ray diffraction peaks. The thermal product at 680 K showed X-ray diffraction peaks of lithium metaphosphate.[8]

The third stage of the decomposition is assumed to be the following reaction:



$${}^{-}O-\underset{\underset{O}{\|}}{\overset{\overset{OLi}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{OLi}{|}}{P}}{}^{+} \longrightarrow {}^{-}O-\underset{\underset{O}{\|}}{\overset{\overset{OLi}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{OLi}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{OLi}{|}}{P}}{}^{+} \qquad (5)$$

The activation energies of the first and second stages for the thermal decomposition for $LiHPO_3NH_2 \cdot 3H_2O$ were determined tentatively from the DTA curves (Kissinger method[9]) and the TG curves (Ozawa method[10,11]) with the heating rate of 1, 3, 5, 7, 9, and 11 $K\,min^{-1}$: 95.3 and 97.1 $kJ\,mol^{-1}$ for the first stage (average; 96.2 $kJ\,mol^{-1}$) and 103.9 and 106.8 $kJ\,mol^{-1}$ for the second stage (average; 105.4 $kJ\,mol^{-1}$) respectively.

We wish to thank Prof. Ikuya Matsuura for the X-ray diffraction analysis, Mr. Kiyoshi Terayama for the DTA–TG and Mr. Yoshiharu Yoneyama for the NMR spectra.

References

1) R. W. Little, "Flameproofing Textile Fabrics," Reinhold Publishing Corp., New York (1957), p. 410.

2) G. S. Buck, "Encyclopedia of Chemical Technology," ed by R. E. Kirk and D. F. Othmer, Interscience Publishers, New York (1951), Vol. VI, pp. 543—558.

3) C. Shimasaki, Y. Oono, F. Takai, M. Shoji, and M. Yoshizawa, *Nippon Kagaku Kaishi,* **1982**, 376.

4) C. Shimasaki, S. Ookawa, and R. Ishizaka, *Bull. Chem. Soc. Jpn.,* **58**, 592 (1985).

5) F. A. Cotton, "Inorganic Syntheses," McGraw-Hill Book Company, New York (1972), Vol. XIII, p. 23.

6) M. Watanabe, T. Inagaki, and S. Sato, *Bull. Chem. Soc. Jpn.,* **56**, 458 (1983).

7) D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.,* **1954**, 493.

8) "Index (inorganic) to the powder diffraction file," American Society for Testing Materials (1968). JCPDS Card 13—438.

9) H. E. Kissinger, *Anal. Chem.,* **29**, 1702 (1957).

10) T. Ozawa, *Bull. Chem. Soc. Jpn.,* **38**, 1881 (1965).

11) T. Ozawa, *J. Therm. Anal.,* **2**, 301 (1970).