Journal of Thermal Analysis, Vol. 38 (1992) 2123-2128

MECHANISM OF THE THERMAL DECOMPOSITION OF HYDROPHOSPHITES OF LITHIUM, SODIUM AND POTASSIUM

Z. Gontarz and W. Wišniewski

DEPARTMENT OF CHEMISTRY, WARSAW TECHNICAL UNIVERSITY,
NOAKOWSKIEGO 3, 00-664 WARSAW, POLAND

The thermal decomposition of some $M^{I}_{2}HPO_3$ (M – Li, Na, K) phosphites under nitrogen atmosphere was investigated. A stepwise mechanism of thermal decomposition has been proposed.

Keywords: hydrophoshites of lithium, sodium and potassium, mechanism of thermal decomposition

Introduction

Results of the investigation of the thermal decomposition of some hydrophosphites of alkali metals are presented in this work. In the HPO_3^{2-} anion there is direct bonding between phosphorus and hydrogen. According to the morphological classification of simple species [1–6], the anion is described by $e_v = 2$, $e_z = 5$ (e_v – number of valence electrons, e_z – number of elementary negative charges formally brought with ligands to the coordination shell).

Evolution of hydrogen from the anionic sublattice of hydrophosphites during thermal decomposition is connected with the formation of volatile products. In this system simple molecules like PH_3, H_2O and H_2 can arise. In our previous paper [6] we have shown that in the case of thermal decomposition of hydrophosphites with counter-ions of 2+ charge (e.g. Mg^{2+}, Ca^{2+}, Zn^{2+}, Sr^{2+}, Cd^{2+}, Ba^{2+}) the only gaseous product is hydrogen. Thus the course of thermal decomposition can be described by the following stoichiometric equation (mechanism I):

$$\sum (6y + 4x)HPO_3^{2-} \rightarrow (3y + 2x)H_2 + (3x + y)PO_4^{3-} + 2yP_2O_7^{4-} + P_{x+y}^{(y-x)-}$$

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

Experimental

The thermal decomposition of hydrophosphites was studied by complex thermal analysis and by identification of the reaction products by means of X-ray phase analysis and infrared absorption spectroscopy.

Complex thermal analysis was performed with the aid of a Paulik-Paulik-Erdey Derivatograph produced by MOM Budapest, which enables simuletaneous recording of T, TG, DTG and DTA curves.

The reactions were carried out in tubular furnaces at temperatures determined from thermogravimetric curves in protective atmosphere of dried, oxygen-free nitrogen.

X-ray phase analysis was performed on the Carl Zeiss TUR apparatus. The infrared absorption spectra were recorded by means of a Carl Zeiss SPECORD 75IR apparatus. Solid samples were prepared in the form of KBr pellets or as suspension in nujol. A ten-centimeter gas cell was used for the determination of gaseous products in the case of lithium hydrophosphite.

The following compounds were used in the present investigations:

– $Li_2HPO_3 \cdot H_2O$ – precipitated from diluted aqueous solutions of K_2HPO_3 and Li_2SO_4 (p. POCh, Poland),

– $Na_2HPO_3 \cdot 5H_2O$ – prepared by neutralization of an aqueous solution of H_3PO_3 with NaOH solution (p.a. POCh, Poland) in the presence of phenolophthalein,

– Na_2HPO_3 – prepared from $Na_2HPO_3 \cdot 5H_2O$ after heating for 2 hours at 250°C,

– $K_2HPO_3 \cdot H_2O$ (p. Hopkins & Williams Ltd, England),

– H_3PO_3 – prepared by hydrolysis of PCl_3 (p. Xenon, Poland) with concentrated hydrochloric acid (p.a. POCh, Poland).

Results and discussion

The results of complex thermal analysis (e.g. TG, DTG, DTA curves) are presented in Figs 1 and 2.

According to the literature [7–13], in good agreement with our investigations, the main solid products of thermal decomposition are crystalline orthophosphates and pyrophosphates, amorphous substances of uncertain composition (probably phosphides).

Investigations of the gas phase are of great importance for the determination of the mechanism of decomposition. In the literature different gaseous products

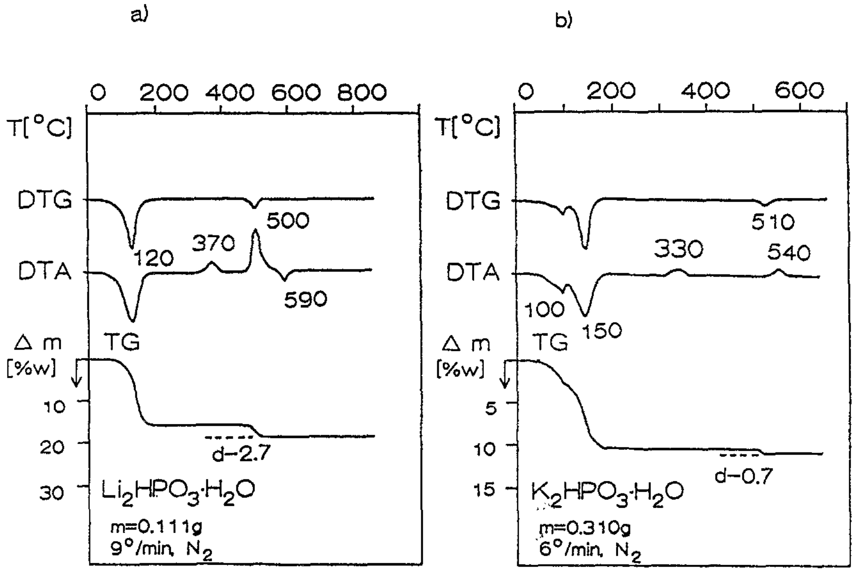

Fig. 1 TG, DTG and DTA curves of: *a*) $Li_2HPO_3·H_2O$, *b*) $K_2HPO_3·H_2O$

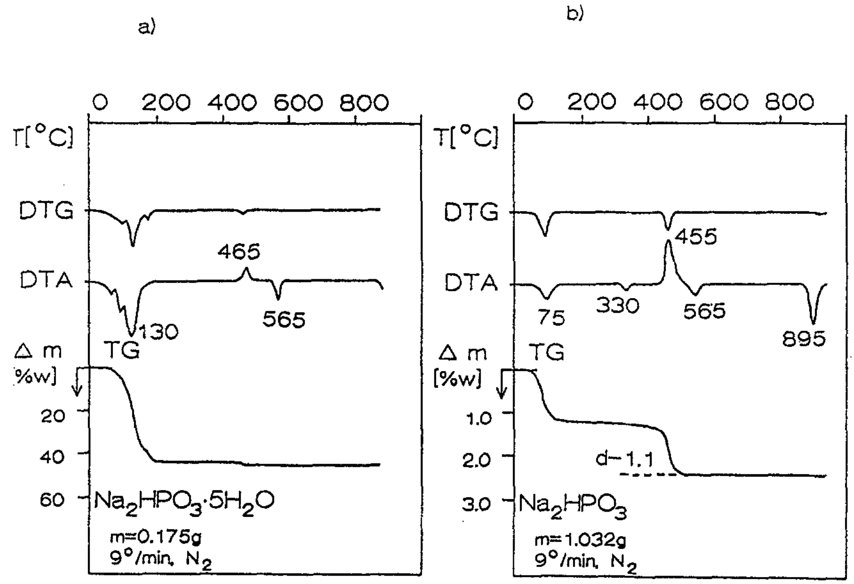

Fig. 2 TG, DTG and DTA curves of: *a*) $Na_2HPO_3·5H_2O$, *b*) Na_2HPO_3

and different stoichiometry of the amorphous substance have been reported [7–13]. Hence, detailed analysis of the evolution of hydrogen was carried out during thermal decomposition of phosphites of alkali metals e.g. Li, Na, K. The results are summarized in Table 1 containing the following parameters:

T_{IR} – temperature of disappearance of the ~2400 cm^{-1} band (which corresponds to the stretching mode of the P-H group) in the IR spectra of solid samples,

T_{DTG} – temperature of the maximum rate of weight loss taken from the DTG curve,

Δm – weight loss taken from the TG curve,

H_{theor} – theoretical weight percentage of hydrogen in anhydrous phosphites.

Only in the case of the potassium salt can we assume that the only gaseous product is hydrogen. During the thermal decomposition of lithium and sodium salts also PH_3 and H_2O are most probably formed. PH_3 was detected in the gas phase by IR study in the case of lithium salt.

Table 1 Results of the investigation of the evolution of hydrogen during thermal decomposition of hydrophosphites

Cation	T_{IR}/°C	T_{DTG}/°C	Δm / %	H_{theor}/%
Li^{1+}	520	500	2.70	1.07
Na^{1+}	500	455	1.10	0.80
K^{1+}	560	510	0.70	0.64

Using morphological classification of simple oxophosphorus species and their hydrogen derivatives [1–6] we can propose an alternative mechanism (II) of the course of the thermal decomposition leading to the formation of PH_3 and H_2O:

(1) $8HPO_3^{2-} \rightarrow 4PO_3^{3-} + 4H_2PO_3^{1-}$

(2) $4PO_3^{3-} + 4H_2PO_3^{1-} \rightarrow 4PO_4^{3-} + 4H_2PO_2^{1-}$

(3) $4H_2PO_2^{1-} \rightarrow 2HPO_2^{2-} + 2H_3PO_2^{0}$

(4) $2HPO_2^{2-} + 2H_3PO_2^{0} \rightarrow 2HPO_3^{2-} + 2H_3PO$

(5) $2HPO_3^{2-} + 2PO_4^{3-} \rightarrow 2PO_3^{3-} + 2HPO_4^{2-}$

(6) $2PO_3^{3-} + 2H_3PO \rightarrow 2PO_4^{3-} + 2PH_3$

(7) $2HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O$

$\sum \; 8HPO_3^{2-} \rightarrow 4PO_4^{3-} + P_2O_7^{4-} + 2PH_3 + H_2O$

In Fig. 3 mechanism II is shown in morphological classification in the $e_v - e_z - e_{zH}$ + system.

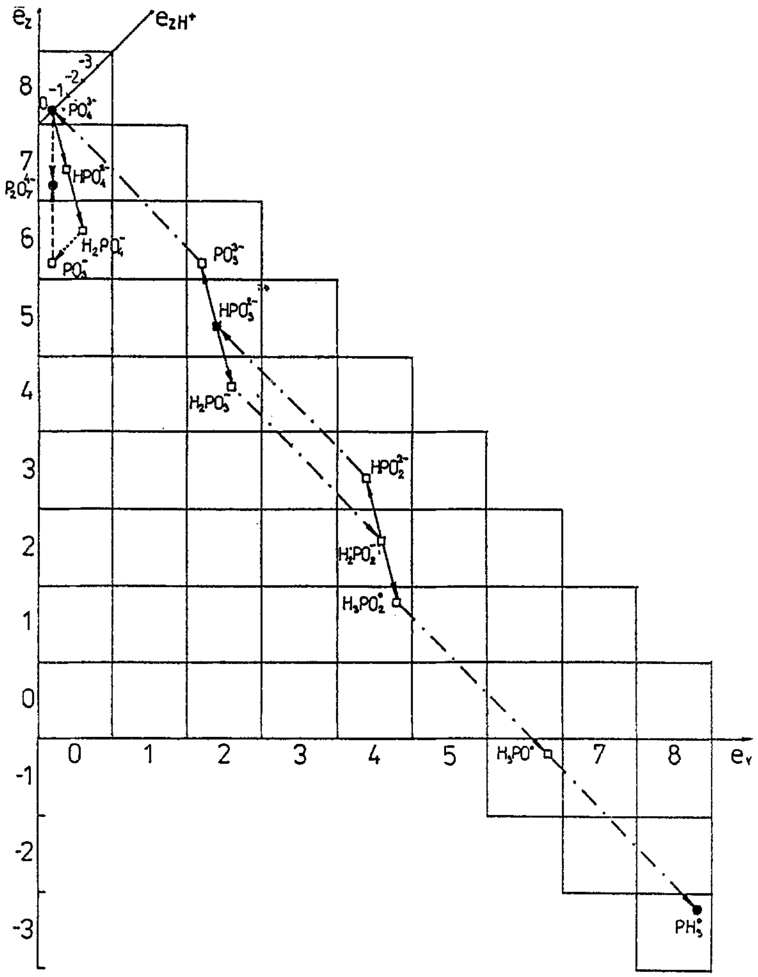

Fig. 3 Mechanism II of thermal decomposition of hydrophosphites in $e_v - e_z - e_{zH}$ + system

Table 2 Theoretical weight loss depending on the type of mechanism of thermal decomposition

Cation	Mechanism I weight%	Mechanism II weight%
Li^{1+}	1.07	11.45
Na^{1+}	0.80	8.53
K^{1+}	0.64	6.80

On the basis of the stoichiometry we can calculate the theoretical weight loss for mechanisms I and II (Table 2).

Comparing experimental values with calculated ones (given in Table 2) for mechanism II deviations of 16 and 4 percent were obtained for lithium and sodium hydrophosphites, respectively. In the case of potassium salt the deviation is negligible.

References

1 A. Górski, Roczniki Chem., 45 (1971) 1981, 2193, 2201; 46 (1972) 127.
2 A. Górski and J. Moszczyńska, Roczniki Chem., 47 (1973) 211, 1313.
3 A. Górski and J. Skiendzielewski, Roczniki Chem., 48 (1974) 1627.
4 Z. Gontarz and A. Górski, Roczniki Chem., 51 (1977) 2483.
5 A. Górski and B. Ziólkowska, Polish J. Chem., 53 (1979) 1165.
6 Z. Gontarz and W. Winiewski, J. Thermal Anal., 36 (1990) 2099.
7 D. Grant, D. S. Payne and S. Skledar, J. Inorg. Nucl. Chem., 26 (1964) 2103.
8 J. P. Ebel, N. Busch and G. Hertzog, Bull. Soc. Chim. France, (1958) 203.
9 H. Estour, M. Porthault and J-C. Merlin, Bull. Soc. Chim. France, (1964) 2843.
10 R. Rudnicki, Zesz. Nauk. Politechn. Warszaw., Chem., 7 (1967).
11 Z. Gontarz and J. Zachara, Zesz. Nauk. Politechn. Sl., Ser. Chem., 109 (1984) 95.
12 D. Zobel and N. Ba, Z. Chem., 9 (1969) 389.
13 B. Krukowska-Fulde, Roczniki Chem., 35 (1961) 1203.

Zusammenfassung — Es wurde die thermische Zersetzung von Phosphiten $M^{I}_{2}HPO_3$ (M – Li, Na, K) in Stickstoffatmosphere untersucht. Die Schritte des Mechanismus der thermischen Zersetzung wurden vorgeschlagen.