MECHANISM OF THERMAL DECOMPOSITION OF HYDROGENPHOSPHITIES

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Evolution of hydrogen during thermal decomposition of some $M^{II}HPO_3$ ($M =$ Mg, Ca, Zn, Sr, Cd, Ba) phosphities under nitrogen atmosphere was investigated. Step mechanism of thermal decomposition has been proposed.

Results of investigation of thermal decomposition of some hydrogenphosphities 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, 2], the anion is described by $e_v = 2$, $e_z = 5$ where e_v - number of valence electrons, e_z - number of elementary negative charges formally brought with ligands to the coordination shell (contribution from O^{2-} and H^+ ligands are 2 and –1, thus for the HPO_3^{2-} anion $e_z = 3 \cdot (2) + 1 \cdot (-1) = 5$). Changes of e_v and e_z numbers are connected with red-ox and ac-bas reactions respectively. The PO_3^{3-} anion ($e_v = 2$, $e_z = 6$) with no protons coordinated around phosphorus is not known so far, although analogs in arsenium chemistry do exist - AsO_3^{3-}. Evolution of hydrogen from the anionic sublattice of hydrogensphosphities during thermal decomposition is connected with the creation of volatile products. In this system simple molecules PH_3, H_2O an H_2 can be generated.

Experimental

The investigated hydrogenphosphities $M^{II}HPO_3 \cdot xH_2O$ (x - number of water molecules in crystalline salts of Mg, Ca, Zn, Sr, Cd, Ba was 6, 1, 2.5, 2.5, 1, 0 respectively) are insoluble and were precipitated from diluted water solutions of K_2HPO_3 (p. Hopkins & Williams Ltd, England) and nitrates

(Zn, Cd - p.a. POCh, Poland) or chlorides (Mg, Ca, Sr, Ba - p.a. POCh, Poland).

Simultaneous registration of T, TG, DTG and DTA curves on a Derivatograph apparatus (MOM, Budapest) under nitrogen atmosphere was the main method of investigation of thermal decompositions. X-ray diffraction, IR spectroscopy and mass spectrometry were used for phase determination.

Results and disscusion

According to the literature [3-8], being in good agreement with our investigations, the main solid products of thermal decompositions are: - crystalline orthophosphates and pyrophosphates, - amorphous phosphides of uncertain composition. Investigations of gas phase are of great importance for the determination of the mechanism of decomposition. In the literature different gas products are reported [4, 6-8]. Because of that, detailed analysis of evolution of hydrogen during thermal decomposition of phosphities of six counter-ions from the 2nd group of the periodic system e.g. Mg, Ca, Zn, Sr, Cd, Ba was undertaken. The results are summarized in Table 1 containing the following parameters:

t-IR - temperature of disappearance of the $\sim 2400 \text{ cm}^{-1}$ band which corresponds to the vibrational stretching mode of the P-H group in IR spectra,

t-TG - temperature of the maximum rate of weight loss taken from the DTG curve,

Δ_mTG - weight loss taken from the TG curve of anhydrous phophities for the sample size ~ 1 g and TG sensitivity 50 mg,

%H-t - theoretical weight percentage of hydrogen in anhydrous phosphities.

Table 1

Cation	t-IR, °C	t-TG, °C	Δ_mTG, %	%H-t, %
Mg^{2+}	500	490	0.90	0.96
Ca^{2+}	590	570	0.87	0.83
Zn^{2+}	450	410	0.63	0.69
Sr^{2+}	600	550	0.55	0.60
Cd^{2+}	490	455	0.54	0.53
Ba^{2+}	530	540	0.52	0.46

In the case of phosphities of magnesium, zinc and strontium mass spectrometry confirm with no doubt the presence of hydrogen in the gas phase.

On the basis of results of experiments and classification analysis we can assume that during thermal decomposition of hydrogenphosphities, with counter-ions of charge $2+$ and no red-ox properties, the only gasous product is hydrogen. The course of thermal decomposition can be described by the following step equations:

1. $(6y + 4x) HPO_3^{2-} \rightarrow (3y + 2x) PO_3^{3-} + (3y + 2x) PO_3^{1-} + (3y + 2x) H_2$

2. $(3y + 2x) PO_3^{3-} + (3y + 2x) PO_3^{1-} \rightarrow (3y + 2x) PO_4^{3-} + (3y + 2x) PO_2^{1-}$

3. $3yPO_2^{1-} \rightarrow 2yPO_3^{1-} + yP^{1-}$

4. $2xPO_2^{1-} \rightarrow xPO_3^{1-} + xPO^{1-}$

5. $xPO^{1-} + xPO_3^{1-} \rightarrow xP^{1+} + xPO_4^{3-}$

6. $2yPO_3^{1-} + 2yPO_4^{3-} \rightarrow 2yP_2O_7^{4-}$

7. $xP^{1+} + yP^{1-} \rightarrow P^{\left(\frac{y-x}{x+y}\right)-}$

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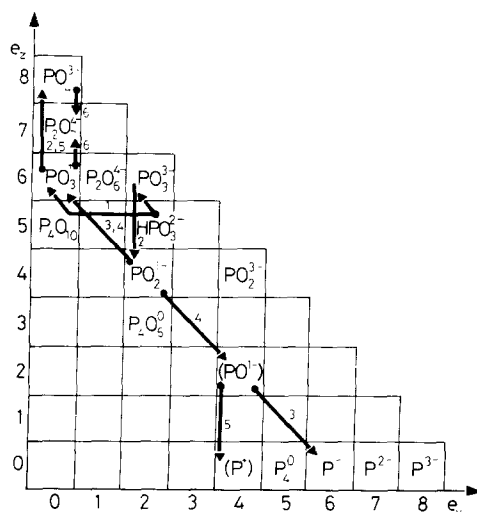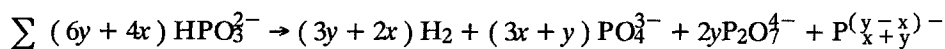

Fig. 1

Using morphological classification of simple phosphorus species we can show the mechanism of thermal decomposition in the e_v vs. e_z system (Fig 1).

References

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Zusammenfassung — Es wurde die Wasserstoffentwicklung während der thermischen Zersetzung einiger Phosphite $M^{II}HPO_3$ (mit $M = Mg$, Ca, Zn, Sr, Cd, Ba) in einer Stickstoffatmosphäre untersucht. Es wurde ein schematischer Mechanismus für die thermische Zersetzungsreaktion gegeben.