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THERMAL PROPERTIES OF AMMONIUM AND POTASSIUM HYDROGENHEXAVANADATES

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ABSTRACT

Thermal properties of $NH_4HV_6O_{16}.3H_2O$ and $KHV_6O_{16}.3H_2O$ have been investigated. It was found by means of IR spectroscopy and X-ray phase analysis that the loss of 3 molecules of water did not change the original arrangement of vanadium and oxygen atoms in anion. Only after the loss of constitutional water the compounds decomposed and other oxovanadates were formed.

INTRODUCTION

Studying the thermal properties of some hydrated hexavanadates authors [1-5] found that given compounds were thermally unstable. They decomposed at higher temperatures to other polyvanadates, V-O bronzes and vanadium oxides. Factors influencing the composition of the product of the thermal decomposition are so far unknown.

MEASURMENT METHODS

$NH_4HV_6O_{16}.3H_2O$ and $KHV_6O_{16}.3H_2O$ were prepared according to [6,7] and purity was verified by chemical analysis and IR spectroscopy.

Thermal properties of hydrogenhexavanadates were studied on the Derivatograph Q 1500 D MOM Budapest (heating rate 10 °C/min, weighed amounts 200 mg). In order to explain individual endo- and exoeffects the heating of the studied compounds was interrupted at chosen temperatures. The substances were cooled to the laboratory temperature and identified by X-ray phase analysis (Philips Diffractometer PW 1058, CuK_α radiation), IR spectroscopy (Perkin Elmer 180 Spectrophotometer, Nujol mulls) and ammonium was determined according to [8].

RESULTS AND DISCUSSION

Within the temperature range from 40° to 270 °C $NH_4HV_6O_{16}.3H_2O$ loses 3 molecules of water and probably a part of ammonium, too (the loss of mass found experimentally was higher by 1,24 % than it responds to the loss of $3H_2O$, the content of NH_4^+ in the sample was lower by 0,35 %). It follows from IR spectra (Fig. 2) and X-ray powder patterns the original structure of the substance is preserved up to 270 °C when the intermediate of the composition $NH_4HV_6O_{16}$ is

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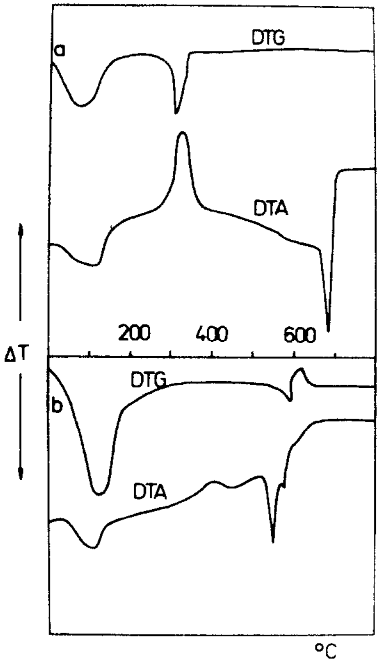

Fig. 1 Thermoanalytical curves
a. $NH_4HV_6O_{16}\cdot 3H_2O$
b. $KHV_6O_{16}\cdot 3H_2O$

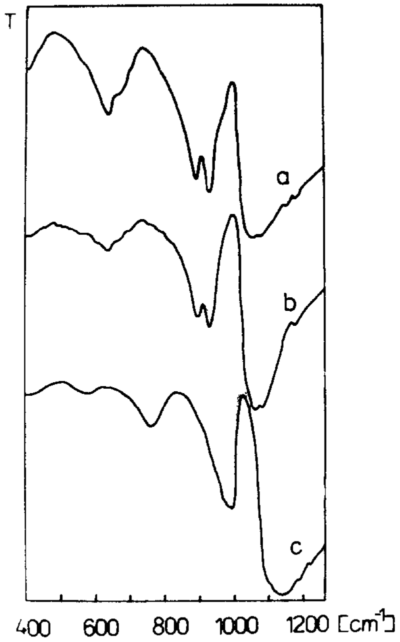

Fig. 2 IR spectra
a. $NH_4HV_6O_{16}\cdot 3H_2O$
b. $NH_4HV_6O_{16}$ (270 °C)
c. V_2O_5 (575 °C)

formed. Complicated exothermic process running in the temperature interval from 270 °C to 380 °C is connected with a loss of ammonium and constitutional water and with vanadium oxide formation. The endothermic deviation with minimum at 670 °C is connected with V_2O_5 melting.

When heating $KHV_6O_{16}\cdot 3H_2O$, continual dehydration takes place within the temperature range from 20° to 330 °C (Fig. 1.b). The decomposition of the compound and complex thermochemical reactions connected with it run as far as after loosing of constitutional water. This is indicated by a relatively broad deviation with

Interplanar distances in nm

Table 1

The products obtained at the temperature [°C]											
390		550		570		390		550		570	
d_{hkl}/I_{rel}	ass.	d_{hkl}/I_{rel}	ass.	d_{hkl}/I_{rel}	ass.	d_{hkl}/I_{rel}	ass.	d_{hkl}/I_{rel}	ass.	d_{hkl}/I_{rel}	ass.
1.04/30	A					0.264/5	D	0.263/5	D		
0.95/20	A+B	0.95/100	D+E	0.98/100	D+E	0.261/30	C			0.261/5	C
		0.76/M	D			0.253/10	B+D	0.252/20	D	0.249/M	D
0.74/45	A+D	0.73/85	E	0.74/25	E	0.248/5					
0.65/25						0.244/M		0.244/10			
0.57/20	C			0.57/15	C	0.2390/M	B+C	0.2381/15	B+E	0.2371/10	D+E
0.52/5	A+B	0.51/5	B			0.2291/5		0.2362/15	D		
0.47/15	B+D	0.47/45	B+D	0.47/15	D	0.2272/5	A	0.2282/5			
0.45/14	D					0.2230/5		0.2209/30			
0.435/55	A+C			0.435/80	C	0.2184/10	C			0.2181/10	C+E
0.407/20	C			0.410/25	C	0.2149/5	C	0.2125/M		0.2143/M	C
0.387/M	B	0.388/20	B			0.2078/30		0.2083/M	E		
0.368/5	A+D	0.364/10	D	0.375/M	E	0.2034/25	B	0.2006/M	B		
0.358/5	B+D			0.354/10	D	0.1987/10	A+B+C	0.1977/25	B+E	0.1991/M	C+E
0.349/20	A+B+C	0.345/25	B	0.349/10	C	0.1933/5		0.1939/5			
0.338/100	C			0.339/30	C	0.1912/10	D	0.1908/10	D	0.1912/10	D
0.335/75	D	0.335/50	D			0.1893/10	C+D	0.1890/10	D+E	0.1898/15	C+D+E
0.328/60	A+D					0.1857/5	C	0.1884/10	E	0.1860/5	C
0.320/10	B	0.321/25	B			0.1822/10		0.1839/M		0.1815/5	
0.315/30	A+B	0.315/45	D	0.315/40	D	0.1795/40	A+B	0.1804/25	B		
0.307/20	B	0.306/80	B+D			0.1778/15	C	0.1767/M		0.1782/5	C
0.299/15	A					0.1752/10	C			0.1757/M	C
0.294/55	D					0.1651/10	C	0.1665/5	B	0.1646/M	C
0.287/80	A+B+C	0.290/50	B+D	0.288/30	C	0.1582/10	C	0.1589/10		0.1576/M	C
0.275/20						0.1559/15		0.1557/20			
0.272/20	A	0.273/35	E	0.273/15	E	0.1530/10	B	0.1530/15	B		
0.268/10	C			0.268/5	C	0.1511/15		0.1522/10			

M - less than 5 B-KV_6O_{15} C-V_2O_5 D-$K_2V_8O_{20.8}$ E-$K_{0.27}V_2O_5$ A-$K_{0.37}V_2O_5$

a maximum at 390 °C. We found that potassium hydrogenhexavanadate decomposes primarily to KVO_3 and V_2O_5 which react together forming bronzes [9] of various composition. At the temperature of exothermic maximum the reaction mixture contains bronzes $K_{0.37}V_2O_5$, KV_6O_{15}, an admixture of $K_2V_8O_{20.8}$ and the rest of V_2O_5 (Table 1). This mixture preserves its composition up to the temperature of 505 °C. However, the content of $K_2V_8O_{20.8}$ rises with temperature increase.

Within the temperature interval from 505° to 615 °C endothermic processes take place. They are indicated on the DTA curve by deviations with minimum at the temperatures of 530°, 560° and 600 °C. The mentioned processes are first connected with small losses and immediately small increases of the mass of the heated substance which points at redox reactions. In addition, vanadium oxide reacts with bronze $K_{0.37}V_2O_5$ forming $K_{0.27}V_2O_5$, bronze KV_6O_{15} decomposes with simultaneous oxidation to $K_2V_8O_{20.8}$ and V_2O_5, and stepwise, the melting of individual components of the mixture takes place, too. The final products of the decomposition of the original compound, e.g. $K_2V_8O_{20.8}$, $K_{0.27}V_2O_5$ and V_2O_5 crystallize from the melt obtained within the range from 600 °C to 800 °C.

In the course of heating of the studied compound, a further so far unidentified admixture is present in the products of thermal decomposition of the studied substance.

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