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THERMAL PROPERTIES OF POTASSIUM, RUBIDIUM and CESIUM HEXAVANADATES

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ABSTRACT

Products of the thermal decomposition of potassium hexavanadate were meta-, pentavanadate and bronze. Main parts of the products obtained by heating rubidium and cesium hexavanadates were the original hexavanadates containing an admixture of V-O bronzes.

INTRODUCTION

Hexavanadates of the $M^{I}_{2}V_{6}O_{16}$ composition are known only for such metals of which the ionic radius is greater than 0.130 nm. These compounds are supposed to be isostructural (ref. 1). According to (ref. 2) the structures of potassium and cesium hexavanadates are of a layer type, alkali cations occupying positions between layers. Consequently it is inevitable to suppose that a stability of such structure depends on the size of interlayer cation.

METHODS

Studied compounds were prepared according to (ref. 3, 4) and their composition was verified by chemical analysis, IR spectra and X-ray diffraction.

The thermal analysis of the compounds was performed on the Derivatograph Q 1500 D (MOM Budapest) in air atmosphere, heating rate 10 degree/min, weighed amounts 200 or 150 mg. The products obtained by interrupted DTA at various temperatures were cooled to laboratory temperature and identified by IR spectroscopy and X-ray phase analysis.

The IR spectra were measured in Nujol mulls using Perkin Elmer 180 Spectrophotometer. X-ray powder patterns were obtained with Philips Diffractometer PW 1058 using CuK$_{\alpha}$ radiation.

Vanadium (V) was determined volumetrically (0.05 mol.dm^{-3} FeSO$_{4}$, diphenylamine), vanadium (IV) by EPR (EPR-spectrometer ER 9 C. Zeiss, Jena), potassium by flame photometry (Flapho 4 C. Zeiss, Jena), rubidium and cesium gravimetrically according to (ref. 5).

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RESULTS AND DISCUSSION

The chemical nature and structure of potassium hexavanadate was retained until this compound was heated to the temperature 415 °C. Within the temperature range from 415 to 560 °C the endothermic effects were connected with a small change of mass of the substance (see Fig.1 a). Within the range of 415 to 480 °C, the original orange colour of the substance changed to dark brown. On the basis of X-ray phase analysis (see Table 1) as well as by comparison of measured (see Fig.2) and published (ref.6,7) IR spectra it may be assumed that potassium hexavanadate decomposes to $K_3V_5O_{14}$ KVO_3 and $K_2V_8O_{20.8}$. This process is connected with a partial reduction of vanadium(V). The latter compound contains 1.3 mol % of vanadium(IV) so that the above mass change of the heated substance can be caused by loosing equivalent amount of oxygen. The given compounds do not react altogether and melt without decomposition in the interval from 480 to 560 °C. Further heating of the melt up to the temperature 800 °C does not result in any changes of the composition of the compounds which crystallize from the melt.

When heating $Rb_2V_6O_{16}$ and $Cs_2V_6O_{16}$ the original hexavanadates are the predominant components of the products which were obtained at various temperatures up to 800 °C. In the products obtained by heating the given hexavanadates above 450 °C, V-O bronzes were identified as admixtures. Small changes on the DTA curves (see Fig. 1b, 1c) are therefore connected with redox reaction running on the surface of the sample whilst forming given bronzes.

In the case of rubidium salt, $Rb_2V_8O_{20.8}$ was identified as an admixture in the product occurring at 470 °C. Expressive endothermic effect corresponding to the melting of given bronze and rubidium hexavanadate has deviation with minimum at 495 and 505 °C. Bronze $Rb_2V_8O_{20.8}$ melts with decomposition (ref. 8), therefore products formed from melt above 600 °C contain a new admixture of $Rb_{0.3}V_2O_5$ composition.

Products formed by heating of cesium salt within the range of 450 to 800 °C contain admixture of $Cs_{0.34}V_2O_5$ and CsV_2O_5; with increased temperature the content of the former compound increases and latter decreases. The endothermic peak with minimum at 508 °C (melting of $Cs_2V_6O_{16}$) indicates the admixture only by its assymetric shape.

Some unassigned diffractions in X-ray patterns as well as the change of the intensity of certain diffractions indicate further admixture in the products which crystallize from the melt of all

Table 1

Interplanar distances in nm

$K_2V_6O_{16}$	B+M+P	$Cs_2V_6O_{16}$	D+H+E	$Rb_2V_6O_{16}$	B+H	$Rb_2V_6O_{16}$	C+H
melt		melt		450 °C		melt	
d_{hkl}/I_{rel}		d_{hkl}/I_{rel}		d_{hkl}/I_{rel}		d_{hkl}/I_{rel}	
1.05/1	M	0.81/54	H+?			0.81/63	
0.94/85	B+M	0.59/25	H	0.78/56	H	0.77/100	H+?
0.79/40	B	0.51/24	H	0.57/47	H	0.57/34	H
0.61/1	B+M	0.444/29	H	0.439/23			
0.50/20	P+M	0.429/35	H+D	0.427/35	H	0.427/28	H
0.472/55	B	0.408/87	H+E	0.422/29		0.412/28	
0.459/15	B	0.395/32	H			0.407/40	C
0.453/1		0.378/42	H	0.399/40	H	0.399/45	H
0.435/1	P	0.367/100	H+D	0.390/31	H	0.389/28	H
0.419/1	P	0.348/18	D+E	0.371/29	H	0.369/27	H
0.397/1	B	0.332/63	H+D	0.360/24	B		
0.392/1	M	0.324/100	H	0.353/100	H	0.354/100	H
0.372/1	P+M	0.310/61	H+E			0.346/45	C
0.365/1	B+M	0.302/64	H+D	0.331/16	B		
0.355/10	B	0.295/63	H+E	0.320/100	H	0.321/100	H
0.336/5	B	0.287/11	D+E			0.309/26	
0.331/10		0.271/86	H+E			0.307/31	C
0.328/35	B+P	0.269/25	H+D	0.302/52	H	0.302/50	H
0.315/100	B+M	0.259/52	H+?	0.291/73	H+B	0.291/57	H
0.306/15	B	0.250/29	H	0.286/100	H+B	0.286/55	H+C
0.302/15	P	0.246/49	H+E			0.271/20	C
0.297/10	B	0.239/19	H+E	0.264/31	H+B	0.264/16	H
0.285/40	B+P+M	0.235/10	H+E	0.260/14	H	0.260/21	H
0.270/1		0.222/25	H+E	0.257/10	B		
0.268/1	M	0.215/36	H+D+E	0.248/65	H	0.247/55	H
0.265/15	B+M	0.214/25	H+E	0.244/29	H	0.244/31	H+C
0.255/5	B+M	0.207/24	H	0.240/64	H+B	0.240/32	H
0.251/20	B+P+M	0.204/25	H+D	0.229/10	H	0.230/15	H+C
0.247/5		0.199/26	H+E	0.220/46	H+B	0.220/26	H+C
0.237/90	B+M	0.196/20	H+D	0.213/57	H+B	0.213/38	H
0.223/1	P+M	0.190/44	H+D	0.211/29	H+B	0.212/20	H
0.217/1	P+M	0.189/20	H+E	0.202/78	H+B	0.202/55	H
0.208/5	P+M	0.183/25	H	0.200/19	H	0.200/22	H+C
0.199/1	M	0.179/25	H+D+E			0.198/11	C
0.196/1	M	0.175/13	H+E	0.195/19	H	0.195/18	H
0.191/25	B+M	0.174/16	H+D+E	0.190/22	H	0.190/21	H
0.190/25	B	0.166/27	H+D+E	0.180/20	H	0.189/22	H+C
0.188/10	P+M	0.163/18	H+D	0.186/21	B		
0.182/10	M	0.160/13	H+D+E	0.184/36	H	0.184/31	H
0.181/10		0.157/13	H+D	0.181/25	H+B	0.180/20	H+C
0.180/5	P+M	0.154/11	H	0.176/13	H	0.176/20	H+C
0.172/1	P			0.174/16	H	0.173/15	H

H = $M^{I}_{2}V_6O_{16}$, B=$M^{I}_{2}V_8O_{20.8}$, C=$Rb_{0.3}V_2O_5$, D=CsV_2O_5, E=$Cs_{0.34}V_2O_5$,

P = $K_3V_5O_{14}$, M = KVO_3, 1 = less than 5

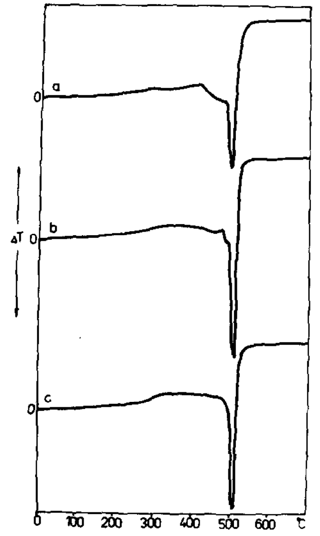

Fig. 1. DTA curves of
a. K-, b. Rb-,
c. Cs-salt

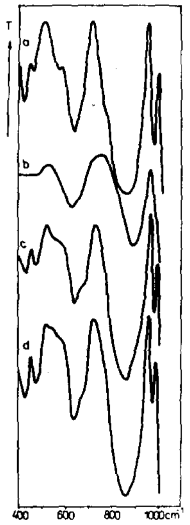

Fig. 2. IR spectra of a. starting hexavanadates, final product of heating
b. K-, c. Rb-, d. Cs-salt

studied substances. However, its composition was not unambiguously identified. This admixture is supposed to be $M^{I}_{2+x}V_6O_{16}$.

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