THERMAL REACTIVITIES OF POTASSIUM AND CADMIUM HYDROGENHEXAVANADATES

L. Ulická

DEPARTMENT OF INORGANIC CHEMISTRY, FACULTY OF NATURAL SCIENCES
KOMENSKY UNIVERSITY, 842 15 BRATISLAVA, CZECHOSLOVAKIA

The thermal reactivities of $KHV_6O_{16} \cdot 3H_2O$ and $Cd(HV_6O_{16})_2 \cdot 12H_2O$ were investigated. By means of IR spectroscopy and X-ray phase analysis it was found that, after dehydration, both compounds decompose to vanadium pentoxide and the corresponding metavanadate. Potassium metavanadate and vanadium pentoxide react together to form bronzes of different compositions. In contrast, vanadium pentoxide and cadmium metavanadate are the predominant components of the reaction products obtained within the temperature range from 300° to 800°C.

Hydrogenhexavanadates have become the subject of detailed research only in the past few years. X-ray diffraction examinations of polycrystalline specimens reveal a lower degree of arrangement in the structure of these compounds. It is evident that information on the structural aspects of hydrogenhexavanadates can be obtained only by means of several mutually complementary methods. A study of the thermal reactivities of the given type of polyvanadates may contribute to an explanation of their nature [1-3].

The present paper deals with the thermal reactivities of the compounds $KHV_6O_{16} \cdot 3H_2O$ and $Cd(HV_6O_{16})_2 \cdot 12H_2O$

Experimental

$KHV_6O_{16} \cdot 3H_2O$ and $Cd(HV_6O_{16})_2 \cdot 12H_2O$ were prepared by the acidic hydrolysis of the corresponding metavanadates at 80° [4].

The potassium contents of the prepared substances were determined by flame photometry [5], and the cadmium contents complexometrically [6]. Vanadium(V) was estimated volumetrically by titrating with 0.05 M iron(II) sulphate using diphenylamine as indicator [7], and vanadium(IV) by titrating with 0.01 M potassium permanganate [7]. The amount of crystal water was estimated by DTA.

7

For $KHV_6O_{16} \cdot 3H_2O$ (655.79 g mol^{-1}) 5.96% K, 46.61% V and 9.61% H_2O* were calculated, and 5.90% K, 46.80% V and 9.21% H_2O were found. For $Cd(HV_6O_{16})_2 \cdot 12H_2O$ (1453.88 g mol^{-1}) 7.73% Cd, 42.05% V and 16.11% H_2O* were calculated, and 7.76% Cd, 41.87% V and 15.87% H_2O were found.

Thermal analysis of the compounds was performed on a Q 1500 derivatograph in air atmosphere, at a heating rate of 10 deg/min, with a weighed amount of 150 or 200 mg. In order to explain the individual endo- and exoeffects, the heating of the studied compounds was interrupted at chosen temperatures (according to the DTA curve). In some cases, isothermal heating of the substances was applied at definite temperatures in a crucible furnace. The products obtained were cooled to room temperature and identified by X-ray phase analysis and IR spectroscopy.

X-ray powder diffraction patterns were taken on a Philips PW 1050 diffracto-graph, equipped with a copper anticathode and a nickel-filter.

The infrared spectra were taken on a Perkin–Elmer 180 spectrophotometer, with the Nujol technique.

Results and discussion

The results of differential thermal analysis of $KHV_6O_{16} \cdot 3H_2O$ are shown in Fig. 1. The first endothermic process is connected with continuous dehydration within the temperature range from 20° to 330°. The chemical nature and to some extent
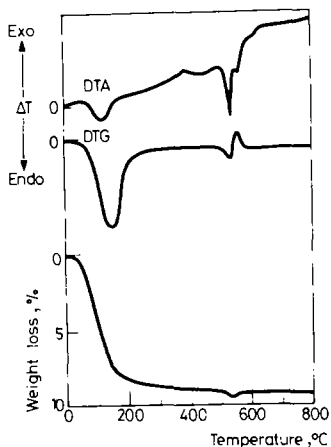

Fig. 1

* crystal and constitutional water.

also the crystal structure of the given hydrogenhexavanadate are not influenced by the loss of 3 molecules of water the X-ray powder patterns of the trihydrate and the anhydrous salt are almost the same. The decomposition of KHV_6O_{16} and the complex thermochemical reactions connected with this proceed only after the loss of constitutional water. These processes are indicated by a relatively broad deviation with a maximum at 390°. The results of isothermal heating permit the conclusion that potassium hydrogenhexavanadate decomposes primarily to KVO_3 and V_2O_5, which react together to form bronzes of various compositions. The product obtained by heating to the temperature of the exothermic maximum contains brones $K_{0.37}V_2O_5$, KV_6O_{15}, an admixture of $K_2V_8O_{20.8}$ and residual V_2O_5 (Tables 1 and 2). The given components are present in all the products obtained within the temperature range from 390° to 505°. However, the content of $K_2V_8O_{20.8}$ increases with temperature rise.

Within the temperature interval from 505° to 615°, endothermic processes take place. These are indicated in the DTA curve by the deviations with minima at 530°, 560° and 600°. These processes firstly involve a small loss, and immediately afterwards a small increase in mass of the heated substance, which points to redox reactions. Further, in the product obtained at 550°, the new component $K_{0.27}V_2O_5$ was identified instead of $K_{0.37}V_2O_5$. It is presumed that this bronze is formed according to the equation:

$$2.7\ K_{0.37}V_2O_5 + V_2O_5 = 3.7\ K_{0.27}V_2O_5 \qquad (1)$$

The possibility of this transformation of $K_{0.37}V_2O_5$ also follows from the fact that V_2O_5 is absent from the product obtained at the above-mentioned temperature. Within the temperature interval from 505° to 550°, melting of one component occurs, too. According to [8] this component could be $K_2V_8O_{20.8}$. When the studied substance is heated to 570°, a further change of the composition of the reaction product takes place. Bronze KV_6O_{15} decomposes with simultaneous oxidation to $K_2V_8O_{20.8}$ and V_2O_5, probably according to the equation:

$$2\ KV_6O_{15} + 0.4\ O_2 = K_2V_8O_{20.8} + 2\ V_2O_5 \qquad (2)$$
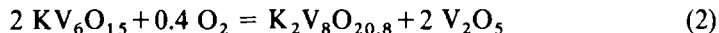
This assumption is in agreement with the low thermal stability of KV_6O_{15} [8], as well as with the identification of V_2O_5 in the product obtained at 570°.

Increase of the temperature of the heated substance above 570° causes total melting of the reaction mixture. The final products of the thermal reactions, i.e. $K_2V_8O_{20.8}$, $K_{0.27}V_2O_5$ and V_2O_5, crystallize from the melt obtained within the temperature range from 600° to 800°.

In the course of heating of the studied compound, a further, as yet unidentified admixture indicated by X-ray powder patterns is present in the products.

7*

Table 1 Interplanar distances in nm

The products obtained at t, °C

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

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

Table 2 Wavenumbers in cm^{-1}

Products obtained at t, °C							
390	550	570	$K_{0.37}V_2O_5^{10}$	$KV_6O_{15}^{10}$	$K_2V_8O_{20.8}^{10}$	$K_{0.27}V_2O_5^{10}$	V_2O_5
420–600 vs	420–600 vs	420–600 vs	420 s	450 600 w	430 w		480 s
			430 s		495 m		
			520 vw		510 s		
					565 vs		590 m
680–780 vs	680–780 vs	680–780 vs	720 vs		740 vs	730 vs	
850 sh	830 sh	830 sh	820 vs		830 sh		820 vs
940 w	940 w	940 w	950 w	945 w	945 w	945 w	
970 s	975 m	970 m		975 s	975 s	975 s	
995 s	980 vs	980 s	1000 s	1005 s	995 s	1005 s	
1020 m	1020 m	1010 m		1025 s		1025 s	1020 m

vs — very strong   s — strong   m — medium   w — weak   vw — very weak   sh — shoulder

The thermal curves of $Cd(HV_6O_{16})_2 \cdot 12H_2O$ are shown in Fig. 2. In contrast to the previously-discussed compound, the dehydration of cadmium hydrogenhexa-vanadate dodecahydrate proceeds in two steps. The weight loss in the first step (11.75%) corresponds to 10 molecules of crystal water. According to the IR spectra, the partially dehydrated substance preserves its original chemical nature and can be
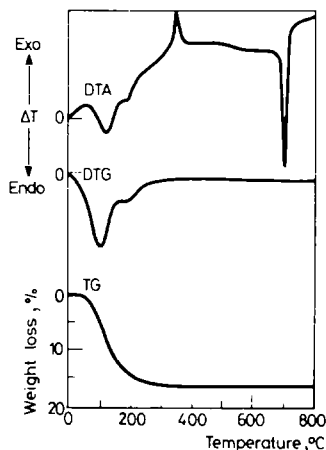

Fig. 2

formulated as $Cd(HV_6O_{16})_2 \cdot 2H_2O$. The X-ray powder pattern of the dihydrate is almost the same as that of the dodecahydrate (two of the highest intensity diffractions shift to higher angles θ). The remaining 2 molecules of crystal water, as well as constitutional water, are lost within the temperature interval from 180° to 300°. Total dehydration of the heated substance results in its decomposition. The decomposition of the hydrogenhexavanadate, together with the ensuing formation of new phases, is indicated by the exothermic effect with maximum at 340°. The X-ray powder pattern (Table 3) indicates that at least a three-component mixture is formed, i.e. V_2O_5, α-$Cd(VO_3)_2$ and a further, so far unidentified substance. The presence of the unknown component in the mixture is also indicated by two absorption bands at 1000 and 1060 cm^{-1} in the IR spectra (Table 4) and by the presence of vanadium(IV) in the product (1.97%). Vanadium pentoxide and cadmium metavanadate are present in the reaction mixture until they melt in the temperature interval from 645° to 715°. These two compounds also crystallize from the melt, but cadmium metavanadate changes its crystal structure to the β-modification [9] (Table 3). From the given results it follows that, under the studied conditions, cadmium metavanadate and vanadium pentoxide do not react together to such an extent as observed in the case of potassium metavanadate.

A small admixture of a different compound was indicated in the product

Table 3 Interplanar distances in nm

300 d_{hkl}/I_{rel}	ass.	400–600 d_{hkl}/I_{rel}	ass.	715–800 d_{hkl}/I_{rel}	ass.
1.10/20					
1.01/20					
0.88/10		0.68/L	A		
		0.57/10	B	0.57/20	B
0.444/60	A+B	0.444/95	A+B	0.439/100	B+C
		0.412/10	B	0.411/10	B
0.353/70	A	0.352/70	A	0.355/10	
				0.351/10	
0.347/90				0.350/10	B
0.341/100	A+B	0.340/100	A+B	0.340/10	C
				0.330/5	C
				0.324/30	
0.301/40	A	0.316/10	A	0.314/5	C
				0.310/30	
				0.305/L	
		0.294/10		0.296/L	B
0.288/40	B	0.288/30	B	0.288/60	
0.283/40					
0.276/25	B	0.276/10	B	0.278/20	B+C
		0.261/10	B	0.269/5	B
				0.261/5	B
0.259/40					
0.250/30	A	0.250/15	A	0.249/5	C
0.238/40	A	0.238/10	A	0.240/5	
				0.237/5	
0.227/20	A	0.228/L	A	0.234/10	C
0.2140/L	A	0.2205/5		0.2259/L	C
		0.2140/L	A	0.2252/L	B
				0.2188/85	C
				0.2150/60	
				0.2046/L	B
		0.1996/5	B	0.1993/L	
0.1968/25	A	0.1968/L	A	0.1951/L	C
				0.1932/10	C
0.1918/40	B	0.1916/10	B	0.1920/40	B
				0.1897/40	
				0.1865/10	
				0.1840/L	B
0.1812/80	A	0.1810/5	A		
		0.1781/10	A	0.1782/10	
		0.1778/L	B	0.1756/15	
				0.1738/10	
		0.1690/L		0.1687/5	
		0.1652/5	A+B	0.1652/L	B
		0.1634/L		0.1632/L	
		0.1608/L		0.1616/L	
				0.1587/L	
				0.1576/L	
0.1566/40	B	0.1568/5	B	0.1565/10	B
				0.1557/10	
				0.1542/10	
		0.1518/5		0.1518/L	

L — less than 5   A — α-Cd(VO$_3$)$_2$ B — V$_2$O$_5$ C — β-Cd(VO$_3$)$_2$

Table 4 Wavenumbers in cm^{-1}

| | Products obtained at t, °C | | | | α-Cd(VO$_3$)$_2$[11] | β-Cd(VO$_3$)$_2$[11] |
	300	400–600	715–800	V$_2$O$_5$		
	475–580 vs	425 580 vs	450–580 vs	480 s	565–585 vs	540–550 vs
				590 m		
	765 sh		770 m			
	800–875 m	770–890 vs	785–875 vs	820 vs	850 vs	845 vs
			885 m			
	930–955 m	955 m			960 m	
	1000 m					
	1020 s	995–1020 vs	1020 m	1020 m		
	1060 m					

vs — very strong   s — strong   m — medium   w — weak   vw — very weak   sh — shoulder

crystallizing from the melt. From the IR spectrum (Table 4), the X-ray powder pattern (Table 3) and the vanadium(IV) content in the product (1.43%), it can be assumed that the composition of this admixture is different from those mentioned above. It is probable that a small amount of bronze is formed during the decomposition of cadmium hydrogenhexavanadate. The composition of the primarily formed bronze is obviously changed on increase of the temperature.

It follows from the results that the main primary products in the thermal decomposition of the two hydrogenhexavanadates have analogous compositions, i.e. vanadium pentoxide and the corresponding metavanadate. It is stated in [10] that these compounds can react together to form bronzes. With respect to the different thermal stabilities of potassium and cadmium bronzes, it is apparent that the final products formed as a consequence of the thermal decompositions of the two hydrogenvanadates have different compositions.

References

1 I. G. Čufarova, A. A. Ivakin, N. I. Petunina, L. A. Pereljaeva and O. V. Korjakova, Zh. Neorgan. Khim., 24 (1979) 953.

2 A. A. Ivakin, I. A. Jacenko and M. V. Kručinina, Zh. Neorgan. Khim., 26 (1981) 2677.

3 M. Drábik, Ľ. Žúrková and I. Goljer, J. Thermal Anal., 26 (1983) 73.

4 Ľ. Ulická, prepared for press.

5 R. Herrman, Plameňová fotometria (Flame photometry), State publishing House of Health, Prague, 1968.

6 R. Přibil, Komplexony v chemické analyse (Complexons in the chemical Analysis), Publishing House of Czech. Acad. Sci., Praque, 1957.

7 O. Tomiček, Kvantitativní analysa, IV. (Quantitative Analysis), State publishing House of Health, Prague, 1958.

8 A. A. Fotjev, V. L. Volkov and V. K. Kapustkin, Oksidnyje vanadijevyje bronzy (Oxo-bronzes of vanadium), Publishing House Nauka, Moscow, 1978.

9 Ľ. Ulická, Chem. Zvesti, 30 (1976) 409.

10 A. A. Fotjev, M. P. Glazyrin, V. L. Volkov, B. G. Golovkin and V. A. Makarov, Issledova-nija kislorodnych vanadijevych sojedinenij (Study of the oxovanadate compounds), Publishing House UFANSSR, Sverdlovsk, 1970.

11 Č. Göczeová, unpublished results.

Zusammenfassung — Die thermische Reaktivität von $KHV_6O_{16} \cdot 3H_2O$ und $Cd(HV_6O_{16})_2 \cdot 12H_2O$ wurde untersucht. IR-Spektroskopie und Röntgenphasenanalyse ergaben, daß beide Verbindungen nach der Dehydratisierung zu Vanadinpentoxid und dem entsprechenden Metavanadat zersetzt wurden. Kalium-metavanadat und Vanadinpentoxid reagieren miteinander unter Bildung von Bronzen unterschiedlicher Zusammensetzung. Dagegen sind Vanadin-pentoxid und Cadmium-metavanadat die im Temperaturbereich von 300–800 °C in den Reaktionsprodukten vorherrschenden Komponenten.

Резюме — Исследована термическая реакционная способность $KHV_6O_{16} \cdot 3H_2O$ и $Cd(HV_6O_{16})_2 \cdot 12H_2O$. Методом ИК спектроскопии и фазового анализа найдено, что после дегидратации оба соединения разлагаются с образованием пятиокиси ванадия и соответствующего метаванадата. Метаванадат калия реагирует затем с пятиокисью ванадия с образованием бронз различного состава. В случае кислого гексаванадата кадмия, пятиокись ванадия и метаванадат кадмия являются главными продуктами реакции в интервале температур 300–800 °C.