

## **THERMAL PROPERTIES OF LITHIUM HYDROGENHEXAVANADATE**

*Ľ. Žurková and S. Korenková*

DEPARTMENT OF INORGANIC CHEMISTRY, KOMENSKÝ UNIVERSITY,  
MLYNSKÁ DOLINA, 842 15 BRATISLAVA, CZECHOSLOVAKIA

(Received January 19, 1987)

The thermal properties of  $\text{LiHV}_6\text{O}_{16} \cdot 5.5\text{H}_2\text{O}$  were studied in air atmosphere by DTA, DTG and TG in the temperature interval 20–800°. The studied compound is thermally unstable. In the course of the third step of mass loss, it decomposed with the formation of new phases. On further heating, reaction between these phases took place. A mixture of  $\text{V}_2\text{O}_5$  and  $\text{LiV}_3\text{O}_8$  was obtained as final product.

The crystal structures of the polyvanadates formulated as  $\text{M}^1\text{HV}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$  [1–3] or  $\text{M}^1_2\text{V}_{12}\text{O}_{13} \cdot y\text{H}_2\text{O}$  [4, 5] are not yet known. Their X-ray patterns exhibit only a small number of diffuse diffractions. Accordingly, it is not possible to draw any conclusions about their structures from X-ray studies. Information about their structures, however, can be obtained from studies of their properties, e.g. their thermal properties.

Except for cesium, all of the alkali metals form hydrogenhexavanadates, but only the thermal properties of sodium and potassium hydrogenhexavanadates have been studied so far [6, 7]. This paper deals with a study of the thermal reactivity of the hydrate of lithium hydrogenhexavanadate.

### **Experimental**

$\text{LiHV}_6\text{O}_{16} \cdot 5.5\text{H}_2\text{O}$  was prepared by adding  $\text{HNO}_3$  ( $c = 1 \text{ mol} \cdot \text{dm}^{-3}$ ) to a solution of  $\text{LiVO}_3$  ( $c = 0.5 \text{ mol} \cdot \text{dm}^{-3}$ ). The degree of acidification  $Z$  was 1.1 ( $Z = n\text{HNO}_3/n\text{LiVO}_3$  where  $n$  is the mass amount). The reaction proceeded at 20°. The lithium hydrogenhexavanadate was isolated from the reaction mixture after 10 days.

The composition of the prepared compound was verified by chemical analysis and via the IR spectrum.

The thermal analysis of the lithium hydrogenhexavanadate was performed on a

Q 1500 Derivatograph (MOM, Budapest); conditions: air atmosphere, sample mass 250 mg, heating rate 10 deg/min, Pt crucible,  $\text{Al}_2\text{O}_3$  as internal standard. Before being measured, the compound was powdered and sifted through a sieve with 4900 mesh/cm<sup>3</sup>. The products obtained during DTA interrupted at various temperatures were cooled to room temperature and identified by IR spectroscopy and X-ray phase analysis.

The IR spectra were measured in Nujol mulls on a Perkin-Elmer 180 spectrophotometer. X-ray diffraction patterns were recorded with a Philips PW 1050 diffractometer;  $\text{CuK}_\alpha$  radiation was used.

Vanadium(V) and vanadium(IV) were estimated volumetrically with  $0.05 \text{ mol} \cdot \text{dm}^{-3} \text{ FeSO}_4$  and  $0.01 \text{ mol} \cdot \text{dm}^{-3} \text{ KMnO}_4$ , respectively. The lithium content was determined by flame photometry (Flapho 4, C. Zeiss, Jena).

## Results and discussion

In order to explain the endo- and exothermic peaks in the DTA curve, the heating of  $\text{LiHV}_6\text{O}_{16} \cdot 5.5\text{H}_2\text{O}$  was interrupted at 168, 248, 325, 562 and 615° (Fig. 1).

In the temperature interval 40–325°,  $\text{LiHV}_6\text{O}_{16} \cdot 5.5\text{H}_2\text{O}$  lost mass in three steps. The total mass loss found was 16.82%; that calculated was 16.16%.

The first step of mass loss is connected with partial dehydration: a lower hydrate of lithium hydrogenhexavanadate is formed. The rest of the water is then released in the temperature interval 168–248°. The IR spectrum of the product obtained at 248° is shown in Fig. 2(b). The product obtained when heating was interrupted at 325°, when the exothermic process with maximum at 292° is already finished, is a mixture of  $\text{V}_2\text{O}_5$  and  $\text{LiV}_3\text{O}_8$ .

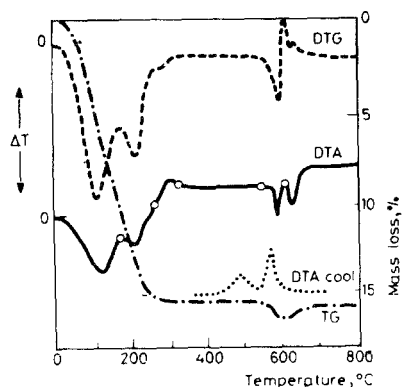


Fig. 1 Thermoanalytical curves of  $\text{LiHV}_6\text{O}_{16} \cdot 5\frac{1}{2} \text{H}_2\text{O}$  (○ interruption of heating)

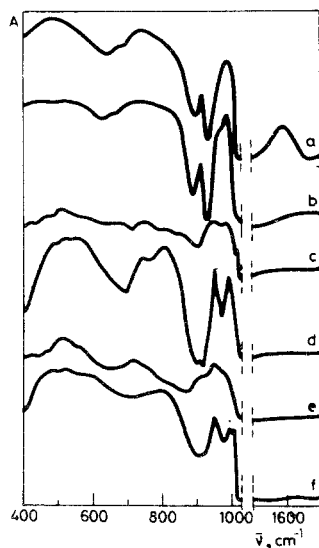


Fig. 2 IR spectra of  $\text{LiHV}_6\text{O}_{16} \cdot 5\frac{1}{2}\text{H}_2\text{O}$  (a) and products of its thermal decomposition at various temperatures: a: 168° (identical with parent compound), b: 248°, c: 325°, d: 562°, e: 615°, f: 800 °C

However, the X-ray pattern indicates that  $\text{Li}_{0.48}\text{V}_2\text{O}_5$  and  $\text{Li}_{0.56}\text{V}_2\text{O}_{15}$  bronzes and a third phase, not identified as yet, are also present in the mixture (Table 1). From these results, we presume that in the temperature interval 248–325° the mass loss is connected with decomposition of the structure of hydrogenhexavanadate to yield new substances. From the presence of vanadium-oxygen bronzes of lithium in the mixture obtained at 325°, as well as from the results of vanadium(IV) estimations (Table 2), it follows that within this temperature interval oxygen is released, too. However, the formation of new phases and oxygen release cannot be excluded in the temperature interval 168–248°, as the second and third steps of mass loss partially overlap. It must further be mentioned that the X-ray patterns of the starting compound and of products obtained at 168 and 248° contain only a small number of diffuse diffractions, and so they are not suitable for X-ray phase analysis.

The product obtained when heating was interrupted at 562° is a mixture of  $\text{V}_2\text{O}_5$ ,  $\text{LiV}_3\text{O}_8$  (in greater amount at 325°), a  $\beta$ -bronze having the formula  $\text{Li}_{0.33}\text{V}_2\text{O}_5$  and a further, unidentified phase whose presence is evidenced by two weak unassigned diffractions in the X-ray pattern (Table 1). This means that in the temperature interval 325–562° thermochemical reactions between the components of the mixture take place, which are accompanied by oxygen release and result in the formation of the  $\beta$ -bronze and  $\text{LiV}_3\text{O}_8$ .

**Table 1** Interplanar distances in products of thermal decomposition of lithium hydrogenhexavanadate at various temperatures

325 °C		562 °C		615 °C		800 °C	
<i>d</i> , nm	<i>I</i> <sub>rel</sub>	<i>d</i> , nm	<i>I</i> <sub>rel</sub>	<i>d</i> , nm	<i>I</i> <sub>rel</sub>	<i>d</i> , nm	<i>I</i> <sub>rel</sub>
0.941	43 B	0.941	30 B	0.947	73 B		
0.865	22						
		0.720	29 B	0.723	100 B		
0.714	64 B'T						
0.630	45 O	0.634	85 O	0.637	46 O	0.631	100 O
0.572	27 O V T	0.575	63 O V	0.577	23 O V	0.575	49 O V
0.510	14 B'						
				0.497	43 B		
0.496	18						
0.472	22 B'	0.472	16 B	0.473	36 B		
0.437	48 V	0.437	100 V	0.438	100 V	0.436	100 V
0.408	22 V	0.408	60 V	0.410	31 V	0.408	100 V
0.379	23 O B'	0.381	29 O	0.386	29 O B	0.381	35 O
		0.362	× B	0.361	87 B		
0.359	18 B'						
		0.348	16 B V	0.344	43 B O	0.347	24 V O
0.339	52 O B'	0.340	100 O V B	0.338	38 B V	0.340	53 V
0.335	90 V T						
		0.322	25 O	0.322	14 O	0.320	48 O
				0.320	17 B		
0.318	33 O	0.314	83 O B	0.315	36 O B	0.314	46 O
0.312	60 T B'						
0.303	46 O T	0.304	17 O B	0.303	100 O B	0.305	13 O
		0.297	10 O			0.296	12 O
		0.295	18 B	0.295	58 B		
0.291	53 O	0.288	100 V O	0.289	39 V O B	0.288	100 V O
0.286	62 V B'						
0.276	18 V	0.276	51 V	0.277	× V	0.276	30 V
				0.273	21 B		
0.271	30 V B'	0.269	19 V			0.268	14 V
0.2606	25 O V	0.2610	50 O V	0.2613	13 O V	0.2607	23 O V
		0.2494	× B	0.2570	10 B		
0.2520	15			0.2522	21		
0.2445	14			0.2446	10		
		0.2402	× V	0.2403	V	0.2398	× V
0.2390	×						
0.2371	×						
				0.2358	13 B		

Table 1 (cont.)

325 °C		562 °C		615 °C		800 °C	
<i>d</i> , nm	<i>I</i> <sub>rel</sub>	<i>d</i> , nm	<i>I</i> <sub>rel</sub>	<i>d</i> , nm	<i>I</i> <sub>rel</sub>	<i>d</i> , nm	<i>I</i> <sub>rel</sub>
0.2286	× O	0.2289	× O	0.2296	× O	0.2287	× O
0.2256	14			0.2254	12 B		
		0.2199	30 O				
0.2193	26 O VT	0.2187	33 V	0.2190	28 O V	0.2185	100 O V
0.2152	24 V T	0.2149	17 B	0.2153	100 B V		
0.2123	17 O	0.2137	27 O V			0.2139	81 V
						0.2105	19 O
		0.2035	11 B	0.2041	12 B	0.2036	12
0.2042	× O						
0.2014	×						
		0.1993	23 V	0.1985	22 V B	0.1989	14 V
0.1978	19	0.1970	× B			0.1966	11
		0.1916	31 V	0.1926	20 V B	0.1917	25 V
0.1910	17 V	0.1900	20 V	0.1903	10 V	0.1896	35 V
				0.1892	13		
				0.1888	13 B		
0.1855	15 V	0.1860	25 V	0.1866	19 V	0.1859	26 V
0.1821	×	0.1841	10 B	0.1839	11 B	0.1838	13
0.1795	41 O	0.1799	25 O	0.1802	21 O B	0.1796	11 O
0.1782	18 V	0.1782	33 V	0.1786	× V	0.1780	16 V
0.1757	11 V	0.1757	18 V	0.1763	11 V	0.1755	15 V
0.1740	11 V	0.1731	× V			0.1737	× V
0.1728	×						
0.1668	×	0.1699		0.1663	×		
0.1648	11 V	0.1651	17 V	0.1650	13 V	0.1650	13 V
0.1633	× V	0.1633	× V	0.1629	11 V	0.1635	× V
0.1606	×	0.1616	×			0.1616	10
0.1576	× V	0.1577	11 V			0.1573	× V
0.1565	× V	0.1563	17 V	0.1559	× V	0.1559	12 V
				0.1548	11		
0.1546	12 V	0.1535	17 V	0.1541	28 V	0.1530	12 V O
				0.1537	26		
0.1526	22 V	0.1529	15 V	0.1523	17 O		

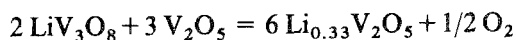
B = β-bronze Li<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub> [8]B' = β'-bronze Li<sub>0.48</sub>V<sub>2</sub>O<sub>5</sub> [8]O = LiV<sub>3</sub>O<sub>8</sub> [9] T = γ-bronze Li<sub>0.56</sub>V<sub>5</sub>O<sub>12</sub> [8]V = V<sub>2</sub>O<sub>5</sub> [8] × = *I*<sub>rel</sub> less than [10]

**Table 2** Composition of products of thermal decomposition of lithium hydrogenhexavanadate at various temperatures and the contents of vanadium(IV)

<i>t</i> , °C	% V(IV)	Composition of the mixtures			
		V <sub>2</sub> O <sub>5</sub>	LiV <sub>3</sub> O <sub>8</sub>	Li <sub>0.33</sub> V <sub>2</sub> O <sub>5</sub>	additional
325	1.11	+	+	–	B' T N
562	1.64	+	++	+	N
615	5.11	+	+	++	N
800	1.17	++	+	–	N

+ = present in the product; – = not present in the product; ++ = the highest content in comparison with another temperatures; B' = Li<sub>0.48</sub>V<sub>2</sub>O<sub>5</sub>, T = Li<sub>0.56</sub>V<sub>5</sub>O<sub>12</sub>, N = unidentified admixture.

The temperature interval 562–615° in the DTA curve is characterized by a marked endothermic peak with minimum at 592°. In this interval the product partially melts. According to [9], the melting point of LiV<sub>3</sub>O<sub>8</sub> is 601°. Although the oxidation of vanadium-oxygen bronzes when they are heated in an air atmosphere does not allow the determination of their exact melting points, we presume that LiV<sub>3</sub>O<sub>8</sub> melts in this temperature interval. The product obtained at 615° contains the same three phases as that at 562°, but their relative amounts differ: the β-bronze content is increased, and those of LiV<sub>3</sub>O<sub>8</sub> and V<sub>2</sub>O<sub>5</sub> are decreased. These facts indicate that the endothermic effect is a result of a superposition of several processes: the melting of at least one component, and redox reactions between the components, resulting in β-bronze formation and the elimination of oxygen (mass loss is evident in the TG and DTG curves). The formation of the compounds mentioned above can be described by following equation:



The other components of the mixture melt within the temperature interval 615–800°. In the course of the melting, the β-bronze is oxidized (mass increase in the TG and DTG curves). The melting points of β-bronze (oxidative) and V<sub>2</sub>O<sub>5</sub> according to [9] are 585° and 675°, respectively. The final product obtained at 800° is a mixture of V<sub>2</sub>O<sub>5</sub> and LiV<sub>3</sub>O<sub>8</sub>. The composition of this mixture is in agreement with data in [8]. During the cooling of a melt of Li<sub>2</sub>O : V<sub>2</sub>O<sub>5</sub> with molar ratio 1 : 6 in an air atmosphere, the β-bronze begins to crystallize first, and is then oxidized to form a eutectic V<sub>2</sub>O<sub>5</sub>–LiV<sub>3</sub>O<sub>8</sub> mixture. The observed DTA curve of cooling of the product obtained at 800° is in agreement with this. The first exothermic peak corresponds to crystallization of the β-bronze, and the second one to the crystallization of the eutectic mixture. The shifts of the temperatures of the maxima in the DTA curve of cooling, as compared with those in the DTA curve of heating,

are caused by a characteristic undercooling in the course of the crystallization of  $V_2O_5$  and vanadium-oxygen bronzes of alkali metals formed in an air atmosphere [8].

$LiHV_6O_{16} \cdot 5.5H_2O$  is a thermally reactive compound. In the temperature interval 40–325°, the mass loss proceeds in three steps. The third step is connected with decomposition of the parent structure and the formation of new phases. At higher temperatures, redox reactions accompanied either by mass loss or mass increase, reactions between the components of the mixture, and successive melting of the individual phases take place. The product obtained at the highest temperature (800°) is a mixture of  $V_2O_5$  and  $LiV_3O_8$ . It must be mentioned, however, that there are 5 weak unassigned diffractions in the pattern of this product, which may be connected with the presence of further components (Tables 1 and 2).

## References

- 1 M. Drábik and Ľ. Žúrková, Chem. Zvesti, 36 (1982) 799.
- 2 Ľ. Žúrková, V. Suchá and M. Drábik, Proc. 9<sup>th</sup> Conf. Coord. Chem., (1983) 495.
- 3 M. Drábik, Ľ. Žúrková and I. Goljer, J. Thermal Anal., 26 (1983) 73.
- 4 A. A. Ivakin, J. G. Čufarova and I. I. Petunina, Zh. Neorg. Khim., 21 (1976) 3192.
- 5 O. V. Korjakova, L. A. Pereljaeva, E. V. Zabolockaja, I. I. Medvedeva and A. A. Ivakin, Zh. Neorg. Khim., 27 (1982) 2521.
- 6 V. Suchá, Ľ. Žúrková and E. Marko, Acta Fac. Rer. Natur. Univ. Comen., (in press).
- 7 Ľ. Ulická and Ľ. Žúrková, Thermochem. Acta, 92 (1985) 481.
- 8 A. A. Fotiev and A. A. Ivakin, Vanadium-oxygen bronzes, Nauka, Moscow, 1978.
- 9 A. A. Fotiev and A. A. Ivakin, Vanadium compounds of alkali metals and conditions of their formation, Trudy Inst. Khimii Akademii Nauk, USSR 19, Swerdlowsk, 1970.

**Zusammenfassung** — Die thermischen Eigenschaften von  $LiHV_6O_{16} \cdot 5.5H_2O$  wurden in Luftatmosphäre im Temperaturintervall von 20 bis 800 °C durch DTA, DTG und TG untersucht. Die untersuchte Verbindung ist thermisch instabil. Im Verlaufe der dritten Stufe des Gewichtsverlustes zersetzt sich die Verbindung unter Bildung neuer Phasen, die bei weiterem Erhitzen miteinander reagieren. Als Endprodukt wurde ein Gemisch von  $V_2O_5$  und  $LiV_3O_8$  erhalten.

**Резюме** — Методом ДТА, ДТГ и ТГ изучены в атмосфере воздуха и температурном интервале 20–800° термические свойства  $LiHV_6O_{16} \cdot 5.5H_2O$ . Изученное соединение термически неустойчивое. На третьей стадии потери веса вещество разлагается с образованием новых фаз, которые при дальнейшем нагревании вступают в реакцию. В качестве конечного продукта реакции получена смесь  $V_2O_5$  и  $LiV_3O_8$ .