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STUDY OF THERMAL PROPERTIES OF THALLIUM HEXAVANADATE

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A DTA study of the thermal properties of $Tl_2V_6O_{16}$ showed that its structure is not decomposed up to 475 °C. It melts at 505 °C. $Tl_2V_8O_{21}$ and $Tl_3V_5O_{14}$ crystallize successively from the melt.

The hexavanadates $M^I_2V_6O_{16}$ or $M^IV_3O_8$ (where M^I is K, Rb, Cs, Tl or NH_4) are well-characterized compounds of vanadium(V). They are isostructural [1, 2], having layer structures in which the cations with suitable radii (0.133–0.165 nm) are situated in the cavities between the anionic layers.

In a previous paper, we described the thermal properties of potassium, rubidium and cesium hexavanadates [3]. The present paper deals with the thermal decomposition of $Tl_2V_6O_{16}$. The aim of the study was to compare the stability of this compound with those of other hexavanadates and to acquire additional data concerning the relationship between the cation radius and the thermal stability of a hexavanadate.

Experimental

Thallium hexavanadate was prepared according to [4] and was identified by means of chemical analysis, and via its IR spectrum and X-ray powder diffraction patterns.

The thermal analysis of the thallium hexavanadate was performed on a Q–1500 derivatograph (MOM, Budapest); conditions: air atmosphere, sample mass 300 mg, heating rate 10 deg/min, Pt crucible, Al_2O_3 as reference material, temperature interval 20–750°. The thermal analysis was interrupted at 325, 475 and 550°. The products obtained during DTA interrupted at various temperatures were

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cooled to room temperature and identified by means of IR spectroscopy and X-ray phase analysis.

The IR spectra were measured in nujol mulls on a Perkin–Elmer 180 spectrophotometer. The diffraction patterns were recorded with a Philips PW 1050 diffractometer; CuK_α radiation was used.

Vanadium(V) and vanadium(IV) were estimated volumetrically with $FeSO_4$ and $KMnO_4$, respectively.

The thallium content was determined by titration with $KBrO_3$.

Results and discussion

The DTA curve of thallium hexavanadate exhibits two endothermic peaks: one in the temperature range 330–470°, with minimum at 375°, and one in the range 480–550°, with minimum at 505° (Fig. 1).

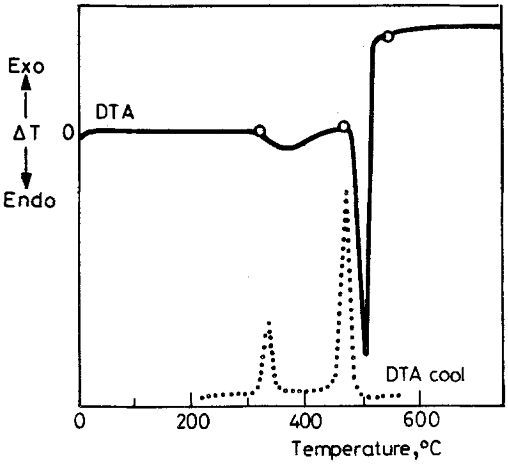

Fig. 1 DTA curves of $Tl_2V_6O_{16}$ (O – interruption of heating)

In order to explain the first endothermic effect, the heating was interrupted at 325 and 475°. The X-ray diffraction patterns of the products obtained were fully identical with the pattern of the starting hexavanadate (Table 1, Fig. 2). The small differences which were observed in the region of end-bonded V–O vibrations in the IR spectrum of the compound obtained at 475° indicate temperature-influenced deformations of these bonds, whereas the structure of $Tl_2V_6O_{16}$ is not decomposed. Such deformation of the V–O bonds can also be explained by the partial reduction of vanadium(V) to vanadium(IV). The presence of vanadium(IV) was not proved analytically, and its amount must be smaller than the sensitivity of the methods used.

The marked endothermic effect in the temperature range 480–550°, with minimum at 505°, corresponds to melting of the compound. This is in agreement with data in [5] and [6]: a phase $Tl_2V_6O_{16}$ melting at 505° was identified in the Tl_2O–V_2O_5 system.

The interruption of heating at 550° and cooling of the melt to room temperature results in the formation of a $Tl_3V_5O_{14}$–$Tl_2V_8O_{21}$ mixture (Table 1, Fig. 2). During

Table 1 Interplanar distances in products of thermal decomposition of thallium hexavanadate at various temperatures

325° or 475 °C		550 °C		550 °C	
d, nm	I_{rel}	d, nm	I_{rel}	d, nm	I_{rel}
0.779	25 H	0.758	17 OP	0.2253	16 OP
0.496	11 H	0.678	12 O	0.2197	8 P
0.440	10 H	0.531	32 O	0.2178	10 P
0.4202	17 H	0.5090	6 P	0.2089	80 OP
0.3965	27 H	0.4988	26 O	0.2032	6 OP
0.3857	26 H	0.4353	20 P	0.1979	5 O
0.3679	31 H	0.4159	45 O	0.1932	11 OP
0.3492	90 H	0.3773	18 OP	0.1901	8 OP
0.3204	100 H	0.3655	61 OP	0.1873	20 O
0.3013	39 H	0.3506	6 O	0.1834	16 O
0.2888	38 H	0.3402	18 O	0.1817	10 O
0.2845	47 H	0.3371	100 O	0.1801	18 OP
0.2631	8 H	0.3314	63 P	0.1769	5 P
0.2571	19 H	0.3179	22 OP	0.1734	5 P
0.2461	40 H	0.3016	50 OP	0.1709	4 O
0.2377	28 H	0.2998	48 O	0.1686	18 OP
0.2304	7 H	0.2933	10 O	0.1653	12 OP
0.2195	6 H	0.2874	40 O	0.1642	11 OP
0.2117	22 H	0.2854	40 P	0.1619	13 P
0.2008	20 H	0.2779	8 O	0.1588	10 OP
0.1933	8 H	0.2730	8 O	0.1568	12 P
0.1881	17 H	0.2574	11 OP	0.1548	11 O
0.1824	22 H	0.2519	60 OP		
0.1792	9 H	0.2486	44 OP		
0.1731	8 H	0.2386	12 O		
0.1697	18 H	0.2369	19 O		
0.1619	5 H	0.2344	12 O		
0.1589	14 H	0.2310	7 O		
		0.2282	12 O		

H = $Tl_2V_6O_{16}$ [4]; O = $Tl_2V_8O_{21}$ [5]; P = $Tl_3V_5O_{14}$ [4].

further heating of the product up to 750°, no changes occur in the composition of the mixture. This is confirmed by the cooling curve (Fig. 1), which exhibits two marked exothermic maxima connected with crystallization of the components of the above mentioned mixture. We assign the first maximum, at 475°, to the crystallization of $Tl_2V_8O_{21}$, with a published melting point of 518° [5, 6], and the second one, at 330°, to the crystallization of $Tl_3V_5O_{14}$. According to [7], $Tl_3V_5O_{14}$ decomposes at temperatures above 360°. The shift of the temperatures of crystallization to values lower than the corresponding melting points is caused by undercooling, which is characteristic for many compounds of vanadium [8].

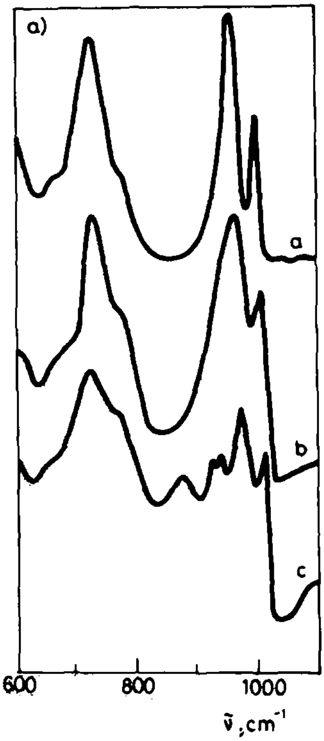

Fig. 2 IR spectra of $Tl_2V_6O_{16}$ (a) and the products of its thermal decomposition at different temperatures: (a) 325° (identical with starting compound), (b) 475°, (c) 550°

Thallium hexavanadate is stable up to its melting point. The crystallization of $Tl_2V_8O_{21}$ and $Tl_3V_5O_{14}$ during the cooling of melted thallium hexavanadate can be explained in the following way: under the given conditions, $Tl_2V_8O_{21}$ has the lowest value of ΔH (crystallization), and therefore this phase is formed first. After its crystallization, the concentration ratio $Tl_2O : V_2O_5$ in the mixture is changed and the optimum conditions for the crystallization of $Tl_3V_5O_{14}$ are established. The phase diagram of Tl_2O–V_2O_5 [6] confirms these conclusions.

The study of the thermal properties of alkali metal hexavanadates $M_2V_6O_{16}$ (M = K, Rb or Cs) [3] and $Tl_2V_6O_{16}$ showed that $K_2V_6O_{16}$ is the thermally most unstable hexavanadate; it is decomposed at 415°, i.e. a temperature below its melting point, to $K_3V_5O_{14}$, $K_2V_8O_{21}$ and KVO_3. Thallium hexavanadate forms a melt at 505°, and during its cooling $Tl_2V_8O_{21}$ and $Tl_3V_5O_{14}$ crystallize out successively. Rubidium and cesium hexavanadates melt at 505° and 508°, respectively.

On the crystallization of the melts, $Rb_2V_6O_{16}$ and $Cs_2V_6O_{16}$ are formed again, but they contain small amounts of vanadium–oxygen bronzes of the corresponding metal as admixtures.

The following conclusion may be drawn from the obtained results. The thermal stability of the hexavanadates is a function of the radius of the cation: the greater the radius, the higher the stability. $Rb_2V_6O_{16}$ and $Cs_2V_6O_{16}$ are the thermally most stable hexavanadates.

Note: The compounds $M^I_2V_8O_{21}$ (where M^I is K or Rb) contain a small amount of vanadium(IV). Therefore, they can also be formulated as $M^I_2V_8O_{20.8}$.

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Zusammenfassung — Eine DTA-Untersuchung der thermischen Eigenschaften von $Tl_2V_6O_{16}$ zeigt, daß seine Struktur bis 475 °C unzerstört bleibt. Der Schmelzpunkt beträgt 505 °C. Nacheinander kristallisieren $Tl_2V_8O_{21}$ und $Tl_3V_5O_{14}$ aus der Schmelze aus.

Резюме — ДТА исследование термических свойств гексаванадата талия ($Tl_2V_6O_{16}$) показало, что структура его сохраняется до температуры 475 °C, а затем он плавится при повышении температуры до 505 °C. Из расплава затем последовательно выкристаллизовываются соединения $Tl_2V_8O_{21}$ и $Tl_3V_5O_{14}$.