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THERMAL PROPERTIES OF PENTAVANADATES

K. GÁPLOVSKÁ and Ľ. ŽÚRKOVÁ

Department of Inorganic Chemistry, Faculty of Natural Sciences, Comensky University, 816 31 Bratislava, Czechoslovakia

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The thermal properties of $K_3V_5O_{14}$,$Rb_3V_5O_{14}$ and $Tl_3V_5O_{14}$ were studied in the temperature range 20–1000° in air atmosphere using DTA. $K_3V_5O_{14}$ is the most stable pentavanadate. $Tl_3V_5O_{14}$ is thermally stable up to 360°; at higher temperature it decomposes to $TlVO_3$ and $Tl_2V_6O_{16}$. $Rb_3V_5O_{14}$ is stable up to 300° at higher temperature it decomposes to $RbVO_3$ and $Rb_2V_6O_{16}$, and at even higher temperature $Rb_2V_6O_{16}$ reacts with part of the $RbVO_3$ and $Rb_2V_4O_{11}$ is formed.

Pentavanadates of the general formula $M_3^IV_5O_{14}$ belong to the not very numerous group of polyvanadates. Only the potassium, rubidium and thallium salts are known to date [1–4]. The physico-chemical properties of these compounds have not been studied extensively. In papers referring to the thermal properties of the pentavanadates, the ranges of existence of the pentavanadates in the phase diagrams of $KVO_3 - V_2O_5$ [5, 6], $RbVO_3 - V_2O_5$ [6] and $Tl_2O - V_2O_5$ [7] were estimated. The aim of our work was to study the thermal properties from the point of view of possible structural transformations, which have not been studied so far.

Experimental

The starting pentavanadates $K_3V_5O_{14}$, $Tl_3V_5O_{14}$ and $Rb_3V_5O_{14}$ were prepared according to [3]. The thermal properties were studied using MOM derivatograph, at different temperatures in the range 20–1000°. The conditions of measurements were the same for all compounds: the weighed amount was 120 mg, the heating rate was 5°/min, and an air atmosphere was used. Before being measured, the compounds were powdered, sifted through a sieve with 4900 mesh/cm^2 and uniformly packed into a Pt-crucible. The products obtained were identified after they had cooled down to room temperature.

The products were identified using IR-spectroscopy (Perkin–Elmer 567 IR-spectrophotometer, nujol suspension) and X-ray phase analysis (Philips X-ray diffractograph equipped with a PW 1058 goniometer, Cu_{K_α} radiation). Vanadium(IV) was qualitatively detected by EPR (EPR-spectrophotometer 9, Carl Zeiss, Jena).

Table 1

Interplanar

$K_3V_5O_{14}$		$Rb_3V_5O_{14}$		
505 °C	1000 °C	390 °C	440 °C	560 °C
0.779 s. B	0.779 m. B	0.779 w. H	0.766 m. H	0.770 s. H
0.495 s. P	0.495 s. P	0.754 w. P	0.565 w. H+M	0.570 w. H+M
0.432 w. P	0.432 w. P	0.526 w. P	0.423 v.w. H+M	0.424 v.w. H+M
0.412 w. P	0.412 w. P	0.432 m. P	0.396 w. H	0.398 w. H
0.389 v.w. B		0.377 w. P	0.384 w. M	0.385 m. M
0.373 m. P	0.373 m. P	0.355 w. H	0.366 v.w. M	0.365 w. M
0.325 v.s. P	0.325 v.s. P	0.334 v.s. P	0.364 v.w. M	0.352 s. H
0.310 w. B		0.321 w. M+H	0.351 v.w. H	0.334 w. P
0.298 s. P	0.298 s. P	0.307 v.s. P	0.318 v.s. H+M	0.319 v.s. H+M
0.282 s. P	0.282 s. P	0.285 v.s. P+M+H	0.308 v.w. M	0.308 v.s. P+H
0.248 s. P	0.248 s. P	0.263 v.s. P+M+H	0.300 m. H	0.301 w. H
0.246 s. P	0.246 s. P	0.251 v.s. P+H	0.290 m. H	0.291 m. H
0.223 v.w. P	0.223 v.w. P	0.240 v.w. H	0.284 v.s. H+M	0.285 v.s. P+H+M
0.216 w. P	0.216 w. P	0.225 s. P+H	0.270 v.w. M	0.271 M
0.207 m. P	0.207 w. P	0.217 w. P	0.262 m. M	0.263 w. P+M+H
0.195 v.w. P	0.195 v.w. P	0.209 s. P+M+H	0.258 w. H	0.260 w. P+H
0.191 w. P	0.191 w. P	0.203 v.w. M+H	0.254 m. M	0.255 m. M
0.187 m. P	0.187 m. P	0.201 v.w. P	0.249 w. M	0.250 m. P+M
0.176 w. P	0.176 w. P	0.193 s. P+M+H	0.245 m. H	0.248 m. H
0.175 w. P	0.175 w. P	0.189 v.w. M+H	0.243 v.w. H	0.239 w. H
0.172 w. P	0.172 w. P	0.184 v.w. H	0.238 w. H	0.234 w. M
0.166 v.w. P	0.166 v.w. P	0.182 w. P	0.233 w. M	0.219 w. P+H
0.164 m. P	0.164 m. P	0.178 v.w. P+M	0.219 w. H	0.216 v.w. M+H
0.163 m. P	0.163 m. P	0.176 v.w. P+H	0.215 v.w. M+H	0.213 w. M+H
0.162 m. P	0.162 m. P	0.173 v.w. P	0.211 w. M+H	0.209 w. M
0.159 v.w. P	0.159 v.w. P	0.171 v.w. P+M+H	0.209 v.w. M	0.201 m. M+H+P
0.155 m. P	0.155 m. P	0.168 v.w. P+M	0.201 m. M+H	0.193 w. P+M
		0.164 s. P	0.193 w. M	0.190 v.w. H
		0.163 v.s. P+H	0.189 w. H	0.188 w. M+H
		0.159 w. H+P+M+H	0.188 w. M+H	0.183 m. H+M
		0.157 w. P+H	0.184 w. M	0.180 v.w. M+P
			0.183 w. H	0.179 w. M
			0.180 w. M	0.175 v.w. H
			0.178 w. M	0.171 m. H+M
			0.174 v.w. H	0.165 v.w. M
			0.170 m. M+H	0.160 w. H+M
			0.165 v.w. M	0.156 v.w. H+M
			0.160 m. H+M	
			0.156 w. H+M	

P$-M_3V_5O_{14}$; H$-M_2V_6O_{16}$; M$-MVO_3$ (M = K, Rb, Tl); B$-KV_6O_{15}$; T$-Rb_2V_4O_{11}$

distances, nm

						$Tl_3V_5O_{14}$					
700 °C			1000 °C			390 °C			1000 °C		
0.521	v.w.	P	0.497	s.	T	0.749	v.w.	P	0.767	w.	H
0.491	m.	T	0.388	m.	M	0.504	w.	P	0.516	m.	H
0.429	w.	P	0.368	m.	M	0.433	s.	P	0.495	v.w.	H
0.346	v.s.	T	0.348	v.s.	T	0.420	m.	P	0.469	v.w.	M
0.342	v.s.	T	0.345	v.s.	T	0.404	v.w.	H+M	0.440	v.w.	H
0.334	s.	P	0.321	v.s.	M	0.398	v.w.	H	0.420	v.w.	H
0.320	m.	M	0.287	s.	T	0.376	v.w.	P+M	0.400	m.	H+M
0.305	m.	P	0.284	v.s.	M	0.368	v.w.	H+M	0.385	m.	H+M
0.283	s.	P+T+M	0.279	v.s.	T	0.351	v.w.	H	0.380	m.	M
0.277	s.	P+T	0.272	w.	M	0.329	v.s.	P	0.363	m.	H+M
0.262	m.	P+M	0.263	w.	M	0.317	w.	P+M+H	0.349	s.	H
0.249	m.	P	0.256	w.	M	0.302	s.	P+M+H	0.317	v.s.	H+M
0.247	s.	T	0.251	w.	M	0.289	w.	H+M	0.300	m.	H+M
0.225	w.	P	0.248	v.s.	T	0.284	s.	P+M+H	0.288	v.s.	M+H
0.220	w.	T	0.243	w.	T	0.253	s.	P+M+H	0.282	m.	H+M
0.218	m.	T	0.234	w.	M	0.251	s.	P	0.268	v.w.	H+M
0.216	w.	T+M	0.221	m.	T	0.248	m.	P+M	0.257	m.	H+M
0.208	w.	P	0.219	m.	T	0.247	w.	H+M	0.251	s.	M
0.200	v.w.	P+M	0.216	w.	M+T	0.240	v.w.	P	0.246	s.	H+M
0.193	w.	P+T+M	0.210	v.w.	M	0.237	v.w.	H	0.237	w.	H
0.186	w.	T	0.202	w.	M	0.231	v.w.	H+M	0.230	w.	H+M
0.185	m.	T	0.194	v.w.	M	0.225	m.	P	0.227	w.	H+M
0.181	v.w.	P	0.186	w.	T	0.218	s.	P	0.218	v.w.	H+M
0.172	w.	T+P+M	0.185	m.	T+M	0.213	v.w.	H+M	0.212	m.	H+M
0.170	m.	T+P+H	0.179	v.w.	M	0.209	s.	P	0.209	w.	M
0.163	w.	P	0.174	w.	T+M	0.200	w.	P+M+H	0.200	m.	H+M
0.162	m.	P+T+M	0.171	m.	T+M	0.193	s.	P	0.193	w.	H+M
0.159	v.w.	P+M	0.165	w.	M	0.189	m.	P	0.189	v.w.	H+M
0.156	m.	T+M+P	0.163	w.	T+M	0.179	m.	P	0.187	w.	H+M
						0.177	w.	P	0.178	w.	H+M
						0.173	v.w.	P	0.176	w.	H+M
						0.169	v.w.	P	0.171	w.	H+M
						0.165	w.	P	0.169	w.	H+M
						0.164	m.	P	0.162	w.	H+M
						0.161	m.	P	0.158	w.	H+M
						0.158	m.	P			
						0.157	m.	P			
						0.154	w.	P			

Results and discussion

$K_3V_5O_{14}$

The DTA curve of potassium pentavanadate (Fig. 1a) is characterized by a marked endothermic effect with maximum at 440° corresponding to melting of the compound. The DTA was interrupted at 410, 505 and 1000°, respectively.

The compound obtained at 410° was $K_3V_5O_{14}$. The product formed at 505° by crystallization of the melt was $K_3V_5O_{14}$, with KV_6O_{15} as admixture. The same product was obtained at 1000°. From comparison of the diffraction intensities corresponding to KV_6O_{15} (Table 1) it follows that with increasing temperature the KV_6O_{15} content of the product decreased. This result was also supported by IR-spectroscopy. In the IR-spectra of the compound formed at 505° (Fig. 2b), in the range 900–950 cm^{-1} absorption bands of KV_6O_{15} are also present, whereas in the IR-spectra of the compound formed at 1000° the presence of this admixture was not observed (Fig. 2a).

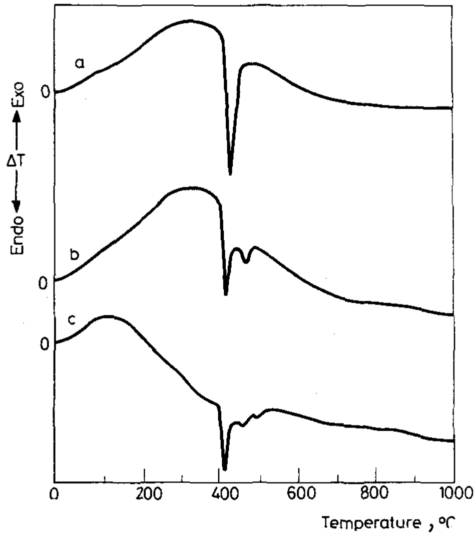

Fig. 1. DTA — curves of the pentavanadates a. $K_3V_5O_{14}$, b. $Rb_3V_5O_{14}$, c. $Tl_3V_5O_{14}$

$Rb_3V_5O_{14}$

The DTA curve of rubidium pentavanadate (Fig. 1b) is characterized by two endothermic effects, with maxima at 400 and 470°, respectively. The DTA was interrupted at 300, 310, 390, 440, 560, 700 and 1000°.

The product formed at 300° was identified as $Rb_3V_5O_{14}$. At all other temperatures the products obtained also contained components of its thermal decomposition. In the products formed at 310 and 390° besides $Rb_3V_5O_{14}$ the presence of $RbVO_3$ and $Rb_2V_6O_{16}$ was also proved.

After the first endothermic process connected with the melting of $RbVO_3$ had finished, at 440° a mixture of $RbVO_3$ and $Rb_2V_6O_{16}$ was obtained. This product was partially melted. The second endothermic process (470°) is connected with the melting of $Rb_2V_6O_{16}$. The product which crystallized out from the melt formed at 560° was a mixture of $RbVO_3$, $Rb_2V_6O_{16}$ and $Rb_3V_5O_{14}$. In the mixture obtained by crystallization of the melt formed at 700°, the presence of $RbVO_3$, $Rb_2V_4O_{11}$ and $Rb_3V_5O_{14}$ was proved. At 1000°, a mixture of $RbVO_3$ and $Rb_2V_4O_{11}$ was identified. The IR-spectra of the products are shown in Fig. 2e–i and their interplanar distances are given in Table 1.

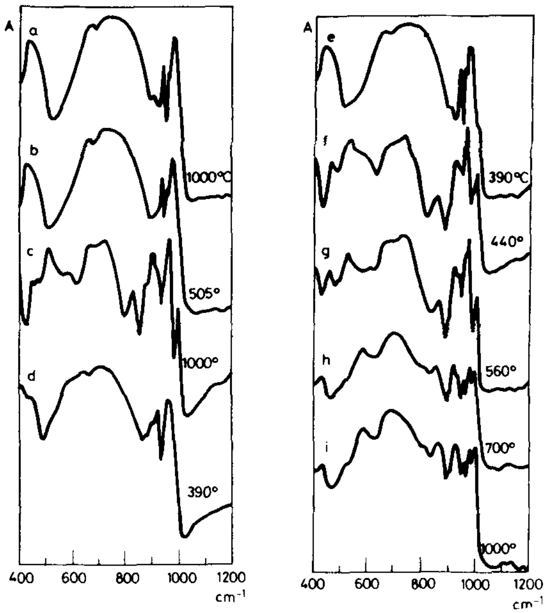

Fig. 2. IR — spectra of products of thermal decomposition of pentavanadates at various temperatures. a.b. $K_3V_5O_{14}$, c.d. $Tl_3V_5O_{14}$, e.—i. $Rb_3V_5O_{14}$

$Tl_3V_5O_{14}$

Three endothermic processes, with maxima at 410, 480 and 520°, were observed in the DTA curve of thallium pentavanadate (Fig. 1c). The DTA was interrupted at 360, 370, 390, 440, 500, 545, 580, 780 and 1000°, respectively.

At 360° $Tl_3V_5O_{14}$ was obtained. In the products formed at 370 and 390° besides $Tl_3V_5O_{14}$ the presence of $TlVO_3$ and $Tl_2V_5O_{16}$ was also proved. The first endothermic effect (410°) corresponds to the melting of $TlVO_3$. The product formed at 440° was partially melted and contained $TlVO_3$ and $Tl_2V_6O_{16}$. The second endothermic process (480°) corresponds to the melting of $Tl_2V_6O_{16}$. At 500° a melt was obtained and the product of its crystallization was proved to be again a mixture of $TlVO_3$ and $Tl_2V_6O_{16}$. This mixture was also formed at higher temperatures. The IR-spectra are shown in Fig. 2c–d, and the interplanar distances are given in Table 1.

Conclusion

The thermal stabilities of the studied pentavanadates decrease from the potassium to the rubidium salt. $K_3V_5O_{14}$ melts at 440° without decomposition; $Tl_3V_5O_{14}$ and $Rb_3V_5O_{14}$ are decomposed before they melt. The products of their thermal decomposition are the meta- and hexavanadates of the corresponding metal. The mixture of $TlVO_3$ and $Tl_2V_6O_{16}$ is stable up to 1000°. In the case of rubidium, at higher temperatures reaction proceeds between the components of the mixture. In this reaction the total mass of the $Rb_2V_6O_{16}$ reacts with part of the $RbVO_3$, and $Rb_2V_4O_{11}$ is formed. The mixture of $RbVO_3$ and $Rb_2V_4O_{11}$ is formed. The mixture of $RbVO_3$ and $Rb_2V_4O_{11}$ is stable up to 1000°.

The results obtained allow us to suppose that the thermal stabilities of the pentavanadates are decisively influenced by the radius of the cation. The thermal stability of the layer structure of the pentavanadates decreases with increasing radius of the cation. It follows from the comparison of the thermal reactivities of rubidium and thallium hexavanadates that $Rb_2V_6O_{16}$ is the more reactive. This fact can be explained by the higher polarisation effects of the Tl^+ ion, which cause the $Tl - O$ bond to be more covalent than the $Rb - O$ bond.

In all products formed at higher temperatures, traces of vanadium(IV) were found. The presence of vanadium(IV) can be explained as a result of the thermal heteropolar splitting of the $V - O$ bonds.

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Résumé — On a étudié les propriétés thermiques de $K_3V_5O_{14}$, $Rb_3V_5O_{14}$ et $Tl_3V_5O_{14}$ par ATD entre 20 et 1000° dans l'air. $K_3V_5O_{14}$ est le pentavanadate le plus stable. $Tl_3V_5O_{14}$ est thermiquement stable jusqu'à 360°; à des températures plus élevées il se décompose en $TlVO_3$ et $Tl_2V_6O_{16}$ · $Rb_3V_5O_{14}$ est stable jusqu'à 300°; à des températures plus élevées il se décompose en $RbVO_3$ et $Rb_2V_6O_{16}$ et à des températures encore plus élevées, $Rb_2V_6O_{16}$ réagit avec une partie du $RbVO_3$ et il se forme $Rb_2V_4O_{11}$.

ZUSAMMENFASSUNG — Die thermischen Eigenschaften von $K_3V_5O_{14}$, $Rb_3V_5O_{14}$ und $Tl_3V_5O_{14}$ wurden im Temperaturbereich von 20 bis 1000° in Luft durch DTA untersucht. $K_3V_5O_{14}$ ist das stabilste Pentavanadat. $Tl_3V_5O_{14}$ ist thermostabil bis zu 360°; bei höheren Temperaturen wird es zu $TlVO_3$ und $Tl_2V_6O_{16}$ zerstetzt. $Rb_3V_5O_{14}$ ist bis zu 300° stabil, bei höheren Temperaturen wird es zu $RbVO_3$ und $Rb_2V_6O_{16}$ zersetzt und bei noch höheren Temperaturen reagiert $Rb_2V_6O_{16}$ mit einem Teil des $RbVO_3$ zu $Rb_2V_4O_{11}$.

Резюме — Методом ДТА изучены термические свойства $K_3V_5O_{14}$, $Rb_3V_5O_{14}$ и $Tl_3V_5O_{14}$ в области температур 20—1000° в атмосфере воздуха. $K_3V_5O_{14}$ является наиболее стабильным пентаванадатом. $Tl_3V_5O_{14}$ термически стабилен до 360°, а при более высоких температурах разлагается до $TlVO_3$ и $Tl_2V_6O_{16}$. $Rb_3V_5O_{14}$ устойчив до 300°, а при более высоких температурах разлагается до $RbVO_3$ и $Rb_2V_6O_{16}$. Это последнее соединение при более высоких температурах частично реагирует с $RbVO_3$ с образованием $Rb_2V_4O_{11}$.