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THERMAL DECOMPOSITION OF DECAVANADATES OF BIVALENT METALS

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The thermal decomposition of $Cd_3V_{10}O_{28} \cdot 16H_2O$ and $Mg_3V_{10}O_{28} \cdot 18H_2O$ has been investigated. It was found by means of IR spectroscopy and X-ray phase analysis that the final products of decomposition of the given compounds are V_2O_5, the corresponding metavanadates and the vanadium bronzes of cadmium and magnesium. Present and previous results allow conclusions on the thermal decomposition of decavanadates of bivalent metals.

The thermal reactivity of decavanadates has become the subject of thorough research only in the last few years. Recent results have brought not only new information but also stimuli for further research.

Analysis of the thermal properties of decavanadates of bivalent metals has been carried out in the cases of $Zn_3V_{10}O_{28} \cdot 16H_2O$ [1], $Ca_3V_{10}O_{28} \cdot 16\,H_2O$, $Sr_3V_{10}O_{28} \cdot 24\,H_2O$ and $Ba_3V_{10}O_{28} \cdot 19\,H_2O$ [2]. Further research into decavanadates proved to be necessary for the explanation of certain phenomena connected with the thermal decomposition of the given compounds and also for purposes of obtaining a larger number of experimental data.

The present paper deals with the problem of dehydration and thermal decomposition of $Cd_3V_{10}O_{28} \cdot 16\,H_2O$ and $Mg_3V_{10}O_{28} \cdot 18\,H_2O$.

Experimental

$Cd_3V_{10}O_{28} \cdot 16\,H_2O$ and $Mg_3V_{10}O_{28} \cdot 18\,H_2O$ were prepared by the reaction of $H_6V_{10}O_{28}$ with the corresponding acetates [3].

The cadmium or magnesium content was determined complexometrically [4]. Vanadium(V) was determined volumetrically by titrating with a 0.1 *N* solution of iron(II) sulphate using diphenylamine as indicator [5], and vanadium(IV) by titrating with a 0.01 *M* solution of potassium permanganate [5], but also qualitatively by using e.p.r. spectra. The amount of crystal water was estimated by drying the substances at 350°, as well as by DTA.

For $Cd_3V_{10}O_{28} \cdot 16\,H_2O$ (1582.84) 21.30% Cd, 32.18% V, 18.21% H_2O were calculated and 21.46% Cd, 32.06% V, 18.77% H_2O found. For $Mg_3V_{10}O_{28} \cdot 18\,H_2O$ (1354.61) 5.38% Mg, 37.61% V, 23.94% H_2O were calculated and 5.39% Mg, 37.35% V, 24.55% H_2O found.

The thermal analysis of the compounds was performed on the Paulik–Paulik–Erdey derivatograph (MOM, Budapest), sample weight 200 mg. Gaseous products were sucked off by a water pump. For the study of the processes connected with heating of the compounds, products obtained by interrupted DTA, by drying over silica gel, and by isothermal heating at definite temperatures in a crucible furnace, were used. The samples obtained isothermally were always heated to constant weight and investigated by means of IR spectroscopy and X-ray phase analysis.

The infrared spectra were taken on a Perkin–Elmer type 221 instrument, with the Nujol technique.

X-ray diffraction patterns were taken on a Philips PW 1058 diffractograph equipped with a copper anticathode and a nickel filter.

The e.p.r. spectra were taken on a Varian instrument of the Strong Pitch type (modulation amplitude 10 G, frequency 9.5 GHz, power of microwave radiation 25 mW, sensitivity $5 \cdot 10^3 - 2 \cdot 10^5$).

Results and discussion

The results of differential thermal analysis of $Cd_3V_{10}O_{28} \cdot 16\,H_2O$ are shown in Fig. 1. The DTA curve indicates two endothermic processes within the temperature range 75–240°. These are immediately followed by an exothermic process (max. at 265°).

By long-term drying of $Cd_3V_{10}O_{28} \cdot 16\,H_2O$ over silica gel, it is possible to obtain $Cd_3V_{10}O_{28} \cdot 8\,H_2O$, with a structure considerably changed in comparison

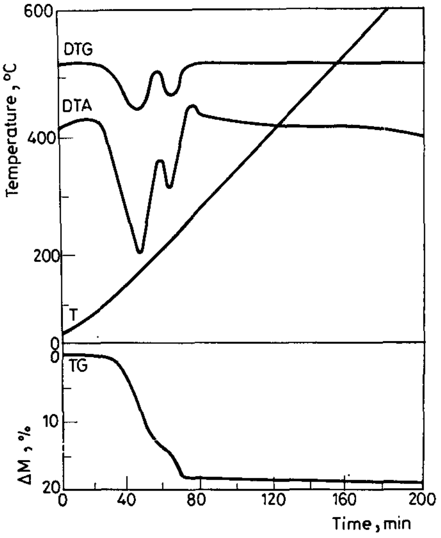

Fig. 1. TG, DTG and DTA curves of $Cd_3V_{10}O_{28} \cdot 16H_2O$

with that of the original compound. By isothermal heating of the starting crystallohydrate of cadmium decavanadate at 130°, the same weight loss (13.5%) is reached as in the TG curve after the first step of thermal decomposition. On the basis of all experimental data obtained, it is impossible to consider this product as a chemical entity. According to the IR spectrum, which in the case of decavanadates is characteristic and independent of the cation [6], the lower hydrate of cadmium decavanadate is the predominant component of the product. However, the occurrence of a weak absorption band beyond 1000 cm^{-1} as well as the presence of vanadium(IV) in the product (Table 2) indicate a further substance. The decavanadate of cadmium can still be identified in the product by means of the IR spectrum after the loss of about 87 per cent of the total crystal water content. The diffraction properties of the products deteriorate with increasing temperature. Total dehydration with formation of crystalline α-$Cd(VO_3)_2$ can be obtained at 200°. This compound can be unambiguously identified by means of IR spectro-

Table 1

Interplanar distances, in nm

$Cd_3V_{10}O_{28}\cdot 16\,H_2O$				Final product		α-$Cd(VO_3)_2$		V_2O_5 [7]	
d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}
0.834	56	0.252	32	0.672	15	0.680	30		
0.704	32	0.247	28	0.565	10			0.570	35
0.538	88	0.237	26	0.439	100	0.443	100	0.438	100
0.502	98	0.231	19	0.404	10			0.409	15
0.489	44	0.224	39	0.351	65	0.352	70		
0.447	100	0.221	36	0.337	90	0.338	35	0.339	85
0.428	74	0.217	53	0.313	60	0.315	55		
0.362	25	0.212	41	0.292	40	0.293	35		
0.352	72	0.199	26	0.286	25			0.287	55
0.338	17	0.197	20	0.276	10			0.276	15
0.327	80	0.194	21	0.266	5			0.268	10
0.325	75	0.191	24	0.260	10			0.261	15
0.323	72	0.189	48	0.251	25	0.251	20		
0.309	11	0.181	18	0.237	70	0.238	40		
0.302	10	0.175	32	0.227	25	0.227	25		
0.294	22	0.172	13	0.213	20	0.213	10		
0.283	16	0.168	12	0.196	15	0.196	10	0.199	10
0.277	64	0.164	36	0.192	5			0.192	15
0.272	24	0.161	11	0.187	15	0.188	15	0.186	10
0.265	34	0.159	13	0.180	30	0.180	15		
0.261	40	0.155	92	0.177	10	0.178	10	0.177	10
0.256	32			0.174	10	0.174	10		
				0.168	10	0.169	5		
				0.165	15	0.163	5	0.165	10
				0.160	10	0.160	10		
				0.156	15	0.156	15	0.156	< 10
				0.151	15			0.151	15

Table 2

Contents of vanadium(IV) in heated samples

Heated compound	Temperature, °C				
	130	200	230	330	600
$Cd_3V_{10}O_{28} \cdot 16\ H_2O$	0.67	1.37			0.13
$Mg_3V_{10}O_{28} \cdot 18\ H_2O$	0.33		1.24	0.90	0.41

scopy and X-ray phase analysis. The stoichiometry of the original decavanadate points to the necessity of formation of at least one more compound in its decomposition. The X-ray diffraction pattern and IR spectrum confirm the correctness of such a requirement. However, due to the unsatisfactory number of very weak unassigned diffraction lines, it is impossible to identify with certainty the further component of the product. The determination of the nature of this unknown compound is facilitated to a certain extent by the presence of vanadium(IV) in the mixture. On this basis it is possible to assume that the further component of the product is either a lower oxide of vanadium or the vanadium bronze of cadmium. In both cases these are compounds in which vanadium in a lower oxidation state is converted in air atmosphere to a higher oxidation state. The above conclusions are in agreement with our experience. The content of vanadium(IV) is maximum at precisely 200°, and decreases with further increasing of the temperature. In the IR spectrum of the product (Table 3), besides the vibrations belonging to α-$Cd(VO_3)_2$, there occur further ones at 1000 and 1015 cm^{-1}. Taking this as well as study of the entire IR spectrum into account, it is possible to elim-

Table 3

Wavenumbers of $Cd_3V_{10}O_{28} \cdot 16\ H_2O$ and of the products of thermal decomposition, in cm^{-1}

$Cd_3V_{10}O_{28} \cdot 16\ H_2O$	Product obtained at t, °C		α-$Cd(VO_3)_2$ [8]	V_2O_5 [8]
	200	300		
400 m				
455 m		480 s		480 s
525 m				
590 m	565–590 vs	565–590 vs	565–585 vs	590 m
740 m				
820 m	820–860 s	820 s		820 s
850 m		860 s	850 s	
940 s	930 m			
965 vs	950 sh	940 s	960 m	
990 m				
	1000 w	1000 sh		
	1015 w	1020 m		1020 m

inate the possibility of the presence of a lower oxide of vanadium in the product [9]. It is therefore reasonable to presume that the vanadium in the oxidation state IV is a constituent of vanadium bronze. There exists only a small amount of information about this particular group of compounds of cadmium. According to some authors [9, 10], bronzes of composition $CdV_{12}O_{30}$ and $Cd_xV_2O_5$ ($x =$ $= 0.0-0.03$ and $0.17-0.25$) are known. They can be prepared by the reaction between V_2O_5 and $Cd(VO_3)_2$ in a stream of inert gas or in vacuum, at high temperatures approaching the melting point of the eutectic mixture of the given compounds. Under different conditions the yield of the reaction is small. If we consider the high reactivity of the dehydrated substance with destroyed structure, however, the occurrence of the bronze seems to be very probable, even at a lower temperature than necessary in the case of the reaction in the two-component system. According to [9], in the IR spectrum of $CdV_{12}O_{30}$, the absorption bands are found at about 1015, 1000 and 965 cm^{-1}. The first two bands are unambiguously present in the spectrum of the product (Table 3), while the third one may overlap with an absorption band of cadmium metavanadate. Although identification of the bronze via the IR spectrum only is not absolutely sufficient, the further thermal reactions confirm its existence. At 250° the presence of V_2O_5, in addition to the above-described compounds, can be identified by means of IR spectroscopy as well as by X-ray phase analysis (Table 1). The content of this oxide increases with the temperature, and at the same time the amount of vanadium(IV) decreases. This fact could be connected with the successive decomposition of an unstable bronze of cadmium [9] to α-$Cd(VO_3)_2$ and V_2O_5.

In the case of the decomposition of the anhydrous substance to α-$Cd(VO_3)_2$ and the bronze of composition $Cd_xV_2O_5$ at 200°, it would be necessary for the oxide of vanadium(V) to be present in the product already at this temperature. We find this to be inconsistent with our experiment.

Analogous conclusions connected with the nature of the products formed by heating of the crystallohydrate of cadmium decavanadate were attained by studying the products obtained by interrupted DTA.

It follows from the investigation of the thermal decomposition of $Cd_3V_{10}O_{28} \cdot$ $\cdot\ 16\ H_2O$ that both endothermic minima in the DTA curve are connected with the dehydration of the compound, the structural changes and the partial reduction of vanadium(V) to vanadium(IV). The exothermic maximum can be assigned to the crystallization of α-$Cd(VO_3)_2$ and formation of the bronze.

The thermal curves of $Mg_3V_{10}O_{28} \cdot 18\ H_2O$ are shown in Fig. 2. As in the previous case, two endothermic effects (40–265°) arise during the heating of this compound. However, in this case a temperature difference of about 100° was found between the second endoeffect and the exoeffect.

The weight loss found in the TG curve, corresponding to 2.5 moles of water, can be reached by drying of the compound at 100°. According to the IR spectrum (Table 4), the product is a pure decavanadate of magnesium, with a slightly altered structure in comparison with the original crystallohydrate, without any admixture containing vanadium(IV). By drying over silica gel, a decavanadate with an even lower content of crystal water (approximately 14 H_2O) was obtained. The X-ray diffraction pattern is likewise only slightly different from that of the initial compound. Major structural changes arise at 130° after the loss of almost 50% of the total amount of water. The product formed at this temperature has a less intense X-ray diffraction pattern than in the case of the higher hydrate. According to the IR spectrum, another component is found in this product besides the deca-

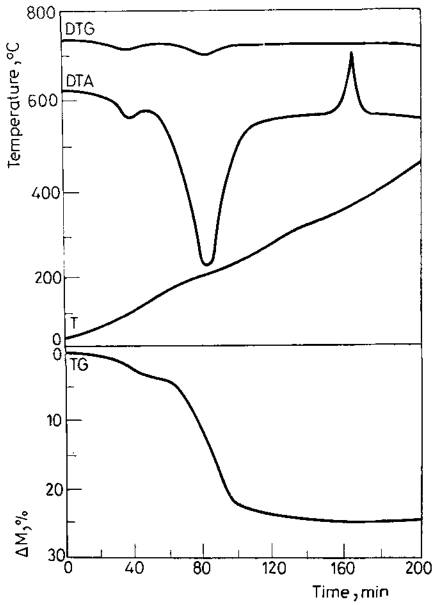

Fig. 2. TG, DTG and DTA curves of $Mg_3V_{10}O_{23} \cdot 18H_2O$

Table 4

Wavenumbers of $Mg_3V_{10}O_{28} \cdot 18\ H_2O$ and of the products of thermal decomposition, in cm^{-1}

$Mg_3V_{10}O_{28} \cdot 18\ H_2O$	Product heated at t, °C		V_2O_5 [8]
	160	330	
415 m		420 s	
450 m		480 s	480 s
515 s	550–700 vs	530–570 vs	590 m
600 s			
740 m			
815 s	820 sh	830–890 s	820 vs
850 m			
960 vs	940–980 vs	985 w	
995 s			
		1020 m	1020 m

vanadate of magnesium. This component contains vanadium(IV), the amount of which increases in the mixture in parallel with increasing temperature. The crystalline nature of the product is then changed. The substance does not diffract at a tempetature of 160° because it releases about 88 per cent of the total water content, and its spectrum is entirely different in comparison with that of the original compound (Table 4). Total dehydration is achieved only at 230°, when the product also retains the greatest amount of vanadium(IV). This intermediate decomposes at 330° to V_2O_5 and $Mg(VO_3)_2$. Both compounds can be identified by the methods used (Tables 4 and 5). In the mixture of substances obtained, however, vanadium(IV) is still present, and its content decreases very slowly with increasing temperature. This fact indicates the presence of a third component of the mixture. The IR spectrum reveals that an oxide of vanadium in a lower

Table 5

Interplanar distances, in nm

$Mg_3V_{10}O_{28} \cdot 18\,H_2O$				Final product		$Mg(VO_3)_2^a$		V_2O_5 [7]	
d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}
0.811	55	0.269	100	0.617	20	0.628	15		
0.774	28	0.261	11	0.570	26			0.570	35
0.748	43	0.255	12	0.433	100	0.432	50	0.438	100
0.524	10	0.244	7	0.407	16			0.409	15
0.508	18	0.243	10	0.338	75	0.340	3	0.339	85
0.479	58	0.234	4	0.323	4	0.324	5		
0.430	11	0.220	6	0.312	59	0.315	25		
0.412	8	0.217	15	0.306	95	0.306	100		
0.398	8	0.215	17	0.286	40	0.291	5	0.286	55
0.392	11	0.213	11	0.275	20	0.276	2	0.276	15
0.354	5	0.205	14	0.274	25	0.273	10	0.268	10
0.348	9	0.203	17	0.260	18			0.261	15
0.333	38	0.195	26	0.230	9	0.232	10		
0.323	10	0.186	12	0.218	17	0.218	20		
0.311	15	0.181	4	0.211	8	0.211	5		
0.301	33	0.172	3	0.208	12	0.208	10		
0.291	13	0.162	22	0.199	7			0.199	10
0.289	15	0.158	4	0.191	16	0.193	2	0.192	15
0.282	18			0.187	18	0.187	5	0.186	10
				0.179	6	0.180	2		
				0.177	14			0.177	10
				0.174	8	0.174	5		
				0.165	15	0.165	15	0.165	10
				0.161	12	0.161	15		

[a] — ref. [11].

oxidation state, similarly to the previous case, can in no way be considered. According to [9], bronzes of composition $MgV_{20}O_{48.5}$ and $Mg_xV_2O_5$ ($x = 0.0-0.11$) are known. The former is very unstable and oxidizes at lower temperatures in comparison with bronzes of other bivalent metals. This fact is inconsistent with our experience, i.e. the slowly decreasing amount of vanadium(IV) in the product. In the case of formation of the bronze $MgV_{20}O_{48.5}$, roughly 10% of the vanadium from the initial compound would have to be reduced. This is probably impossible under the given conditions in the case of magnesium salt. The occurrence of a bronze of type $Mg_xV_2O_5$ seems to be more realistic, because at most a 2.2% reduction of the vanadium is required for its formation. This degree of reduction corresponds to the 1.07% content of vanadium(IV) in the product. This bronze is probably more thermally stable than the previous one and therefore decomposes more slowly.

The same conclusions regarding the thermal decomposition of $Mg_3V_{10}O_{28} \cdot 18\,H_2O$ were reached by studying products obtained by interrupted DTA. Taking this into account, the first endothermic effect can be considered to be connected with the dehydration of the decavanadate as well as with the small structural changes, and the second effect with the dehydration, the major structural changes and the reduction of vanadium(V). The exothermic effect is connected with the crystallization of V_2O_5 and $Mg(VO_3)_2$.

The investigation of the thermal properties of the decavanadates of the bivalent metals has enriched our knowledge of the subject. There is only a small probability that research of other compounds of this type would lead to different results than those achieved thus far.

Above all, it is evident that the crystal water in the structure of the decavanadates has a stabilizing effect. However, it is impossible to generalize on the number of molecules of water sufficient for the stabilization, because it is dependent on the bonding properties of the given cation. After loss of this required amount of water, the structure of the decavanadates is destroyed and the conditions for the creation of the other type of vanadates arise. In the case of the decavanadates of bivalent metals studied so far, the noncrystalline intermediate comes into existence. Its further reactivity is dependent on the cation present in the initial compound. The intermediates formed after dehydration of the decavanadates of calcium, cadmium and barium decompose at either the same or only a slightly higher temperature than that of total dehydration. In contrast, the noncrystalline products formed following dehydration of the decavanadates of strontium, zinc and magnesium are stable within the temperature range 100–170°. The chemical nature of these intermediates is still unknown. Further research could be recommended mainly in the cases of the zinc and magnesium salts, because of the relatively high thermal stabilities of the anhydrous noncrystalline substances.

The products of thermal decomposition of the decavanadates of the bivalent metals were in all cases V_2O_5, the corresponding metavanadates and bronzes. With regard to present knowledge on the bronzes of the bivalent metals, it may be assumed that the composition of the compounds formed during the thermal decomposition of the decavanadates will depend on the possible degree of reduction of vanadium under the given reaction conditions (temperature and type of cation).

It also follows from the results that the chain structures of the anhydrous metavanadates of bivalent metals are thermally stable. Participation of the bivalent metals in formation of the layer structures of the hexa- and pentavanadate types seems only slightly probable. So far, these compounds are known in the case of univalent metals, and are formed, apart form other methods, by the thermal decomposition of some decavanadates [12].

References

1. Ľ. Ulická and Ľ. Zúrková, Proc. 6th Conf. on Coord. Chem. Bratislava—Smolenice, 1976, p. 263.
2. V. Suchá and Ľ. Zúrková, Acta F.R.N. Univ. Comen., Chimia 26 (1978) 23.
3. K. F. Jahr and F. Preus, Chem., 98 (1965) 3297.
4. R. Přibil, Komplexony v chem. analyse, (Complexons in the chemical analysis), Publishing House of Czech. Acad. Sci. Praha, 1957.
5. O. Tomíček, Kvantitativni analysa, IV. (Quantitative analysis), Edn., State Publishing House of Healt, Praha, 1958.
6. Ľ. Ulìcká and M. Dillinger, Collection Czech. Chem. Commun. 36 (1971) 2036.
7. L. I. Mirkin, Spravocnik po rentgenostrukturnomu analizu polikristallov, (Reference book of the X-ray analysis of polycrystals), Gosud. izd. fiziko-matem. liter. Moscow, 1961.
8. Ľ. Ulická, Chem. Zvesti, 30 (1976) 409.
9. A. A. Fotjev, M. P. Glazyrin, V. L. Volkov, B. G. Golovkin and V. A. Makarov, Trudy instituta chimii Ufan SSSR, 22 (1970) 49.
10. J. Galy, M. Pouchard, A. Casalot and P. Hagenmuller, Bull. Soc. Franc. Mineral. Crist., 90 (1967) 544.
11. E. Pollert, Silikaty, 4 (1973) 337.
12. Ľ. Žurková, Ľ. Ulická and V. Suchá, Proc. 7th Conf. on Coord. Chem., Bratislava—Smolenice, 1978, p. 297.

Résumé — On a étudié la décomposition thermique de $Cd_3V_{10}O_{28} \cdot 16\,H_2O$ et $Mg_3V_{10}O_{28} \cdot 18\,H_2O$. A l'aide des techniques de spectroscopie IR et de rayon X, on a établi que les produits finaux de la décomposition de ces composés sont V_2O_5, les métavanadates correspondants et les bronzes au vanadium, de cadmium et magnésium. Les résultats présents et antérieurs permettent de tirer des conclusions sur la décomposition thermique des décavanadates des métaux divalents.

Zusammenfassung — Die thermische Zersetzung von $Cd_3V_{10}O_{28} \cdot 16\,H_2O$ und $Mg_3V_{10}O_{28} \cdot 18\,H_2O$ wurde untersucht. Durch IR-Spektroskopie und Röntgen-Phasenanalyse wurde festgestellt, daß die Endprodukte der Zersetzung der gegebenen Verbindungen V_2O_5 ist, entsprechend den Metavanadate und den Vanadiumbronze von Cadmium und Magnesium. Die gegenwärtigen und früheren Ergebnisse gestatten Folgerungen bezüglich der thermischen Zersetzung von Dekavanadaten zweiwertiger Metalle.

Резюме — Исследовано термическое разложение $Cd_3V_{10}O_{28} \cdot 16\,H_2O$ и $Mg_3V_{10}O_{28} \cdot 18H_2O$. С помощью ИК спектроскопии и рентгеновского фазового анализа, было найдено, что конечными продуктами разложения данных соединений являются V_2O_5, соответствующие метаванадаты и ванадиевые бронзы кадмия и магния. Представленные результаты, а также предыдущие результаты, позволили вывести заключения о термическом разложении декаванадатов двухвалентных металлов.