

Thermal decomposition of ammonium cadmium decavanadate

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This paper is concerned with the thermal decomposition of decavanadate of the composition $(\text{NH}_4)_4\text{CdV}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$. By X-ray phase analysis and infrared spectroscopy it was found that this compound decomposed even before the completion of dehydration to give other polyvanadates. The decomposition reaction proceeded in several steps, the final product being a mixture of vanadium(V) oxide and cadmium metavanadate.

Изучалось термическое разложение декаванадата состава $(\text{NH}_4)_4\text{CdV}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$. При помощи рентгенофазового анализа и ИК спектроскопии было обнаружено, что указанное соединение разлагается с образованием других поливанадатов еще до окончания дегидратации. Происходят многоступенчатые реакции разложения, которых конечным продуктом является смесь пентоксики ванадия и метаванадата кадмия.

It follows from the thermal decomposition of decavanadates of some uni- and bivalent metals [1, 2] that the kind of cation is one of the factors which exerts influence upon the composition of the final decomposition product. The investigation of binary decavanadates gives supplementary information in this respect. These substances do not only contain two different kinds of cations but the ratio of these cations may be also altered ($M^I : M^{II} = 2 : 2$ or $4 : 1$). Our present knowledge of the decomposition of these substances has been achieved by studying the binary decavanadates of such univalent cations which form thermally stable hexavanadates and of such bivalent metals which give metavanadates as polymer vanadates with the best thermal stability. For instance, $\text{K}_2\text{Cd}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$ and $\text{Cs}_2\text{Zn}_2\text{V}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$ decompose to give the hexavanadate of alkali metal and cadmium or zinc metavanadate [3, 4]. The NH_4^+ ion also forms hexavanadate [5] which in contrast to the hexavanadates of some univalent metals is stable only at lower temperatures, but in comparison with other ammonium vanadates it is the most stable compound [6]. Therefore there are two reasons for studying $(\text{NH}_4)_4\text{CdV}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$. It is to determine its thermal stability and make a comparison with other binary decavanadates as well as to find out whether its thermal decomposition is analogous to the decomposition of the above-mentioned salts.

Experimental

$(\text{NH}_4)_4\text{CdV}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$ was prepared by the reaction of a 0.2 M solution of ammonium metavanadate acidified with acetic acid to pH 4.50 with a 1 M solution of cadmium acetate used in requisite molar ratios. The reaction solution was concentrated in a vacuum rotary evaporator approximately to 1/3 of the original volume. The orange crystals showed a sheet form.

$(\text{NH}_4)_2\text{V}_6\text{O}_{16}$, and the α - and β -modification of $\text{Cd}(\text{VO}_3)_2$ were prepared according to [5, 7].

The content of ammonia in the compounds was determined by titration after its release by sodium hydroxide and absorption in sulfuric acid [8]. Cadmium was determined gravimetrically as sulfate [8], vanadium volumetrically by titrating with a 0.1 N solution of iron(II) sulfate using diphenylamine [8] as indicator and the content of water was estimated by drying the substances to 350°C in a stream of oxygen.

For $(\text{NH}_4)_4\text{CdV}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$ (1394.16) calculated: 5.17% NH_4^+ , 8.06% Cd, 36.54% V, 20.67% H_2O^* ; found: 5.23% NH_4^+ , 7.74% Cd, 36.27% V, 20.18% H_2O^*

The differential thermal analysis of the compound was performed on a derivatograph of the system F. Paulik, J. Paulik, L. Erdey MOM, Budapest (sensitivity DTA 1/10, DTG 1/10, TG 200, time 200 min, weighed amount 500 mg). Gaseous products were sucked by a water pump.

The isothermal dehydration was carried out in a vacuum apparatus to constant weight in a stream of oxygen. On reaching a constant weight, an eventual change in the structure of the substance was investigated as a function of time.

The infrared spectra were measured on an instrument UR-20 (Zeiss, Jena) using the Nujol mill technique.

The powder diffraction patterns were made with an X-ray diffractometer (Philips) equipped with a goniometer PW 1058 using the CuK_α rays.

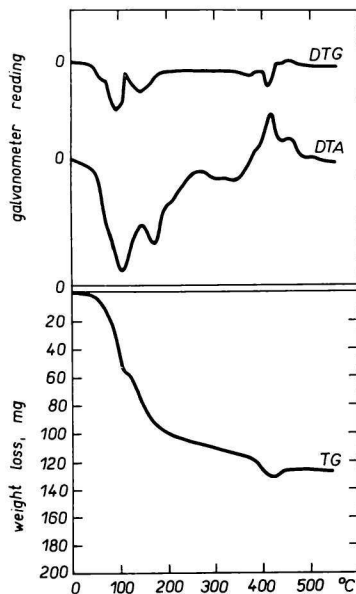
The e.p.r. spectra were taken on an instrument Varian, type Strong Pitch (modulation amplitude 10 G, frequency 9.5 GHz, the power of microwave radiation 25 mW, sensitivity 5×10^3 — 2×10^5).

Results and discussion

According to the results of the thermal analysis of $(\text{NH}_4)_4\text{CdV}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$ shown in Fig. 1 the transformation of this compound proceeds in several steps with two distinct endo-effects showing minima at 115 and 185°C and two also distinct exo-effects at 420 and 460°C. From the TG curve the following weight falls were determined for individual steps: step 1 11.60%, steps 1 and 2 18.50%, steps 1—3 24.50%, steps 1—4 26.10%, and steps 1—5 24.50%.

By drying ammonium cadmium decavanadate at 60°C in a vacuum apparatus its weight decreased by 11.54% which may be unambiguously attributed to the loss of 9 moles of water (during experiment the escape of ammonia was qualitatively detected). The lower hydrate formed may be also considered to be decavanadate because its infrared spectrum did not practically change. This ensues from the

* The amount of water corresponds to 16 moles of water from which 14 moles represent crystal water.

Fig. 1. Thermograms of $(\text{NH}_4)_4\text{CdV}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$.

knowledge that the infrared spectra of all decavanadates have the same character [9]. The first degree of dehydration brings about some structural transformations which are reflected in Fig. 2.

Upon heating ammonium cadmium decavanadate to 80°C another molecule of water is liberated and an amorphous substance is formed. However, the constitution of the anion remains preserved because the original character of infrared spectrum does not change. Nevertheless, the thermal stability of this intermediate is low since it decomposes upon heating to 90°C. Afterwards a mixture arises. It was unambiguously proved by X-ray phase analysis (Table 1) and infrared spectroscopy (Table 2) that ammonium hexavanadate was one of the components

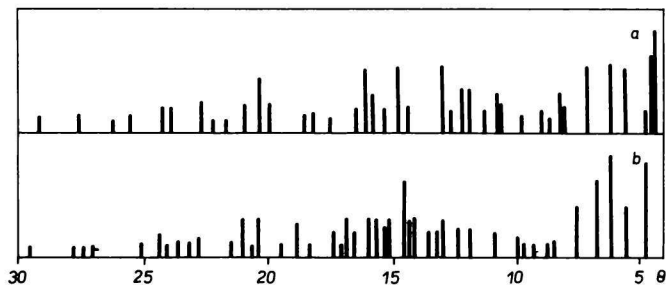


Fig. 2. X-ray diffraction pattern.
a) $(\text{NH}_4)_4\text{CdV}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$; *b*) compound dried at 60°C.

Table 1 Interplanar distances of the decomposition products of ammonium cadmium decavanadate in nm

Product obtained at t , °C		240		350		550		$(\text{NH}_4)_2\text{V}_6\text{O}_{16}$		$\text{V}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$		$\alpha\text{-Cd}(\text{VO}_3)_2$		$\beta\text{-Cd}(\text{VO}_3)_2$	
d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}
0.889	60							0.787	100						
0.787	85	0.787	30	0.681	20	0.649	<10					0.680	30	0.648	10
0.635	10	0.679	<10	0.573	35	0.573	30	0.573	95	0.570	35				
0.576	80	0.575	15					0.500	10						
0.501	15			0.474	10							0.476	10		
						0.448	60							0.448	65
		0.441	25	0.444	100							0.444	100		
		0.437	25	0.439	100	0.439	100			0.438	100			0.436	10
				0.410	35	0.410	20			0.409	15				
0.391	15							0.391	20						
0.355	35	0.354	25					0.354	80						
		0.351	15	0.352	35							0.352	70		
0.346	30	0.338	25	0.340	100	0.340	75			0.339	85			0.330	60
0.326	60					0.330	50							0.324	100
0.322	100	0.322	30			0.324	100			0.322	100			0.315	55
		0.313	15	0.315	30	0.311	50							0.311	55
0.301	50														
0.290	75	0.292	20	0.293	40			0.290	90			0.293	35		
0.286	35	0.287	<10	0.287	60	0.288	40			0.286	45	0.287	55		
						0.278	30							0.278	35
				0.276	30	0.276	20								
				0.268	10	0.269	<10								
				0.261	30	0.261	10								
				0.251	10										
0.253	15											0.251	20		
0.251	15					0.249	10							0.249	10
0.249	15							0.249	20						
0.245	10					0.245	15								
0.239	25	0.238	10	0.238	30			0.239	15						
		0.227	10	0.227	15	0.234	20					0.238	40	0.234	25
						0.224	10					0.227	25	0.224	10
												0.221	10		

Table 1 (Continued)

	0.213	10	0.217	15		0.213	10	0.216	15
	0.199	10	0.199	<10		0.199	10		
	0.196	<10	0.195	10				0.195	10
			0.193	20				0.193	30
	0.192	20	0.192	10		0.192	15		
	0.186	<10	0.186	<10		0.186	10		
	0.180	15						0.180	15
0.179	25	0.180	25	0.178	15	0.180	10	0.178	10
		0.164	10	0.165	<10			0.165	10
0.155	10	0.156	10	0.156	10	0.154	15	0.156	<10
									0.156
									10

Table 2 Wavenumbers of ammonium cadmium decavanadate and of the products of its decomposition in cm^{-1}

$(\text{NH}_4)_4\text{CdV}_{10}\text{O}_{28} \cdot 14\text{H}_2\text{O}$	Product obtained at $t, ^\circ\text{C}$					$\alpha\text{-Cd}(\text{VO}_3)_2$ [11]	$\beta\text{-Cd}(\text{VO}_3)_2$ [11]
	90	240	350	550			
415 m	420 s				420 s		
460 m	465 s	480 w	480 vs	480 s	465 s		
525 s	535 vs		570—600 vs	525—535 s	535 vs	565—585 vs	540—550 vs
595 s	550—605 vs	560—615 vs		620—645 vs	605 s	590 m	590—595 s
		685—700 s					
755 s	725—760 vs				724 s		
					780 w		
815 s							
840 s	870 m	825—850 s	820—850 s	825—850 s		820 vs	850 vs
932 s	904 m						
952 vs	942 m	955 w	952 m				960 m
	962 vs	967 m					
	1007 m	1007 w					
		1020 m	1020 m	1020 m		1020 m	

s — strong, vs — very strong, m — medium, w — weak.

of this mixture. Cadmium polyvanadate is another component of the mixture. However, it is not metavanadate as it was originally assumed. This means that the decomposition of ammonium cadmium decavanadate is not analogous with the decomposition of potassium cadmium decavanadate or cesium zinc decavanadate. In this case the substance contains crystal water still at 90°C. It is known from the study of the hydrate of cadmium metavanadate [7] that this substance dehydrates already at 60°C. Therefore, the formation of hydrate can be left out of consideration and an anhydrous salt has not been identified, either. The presence of water in the substance investigated enables us to assume that cadmium hexavanadate is another product of the decomposition of ammonium cadmium decavanadate. This assumption is based on the fact that the hydrate of calcium hexavanadate does exist [2] and that there is a certain analogy between calcium and cadmium polyvanadates because the radii and charges of calcium cation and cadmium cation are alike. Therefore it may be assumed that the existence of hydrate of cadmium hexavanadate is also well-founded. This assumption is, to a certain degree, also confirmed by the character of decomposition of the intermediate at higher temperatures. At 240°C, it is already possible to identify anhydrous cadmium metavanadate in the mixture. This compound might arise by the decomposition of dehydrated cadmium hexavanadate. This is in agreement with the statement that the hexavanadates of some bivalent metals are stable merely in the form of hydrates and decompose after the loss of water to yield vanadium(V) oxide and the corresponding metavanadate [12].

In the temperature interval from 240 to 300°C ammonium hexavanadate decomposes, too. The weight loss of 24.45% found is lower than it would correspond to a full decomposition of this hexavanadate under the formation of vanadium(V) oxide which might indicate the formation of ammonia-vanadium bronzes (tetravalent vanadium detected by the e.p.r. method). Such a step-wise course of the decomposition of ammonium hexavanadate is also described in [13].

During heating the substance to 350°C its weight decreases at first continuously (maximum loss 25.87%) and afterwards it rises slightly (final loss 25.12%). This phenomenon may be explained by a partial reduction of vanadium by ammonia which is liberated during the decomposition of vanadium bronze. By a prolonged ignition vanadium is oxidized again, but not to a full extent as it is obvious from the reduced content of vanadium(V) (by 1.31% at 350°C and by 0.99% at 550°C) and the presence of vanadium(IV) detected by the e.p.r. method. Vanadium in the oxidation state (IV) is present in the mixture already at 90°C. Its full oxidation is not achieved even above 500°C when the α -modification of cadmium metavanadate is transformed into the β -modification.

The decomposition of ammonium cadmium decavanadate in a stream of oxygen is analogous with the decomposition in a vacuum apparatus, the only difference being in a lower content of vanadium(IV) in the mixture. In this case the decomposition is slower and the compounds formed diffract better.

In the thermal decomposition of ammonium salts the heating program is of a great importance because some intermediates were not identified at all at a rapid temperature rise.

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