Influence of temperature, vanadium concentration, and degree of solution acidification on composition of the solid products
X. Products of the reactions taking place in acidified solutions of manganese(II) metavanadate

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The influence of temperature, vanadium concentration, degree of solution acidification, and reaction time on composition of the solid polyvanadates arising from the system $Mn(VO_3)_2$—HNO_3—H_2O was studied. Besides some products of varying composition, a compound of the composition $Mn(HV_6O_{16})_2 \cdot 14H_2O$ was obtained from the system. It results from the study of thermal properties of this substance that the process of water liberation is of gradual character and the full dehydration is succeeded by a decomposition of original structure yielding V_2O_5 and $Mn(VO_3)_2$.

Изучено влияние температуры, концентрации ванадия, степени насыщенности раствора кислородом и времени протекания реакции на состав твердых поливанадатов, образующихся в реакционной системе $Mn(VO_3)_2$—HNO_3—H_2O. В изучаемой системе кроме продуктов переменного состава было получено соединение состава $Mn(HV_6O_{16})_2 \cdot 14H_2O$. На основании изучения термических свойств этого соединения установлено, что процесс отщепления воды происходит постепенно, и после полной дегидратации наступает разложение исходного соединения с образованием V_2O_5 и $Mn(VO_3)_2$.

The formation of solid polyvanadates from acidified solutions is affected by many factors. Besides temperature, vanadium concentration, and degree of solution acidification, the reaction time and solubility of vanadates of the investigated cation in a given heterogeneous system also play an important part [1—6]. It is easier to investigate these factors in three-component systems metavanadate—acid—water [7—12] because the presence of single cation eliminates the possibility of formation of binary vanadates or mixture of vanadates with two different cations. The influence of vanadium concentration and degree of acidification in moderately acid solutions of the four-component system (sodium, potassium, lithium metavanadate—manganese(II) salt—acid—water) at 22 °C on the composition of solid vanadates was studied by *Zolotavin et al.* [13, 14]. The influence of temperature on the composition of solid manganese(II) polyvanadates arising from the strongly acidified solutions has not yet been investigated.

This paper deals with the influence of temperature, vanadium concentration, and degree of solution acidification on the composition of solid products formed in more acidic solutions of manganese(II) metavanadate.

Experimental

Manganese(II) metavanadate was prepared by the crystallization from the $(CH_3COO)_2Mn$—CH_3COOH—$NaVO_3$—H_2O system according to [15]. Its composition corresponded to the formula $Mn(VO_3)_2 \cdot 4H_2O$. Other chemicals were anal. grade reagents of Czechoslovak production.

Vanadium(V) was estimated volumetrically with the solution of $FeSO_4$ ($c = 0.1$ mol dm^{-3}) by using diphenylamine as indicator [16]. Manganese was determined chelatometrically with complexone III ($c = 0.01$ mol dm^{-3}) by using Eriochrome Black T as indicator. This determination was carried out in alkaline medium in the presence of ascorbic acid and tris(hydroxyethyl)amine [17].

The infrared spectra were taken on an instrument Perkin—Elmer 598 or Specord 71 (Zeiss, Jena) by using the technique of nujol suspension. The powder diffraction patterns were obtained on a diffractograph Philips PW 1050 by using the Cu$K\alpha$ radiation. The thermoanalytical curves were recorded on a derivatograph Q 1500 D (MOM, Budapest) in air atmosphere, temperature interval 20 °C—1000 °C. The weighed amounts varied in the range 150—200 mg and the rate of heating was 10 °C min^{-1}.

The reactions in the $Mn(VO_3)_2$—HNO_3—H_2O system took place at 40 °C, 60 °C, and 80 °C. The concentrations of vanadium in the reaction system were $c(V) = 0.01$ mol dm^{-3} and 0.02 mol dm^{-3}. The reaction time was 24 h and 120 h.

Preparation of the reaction solution

$Mn(VO_3)_2 \cdot 4H_2O$ which was poorly soluble in water was dissolved in dilute H_2O_2 ($V(H_2O_2) : V(H_2O) = 1:20$). Such quantity of HNO_3 ($c = 1$ mol dm^{-3}) was added that the necessary degree of acidification ($Z = n(HNO_3)/n(V)$: 0.6; 0.7; 0.8; 1.0; 2.0; 3.0) was attained. The peroxidic bond of the formed intermediate was eliminated by boiling. The solution was warmed to a given temperature and its volume was so filled up that a chosen concentration of vanadium was attained. The temperature and volume were held constant during the reaction and the reaction solution was stirred. The reaction product was always of dark-brown colour. In some cases, the precipitate started to appear as soon as in 15 min, another time as late as after a few days. Sometimes, no precipitate formed in the solution even after five days (Table 1). The product obtained was washed with ice-cold water, dried in air at laboratory temperature and characterized by chemical analysis, X-ray diffraction pattern and infrared spectroscopy.

Table 1

Results of syntheses in the $Mn(VO_3)_2$—HNO_3—H_2O system

θ	Z	$c(V) = 0.02\ mol\ dm^{-3}$		$c(V) = 0.01\ mol\ dm^{-3}$	
		$t = 24$ h	$t = 120$ h	$t = 24$ h	$t = 120$ h
80 °C	0.6	+	H, M	–	+
	0.7	+	P^1	–	P^1
	0.8	P^1	P^1	+	P^1
	1.0	HH	P^1	P^1	P^1
	2.0	HH	HH	P^1	P^1
	3.0	HH	P^1	P^2	P^2
60 °C	0.6	–	+	–	–
	0.7	+	P^1	–	+
	0.8	P^1	P^1	+	P^1
	1.0	HH	HH	P^1	P^1
	2.0	P^1	HH	P^2	P^1
	3.0	HH	HH	P^2	P^2
40 °C	0.6	–	–	–	–
	0.7	–	+	–	–
	0.8	–	P^1	–	–
	1.0	–	P^1	–	+
	2.0	P^1	P^2	–	HH
	3.0	P^1	HH	–	HH

– Product is not formed; + small yield; HH $Mn(HV_6O_{16})_2 \cdot 14H_2O$; P^1 product with $n(Mn):n(V) > 0.52:6$; P^2 product with $n(Mn):n(V) < 0.48:6$; M $Mn(VO_3)_2 \cdot 4H_2O$; H probably $MnV_6O_{16} \cdot nH_2O$.

Results and discussion

Only one compound of constant composition $Mn(HV_6O_{16})_2 \cdot 14H_2O$ was obtained in all syntheses (Table 1). The mass fractions calculated for $Mn(HV_6O_{16})_2 \cdot 14H_2O$ are w_i(calc.): 3.85 % Mn, 42.68 % V, 17.61 % H_2O while the corresponding experimental values are w_i(found): 3.84 % Mn, 42.97 % V, 17.50 % H_2O. This formula has been derived not only on the basis of chemical analysis but also on the basis of infrared spectra, X-ray diffraction patterns, and thermal properties. The hydrogen hexavanadates hitherto prepared $M^IHV_6O_{16} \cdot nH_2O$ [8, 10, 12] and $M^{II}(HV_6O_{16})_2 \cdot nH_2O$ [7, 9, 11] ($M^I = Na$, NH_4^+, Rb; M^{II} = Ca, Sr, Ba) exhibit characteristic infrared spectra. The absorption band at $\tilde{\nu} = 920\ \mathrm{cm}^{-1}$ corresponding to bending vibrations δ(V—O—H) is characteristic of the $HV_6O_{16}^-$ anion [9—12, 18]. The prepared compound was formulated as hydrogen hexavanadate primarily on the basis of analogy of infrared spectra.

The formation of $Mn(HV_6O_{16})_2 \cdot 14H_2O$ is favoured by higher concentration of vanadium in the solution ($c(V) = 0.02\ \mathrm{mol\ dm}^{-3}$) and a shorter reaction time is sufficient at 80 °C (24 h) while a longer reaction time is necessary at 60 °C (5 days).

An intensive maximum at $\tilde{\nu} = 1000\ \mathrm{cm}^{-1}$ exhibiting a shoulder in the region of lower wavenumbers appears in the spectrum of $Mn(HV_6O_{16})_2 \cdot 14H_2O$ (Fig. 1*a*). Its position was exactly determined by graphical separation ($\tilde{\nu} = 955\ \mathrm{cm}^{-1}$). Both maxima belong to stretching vibrations of the V—O bonds (ν(V—O)). The absorption band at $\tilde{\nu} = 920\ \mathrm{cm}^{-1}$ corresponds to the bending vibrations δ(V—O——H). Moreover, a broad maximum in the region $\tilde{\nu} = 720\ \mathrm{cm}^{-1}$ distorted by the absorption band of nujol) exhibiting a shoulder in the region $\tilde{\nu} = 840\ \mathrm{cm}^{-1}$ and $670\ \mathrm{cm}^{-1}$ appears in the infrared spectrum. These maxima may correspond to the symmetrical and antisymmetrical vibrations ν(V—O—V). The broad band at $\tilde{\nu} = 480\ \mathrm{cm}^{-1}$ belongs to the bending vibrations δ(V—O) and δ(V—O—V). As for the region of the stretching vibrations ν(O—H), there is a little distinct broad absorption band in the region $\tilde{\nu} = 3200—3500\ \mathrm{cm}^{-1}$. The bending vibrations δ(H—O—H) with the maximum at $\tilde{\nu} = 1595\ \mathrm{cm}^{-1}$ are also little distinct. The X-ray powder diffraction pattern of $Mn(HV_6O_{16})_2 \cdot 14H_2O$ also indicates an X-ray-amorphous substance. The diffractions are broad non-sharp and only the following maxima can be distinguished

d/nm	0.671	0.452	0.346	0.328	0.298	0.258	0.191	0.179
I_{rel}	15	20	100	45	20	28	28	60

A compound of similar composition was prepared by *Ivakin et al.* [19, 20] by ion-exchange reaction of solid hydrated V_2O_5 with solutions of manganese(II) salts at 22 °C. The authors formulate this compound as dodecavanadate of the composition $MnV_{12}O_{31} \cdot 12H_2O$. The infrared spectrum of this substance is different from the infrared spectrum of our substance. Likewise, the thermal properties of the discussed compounds are different.

Other substances forming in the reaction system were not of constant composition. The ratio $n(Mn)/n(V)$ of these substances varied according to the degree of acidification of the solution they arose from. For substance P^1, it holds $n(Mn):n(V) > 0.52:6$ (the highest value 0.78:6) whereas it is valid $n(Mn):n(V) < 0.48:6$ (the lowest value 0.41:6) for substance P^2. The infrared spectrum of substance P^1 differs from the infrared spectrum of manganese(II) hydrogen hexavanadate in the region of stretching vibrations ν(V—O)

($\tilde{\nu}=950$—$1020\ \mathrm{cm}^{-1}$). A shoulder the intensity of which increases with increasing ratio $n(\mathrm{Mn}):n(\mathrm{V})$ appears in the region of lower wavenumbers for the absorption band at $\tilde{\nu}=1000\ \mathrm{cm}^{-1}$. The couple of absorption bands in this spectral region is characteristic of hexavanadates [7—12]. The substance P^1 is likely to be a mixture of manganese(II) hexavanadate and hydrogen hexavanadate while the predominating component is hydrogen hexavanadate. Substance P^2 resembles hydrogen hexavanadate by its $n(\mathrm{Mn}):n(\mathrm{V})$ ratio, infrared spectrum and X-ray diffraction pattern. In this case, the base component is also $\mathrm{Mn(HV_6O_{16})_2\cdot 14H_2O}$. Some substances of similar composition formed in the $\mathrm{Sr(VO_3)_2}$—$\mathrm{HClO_4}$—$\mathrm{H_2O}$ reaction system, too [9].

However, a substance of different character was prepared under the following conditions: 80 °C, $c(\mathrm{V}) = 0.02\ \mathrm{mol\ dm^{-3}}$, $Z = 0.6$, and reaction time 5 days. According to its infrared spectrum, it could be hexavanadate [7—9, 11]. It resulted from the X-ray diffraction pattern that this substance contained a small amount of $\mathrm{Mn(VO_3)_2\cdot 4H_2O}$. In order to obtain this substance in pure state, we carried out a great number of syntheses by varying concentration and reaction time at 80 °C and $Z=0.6$. The discussed substance always came into existence in a mixture with manganese(II) metavanadate.

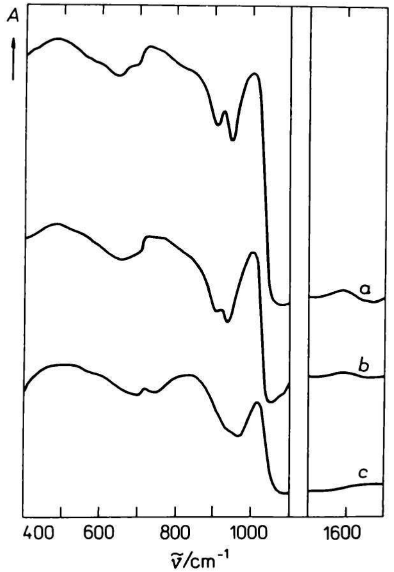

Fig. 1. Infrared spectra.
a) $\mathrm{Mn(HV_6O_{16})_2\cdot 14H_2O}$; *b)* product obtained from $\mathrm{Mn(HV_6O_{16})_2\cdot 14H_2O}$ after interruption of DTA at 275 °C; *c)* product of decomposition after heating to 965 °C.

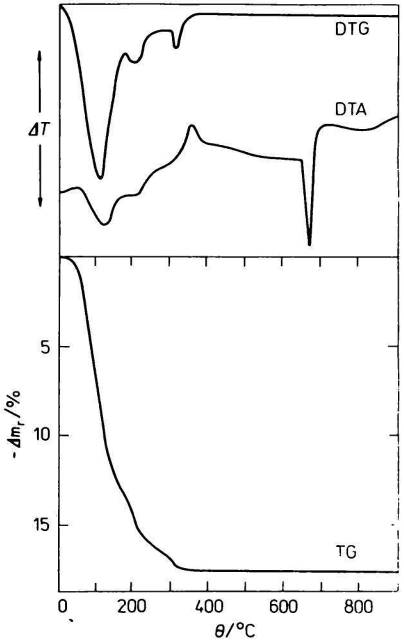

Fig. 2. Thermoanalytical curves of $\mathrm{Mn(HV_6O_{16})_2\cdot 14H_2O}$.

Table 2

Products of thermal decomposition of $Mn(HV_6O_{16})_2 \cdot 14H_2O$

Product of thermal decomposition of $Mn(HV_6O_{16})_2$ at 965 °C		V_2O_5 [21]			$Mn(VO_3)_2$ [15]	
d/nm	I_{rel}	*d*/nm	I_{rel}	*hkl*	*d*/nm	I_{rel}
0.6189	1.8				0.620	7.5
0.5719	21.5	0.576	40	200		
0.4375	100.0	0.438	100	001	0.441	20.7
0.4073	37.8	0.409	35	101		
0.3477	4.9	0.248	8	201		
0.3398	18.7	0.340	90	110		
0.3266	4.2				0.3264	6.8
0.3155	18.7				0.313	100.0
0.3081	2.2				0.308	6.4
0.3027	17.0				0.3025	50.0
0.2878	70.0	0.288	65	400		
0.2755	9.7	0.276	35	011		
0.2736	6.7				0.2735	7.9
0.2684	3.8	0.2687	16	111		
0.2608	8.0	0.2610	40	310		
0.2440	0.5				0.2438	1.9
0.2400	4.2	0.2405	8	401		
0.2322	4.6				0.2324	14.3
0.2184	31.9	0.2185	18	002	0.2205	12.5
0.2146	16.5	0.2147	12	102	0.2149	5.6
0.2077	4.8				0.2074	17.7
0.1991	5.1	0.1992	18	411		
0.1916	24.7	0.1919	25	600	0.1916	3.4
0.1898	22.7	0.1900	18	302	0.1898	20.7
0.1863	5.4	0.1864	14	012		
0.1779	5.7	0.1778	4	020		
0.1757	10.2	0.1757	30	601	0.1762	3.2
0.1742	2.6	0.1740	14	402		
0.1685	2.1				0.1684	6.4
0.1650	3.7	0.1648	12	021	0.1645	4.2
0.1634	2.1	0.1632	8	121		
0.1597	0.8				0.1596	2.0
0.1571	2.2	0.1576	10	611	0.1578	2.3
0.1555	4.6	0.1564	12	412		
0.1537	2.6	0.1540	4	701	0.1541	8.4

Thermal properties of $Mn(HV_6O_{16})_2 \cdot 14H_2O$

The thermoanalytical curves of $Mn(HV_6O_{16})_2 \cdot 14H_2O$ (Fig. 2) show that the dehydration proceeds in three steps. The total relative mass decrease $-\Delta m_r$ is 17.5 % ($-\Delta m_r$(theor) = 17.6 %). In the first step, *i.e.* up to 185 °C ($-\Delta m_r = 14$ %), 12 moles of water are released. However, we did not observe any conspicuous change in the infrared spectrum and X-ray diffraction pattern obtained after cooling this sample to laboratory temperature.

In the second step of dehydration, *i.e.* up to 275 °C ($-\Delta m_r = 2.5$ %), another two moles of water are released. The absorption bands δ(H—O—H) at $\tilde{\nu} = 1595\ \text{cm}^{-1}$ and δ(V—O—H) at $\tilde{\nu} = 920\ \text{cm}^{-1}$ remain preserved in the infrared spectrum (Fig. 1*b*). The absorption band ν(V—O) at $\tilde{\nu} = 955\ \text{cm}^{-1}$ present with the original substance is shifted to $\tilde{\nu} = 972\ \text{cm}^{-1}$ (obtained by graphical separation). This change may be due to the shortening of internuclear distances in the bond vanadium—terminal oxygen appearing after the decay of hydrogen bonds. The character of the compound does not change as long as the last mole of water is not released in the third step (up to 340 °C, $-\Delta m_r = 1$ %). That stoichiometrically corresponds to the water firmly built in the structure of the compound. After liberation of this water, an exothermic maximum is to be observed on the DTA curve before 390 °C. This maximum is caused by the decomposition of original structure and formation of new substances. The X-ray diffraction pattern is changed considerably. The X-ray phase analysis has shown that the substances obtained by interruption of heating at 395 °C and 595 °C are mixtures of V_2O_5 and $Mn(VO_3)_2$ (Table 2). All maxima corresponding to vibrations of the OH groups have disappeared in the infrared spectrum (Fig. 1*c*). An absorption maximum ν(V—O) at $\tilde{\nu} = 978\ \text{cm}^{-1}$ with a shoulder in the region of higher wavenumbers appears in the infrared spectrum. The graphical separation has shown that this shoulder belongs to the maximum at $\tilde{\nu} = 1020\ \text{cm}^{-1}$ which is typical of ν(V—O) in V_2O_5.

The conspicuous endothermic deflection with the minimum at 662 °C on the DTA curve corresponds to melting of V_2O_5 while the little distinct deflection approximately at 800 °C is produced by melting of $Mn(VO_3)_2$. The substance which has crystallized from the melt is also a mixture of $Mn(VO_3)_2$ and V_2O_5 (Table 2, Fig. 1*c*).

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