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THERMAL REACTIVITY AND ^{1}H NMR SPECTROSCOPY OF $Sr_{1-x}H_{2x}V_6O_{16} \cdot aq$

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The results of study of the thermal reactivity and ^{1}H NMR spectroscopy of solid polyvanadates of general formula $Sr_{1-x}H_{2x}V_6O_{16} \cdot aq$ are presented. Compounds with $x = 0$ (a), $x \in (0.3–0.6)$ (b) and $x = 1$ (c) were studied. The protons are bonded in V – OH (b, c) and V – O . . . H (a, b, c) groups, in H_2O molecules (a, b, c) and in $H_2O \ldots H_2O$ systems (a, b, c). Dehydration of the studied compounds proceeds stepwise. Total dehydration causes decomposition of the original structures and $Sr(VO_3)_2$, $SrV_{12}O_{30}$ and V_2O_5 are formed. The results confirm the role of crystal water in stabilizing the structures of the studied compounds.

In acidic aqueous solutions of vanadates, either decavanadates or (at higher temperatures) other polymeric compounds of vanadium(V) are formed, the natures of which remain uncertain. The results of X-ray structure analysis of the potassium and cesium salts [1, 2] showed that for large univalent cations anhydrous hexavanadates with layer structures are formed. The polyvanadates of small univalent and bivalent cations formed under given conditions contain crystal water [3–5]. In paper [3], these compounds were classified as hexavanadates and dodecavanadates. However, the results of studies of hydrated sodium and calcium polyvanadates and polyvanadic acid [4, 5] are not in agreement with this classification. It seems that the charge and cation radius are the main factors determining whether water molecules are present in the crystal structure of the discussed polyvanadates or not. The large univalent cations (K^+, Rb^+, Cs^+, Tl^+, NH_4^+) form anhydrous hexavanadates, while other univalent and bivalent cations form only crystallohydrates of polyvanadates.

This paper deals with a study of the thermal reactivity and ^{1}H NMR spectroscopy of hydrated strontium polyvanadates and polyvanadic acid prepared from acidic solutions.

Experimental

The methods of preparation and identification of the studied compounds were published in [7, 10]. Hydrated hexavanadic acid was prepared by drying the gels obtained according to [6]. The presence of V – OH groups in this compound was proved by IR spectroscopy [10].

The thermal curves of the studied compounds were obtained on an OD 102 derivatograph (MOM, Budapest) in air atmosphere, in the 20–600° temperature range; heating rate 5 degree/min; weighted amounts 150 or 300 mg.

The natures of the endo- and exothermic effects observed in the DTA curves were studied by using two independent methods of identification (IR spectroscopy and X-ray qualitative phase analysis) of the compounds obtained when thermal decomposition was interrupted at the temperatures corresponding to the observed effects. The products were identified after being cooled down to room temperature.

To confirm the results of the study of thermal behaviour, the compounds were also heated isothermally in the range 50–300° (10° intervals). The samples were heated to constant weight, and the compounds formed were cooled and identified by the methods mentioned above.

The IR spectra were measured with a Perkin–Elmer PE 180 spectrophotometer, and the powder diffraction patterns were obtained on a Philips diffractometer with a PW 1058 goniometer, using $Cu_{K\alpha}$ radiation.

The broad-line ^{1}H NMR spectra of the studied compounds were taken on a Jeol JNM-PW-40-3X instrument within the temperature range from – 135° up to 25°; the temperature was held constant within ±1°. The powdered samples were placed in 18 mm OD tubes. Further conditions (first for spectra taken at temperatures below – 115°, second for spectra taken at temperatures above – 115°: range (gs) = = 100, 0.5–10; modulation (gs) = 0.8–1.25, 0.02–0.25; scanning speed (gs s^{-1}) = = 6.25–12.5, 0.065–1.25; time constant (s) = 3, 1 or 3.

Results and discussion

$SrV_6O_{16} \cdot aq$ (a) and $Sr_{1-x}H_{2x}V_6O_{16} \cdot aq$ (where $x \in (0.3–0.6)$) (b) are partly dehydrated on dynamic heating up to 270° and on isothermal heating to 170°. It follows from thermal curves (Fig. a) that in compound (a) the water molecules are bonded in two different manners having relatively similar bond energies. The IR spectra (Table 1) show that the dehydration of compound (a) under dynamic conditions is completed at 300°, while isothermally it is finished at 250°. The dehydration of compound (b) proceeds in three steps (Fig. b). The first two are analogous to those observed in compound (a). The third step, corresponding to the irreversible release of water bonded in the form of OH groups from the compound, is finished at 350° for dynamic heating, or at 280° under isothermal conditions (Fig. b, Table 1). The presence of V – OH groups in compound (b) was also proved by IR spectroscopy [7].

Table 1 Absorption bands (cm^{-1}) in IR spectra of $Sr_{1-x}H_{2x}V_6O_{16} \cdot aq$ compounds during the thermal reactions; if $x = 0$ (a), $x \in (0.3–0.6)$ (b), $x = 1$ (c)

a			b			c	
20–150°C	200–300°C	400°C	20–150°C	250–350°C	400°C	20–150°C	300°C
540 vs	545 vs	540–555 s M	525 vs	525 vs	530 m M	500–520 m	
		585 m O			585 m O		580 w O
			685 sh	680 sh			
	725 w O	720 w O			720 m O		725 s O
735–755 m	745–755 m		750–775 vs	740–775 vs		770 vs	
	825 sh O	825 m O		820 sh O	820 m O		820 vs O
		845 s M			840 w M		
	890 sh M	890 s M			890 m M		
			920 m	920 vw		925 m	
		930 m M,B			930 w M,B		
		950 vs M			950 m M		
965 vs	970 vs			970 sh		975 sh	
		985 vs M,B		985 w M,B	985 s M,B		
1000 s	1005 s B?	1005 sh B	1010 vs	1005 vs B?	1005 sh B	1010 vs	
		1020 sh O			1020 m O		1020 vs O
1620 m	1620 vw		1620 m	1620 vw		1620 m	

no sign – band of original compound, O – V_2O_5, M – $Sr(VO_3)_2$, B – $SrV_{12}O_{30}$
intensities: vs – very strong, s – strong, m – middle, w – weak, vw – very weak, sh – shoulder

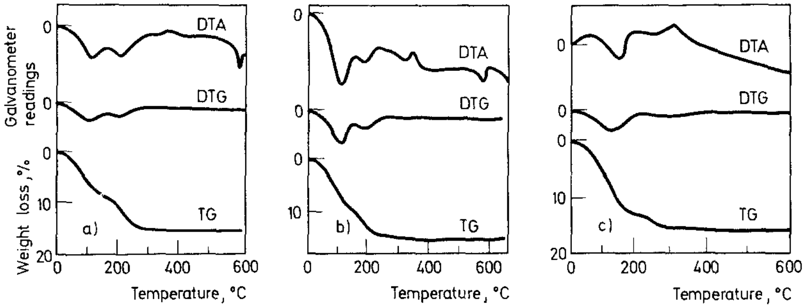

Fig. 1 Thermoanalytical curves of polyvanadates

From the IR spectra of almost completely dehydrated compounds (a) and (b) it follows that during the release of the last water molecules their structural decomposition simultaneously begins (Table 1). In samples isothermally heated above 280° and at temperatures, higher than 40, when all the exothermic processes observed in the DTA curves are finished, $Sr(VO_3)_2$, $SrV_{12}O_{30}$ and V_2O_5 were unambiguously identified as final products of decomposition (Tables 1, 2). The formation of anhydrous hexavanadates was not observed. The small weight loss up to these temperatures (Figs a, b) is caused by release of oxygen in the partial reduction of V(V) to V(IV) during the formation of $SrV_{12}O_{30}$.

The dehydration of $H_2V_6O_{16} \cdot aq$ proceeds in two steps (Fig. c) and is completed by the loss of water molecules bonded in the form of OH groups at 280° (dynamic heating) or at 230° (isothermal heating). The exo effect with maximum at 300° in the DTA curve corresponds to structural decomposition of hexavanadic acid and V_2O_5 formation, which was identified by its IR spectrum and powder diffraction pattern (Tables 1, 2).

The broad-line ^{1}H NMR spectra of the studied compounds were treated by methods described in [11]. Within the temperature range from 25 to − 110°, the "structureless lines of protons" were observed, $\delta_H \in (0.1\text{–}0.7\ \text{gs})$, similarly as by other authors [4]. The results of broad-line ^{1}H NMR spectroscopy of $Sr_{1-x}H_{2x}V_6O_{16} \cdot aq$ (where $x \in \langle 0; 1 \rangle$) and those partly dehydrated within the temperature range from − 115 to − 135° helped to explain the role of water in these compounds. The relation of the ^{1}H NMR data to the manners of proton incorporation in $Sr_{1-x}H_{2x}V_6O_{16} \cdot aq$ (where $x \in \langle 0; 1 \rangle$) are presented in Table 3.

The line shapes of the original samples indicate a qualitative similarity of the proton incorporations in the studied compounds. Comparison of the values of the individual linewidths with data in papers [4, 8, 9] shows that in the structures of the studied compounds the protons are incorporated in several manners (Table 3). From the agreement of the second moment values (24.7–30.5 gs^2) with those published in papers [8, 9], it can be presumed that a predominant proportion of the protons are

Table 2 Interplanar distances (nm) of final products of thermal reactions of $Sr_{1-x}H_{2x}V_6O_{16} \cdot aq$ compounds, where $x = 0$ (a), $x \in (0.3–0.6)$ (b), $x = 1$ (c)

a		b		c	
0.599	O	0.574	O	0.571	O
0.462	B	0.467	B		
0.448	B	0.453	B		
0.439	B	0.438	B		
0.435	O	0.427	B,O	0.435	O
0.420	B				
0.410	O	0.408	O	0.407	O
0.390	M,B	0.387	M,B		
0.374	B	0.380	B		
0.355	M,B	0.353	M,B		
0.344	B,O	0.346	B,O	0.339	O
0.332	M,O	0.335	M,O		
0.326	M	0.327	M		
0.319	M,B	0.319	M,B		
0.299	B,O	0.303	B,O	0.296	O
0.285	M,O,B	0.289	B		
		0.280	M,O	0.275	O
0.269	M,O	0.270	M,O	0.267	O
0.263	O	0.261	O	0.261	O
0.255	M	0.256	M		
0.245	M	0.244	M		
0.225	M	0.225	M		
0.221	B				
0.220	M	0.220	M,O,B		
0.219	O			0.218	O
0.213	M,O	0.215	O	0.214	O
		0.209	M		
0.204	M	0.204	M		
0.193	M,B	0.197	M,B		
0.191	M,O	0.191	M,O	0.191	O
0.188	O	0.186	M,O	0.189	O
0.184	M				
0.181	M,B	0.180	M,B		
0.178	M,O	0.178	M,O	0.178	O

O – V_2O_5, M – $Sr(VO_3)_2$, B – $SrV_{12}O_{30}$

bonded in H_2O molecules and a smaller number are incorporated in the one-proton V – OH or V – O . . . H, and the four-proton H_2O . . . H_2O systems.

It follows from the study of the thermal reactivity and IR spectra that the original nature of the compounds remains unchanged during the first step of dehydration. In the broad-line ^{1}H NMR spectra of the partly dehydrated compounds (isothermally at 100°) there are no lines present with linewidths assigned to protons in hydrogen-bonds

Table 3 Relations of linewidths – δ_H(gs) – in NMR ^{1}H spectra of $Sr_{1-x}H_{2x}V_6O_{16} \cdot aq$ compounds to manners of proton incorporation if $x = 0$ (a), $x \in (0.3–0.6)$ (b), $x = 1$ (c)

	$Sr_{1-x}H_{2x}V_6O_{16} \cdot aq$, $x \in \langle 0; 1 \rangle$		
δ_H(gs)	a	b	c
1.5–2.5	V – O . . . H *	V – OH V – O . . . H *	V – OH V – O . . . H *
12.1–13.6	HOH	HOH	HOH
20.3–21.7 *	HOH * : HOH	HOH * : HOH	HOH * : HOH

* are not present in partly dehydrated compounds

(* in Table 3). Only lines with linewidths assigned to proton incorporations in H_2O molecules and V – OH groups were observed (Table 3). The second moments of the spectra of the partly dehydrated samples are decreased (20.4–22.7 gs^2). These facts allow the conclusion that hydrogen-bonds are not present in the partly dehydrated compounds and the protons in the H_2O molecules and V – OH groups undergo no changes. The H_2O molecules and V – OH groups play the main role in stabilizing the structures of $Sr_{1-x}H_{2x}V_6O_{16} \cdot aq$ (where $x \in \langle 0; 1 \rangle$).

The obtained results confirm that all the studied compounds belong to the same type of polyvanadates: hydrated hexavanadates with layer structures [5, 7]. The dehydration of all the studied compounds proceeds in several steps. The process of water release in the first step is reversible and the original nature of the compounds is conserved in this step. It is not possible to prepare anhydrous hexavanadates by thermal decomposition, for the hexavanadates are decomposed before dehydration is finished. The crystal water, both as H_2O molecules and as OH groups, stabilizes the structures of the studied compounds.

We assume that the small ionic radius of the Sr^{2+} cation and its small amount (in compound (c) it is absent) with respect to the $V_6O_{16}^{2-}$ unit of hexavanadates can be compensated by the hydration of the cations and by the partial protonation of end-bonded oxygens in V – O layers. Such interactions can be regarded as a main factor in stabilizing the structures of hexavanadates with cations of small radius and low amount.

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Zusammenfassung — Die Ergebnisse einer ^{1}H-NMR-spektroskopischen Untersuchung der thermischen Reaktivität von festen Polyvanadaten der allgemeinen Formel $Sr_{1-x}H_{2x}V_6O_{16} \cdot H_2O$ werden dargelegt, bei denen $x = 0$ (a), $x = 0.3–0.6$ (b) and $x = 1$ (c) ist. Die Protonen sind in V – OH-Gruppen (b, c) und V – O . . . H-Gruppen (a, b, c), H_2O molekulen sowie in $H_2O \ldots H_2O$-Systemen (a, b, c) gebunden. Die Dehydratisierung der untersuchten Verbindungen erfolgt stufenweise. Vollständige Dehydratisierung führt zur Zersetzung der ursprünglichen Strukturen und zur Bildung von $Sr(VO_3)_2$, $SrV_{12}O_{30}$ und V_2O_5. Die Ergebnisse bestätigen die Rolle des Kristallwassers bei der Stabilisierung der Strukturen der untersuchten Verbindungen.

Резюме — Представлены резултаты исследования термической реакционной способности твердых поливанадатов общей формулы $Sr_{1-x}H_{2x}V_6O_{16}$ • вода и их ПМР спектроскопия. Были изучены соединения с $x = 0$ (а), $x = 0.3–0.6$ (б) и $x = 1$ (в). Протоны связаны в V—OH (группа соединений б, в) и V—O . . . H (соединения а, б, в), в молекулы H_2O (соединения а, б, в) и в системы $H_2O \ldots H_2O$ (соединения а, б, в). Дегидратация исследованных протекает ступенчато. Полная дегидратация вызывает разложение исходных вещуств с образованием $Sr(VO_3)_2$, $SrV_{12}O_{30}$ и V_2O_5. Результаты подтверждают роль кристаллизационной воды в стабилизации структур исследованных соединений.