Synthesis and Properties of Tripropylammonium Decavanadates

[a]Ľ. ŽÚRKOVÁ, [a]Š. ŠPAČEK, and [b]I. TKÁČ

[a]*Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, SK-842 15 Bratislava*

[b]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-842 36 Bratislava*

$[TPAH]_4H_2V_{10}O_{28} \cdot nH_2O$ (A) and $[TPAH]_3H_3V_{10}O_{28}$ (B) were prepared by dissolving of V_2O_5 in an aqueous solution of tripropylamine (TPA). The IR spectra of the hydrogendecavanadates prepared exhibit small differences in their metal-oxygen framework structures. In course of the thermal decomposition of A the anhydrous $[TPAH]_4H_2V_{10}O_{28}$ was formed at 100 °C.

It is known that voluminous, highly condensed decavanadate anions $H_nV_{10}O_{28}^{(6-n)-}$ (n = 0—3) are formed by ten VO_6 octahedra. All hydrogen atoms in these polyanions are supposed to be bonded to bridging oxygen atoms [1]. Various cations do not influence essentially the structure of this polyanion. A greater deformation of its structure can be expected on protonation of bridging oxygen atoms in $H_nV_{10}O_{28}^{(6-n)-}$.

All decavanadates with inorganic cations are crystallohydrates [2] or crystallosolvates [3], whereas decavanadates with organic cations are known also in the form of anhydrous compounds [4, 5]. Thus, the hydrogen bonds formation between crystal water molecules or organic cations and bulky anion has a stabilizing effect on the crystal structure of decavanadates.

A systematic study on the relation between properties of the various protonated decavanadates of the same cation was not yet performed. The aim of this work is the synthesis and the characterization of tripropylammonium hydrogendecavanadates.

EXPERIMENTAL

V_2O_5 was prepared by thermal decomposition of previously purified NH_4VO_3. All the other chemicals used were of anal. grade.

The elemental analysis was performed on CHN analyzer 1106 (Erba, Milan). The total content of vanadium w(V, total) was determined gravimetrically as V_2O_5.

The EPR spectra of some samples were measured with the Varian E-4 instrument at X-band frequency at room temperature.

pH was measured on a TTT-2 pH-meter (Radiometer) using GK 2401 C electrode or on Piccolo HI-1280 pH-meter (Hanna).

^{51}V NMR spectra of TPA—V_2O_5—H_2O solutions were measured on Bruker AM 300 spectrometer operating at the frequency of 78.94 MHz. Chemical shifts are referred to external neat $VOCl_3$. For the quantitative results the repetition time of 0.15 s was sufficiently long to avoid saturation, so up to 4000 scans were accumulated in 6 min.

The IR spectra in Nujol mulls or KBr pellets were measured on Specord M 80 spectrophotometer (Zeiss, Jena).

The X-ray powder diffraction patterns were registered on a Philips PW 1050 diffractometer using $CuK\alpha$ radiation. The thermal analysis was performed on a derivatograph Q-1500 (MOM); conditions: air atmosphere, sample mass 100 mg, heating rate 5 K min^{-1} resp. 2 K min^{-1}, Pt-crucible, Al_2O_3 reference material, temperature interval 20—700 °C. The thermal analysis of A was interrupted at $\theta/°C$ = 100, 210, 340, 545, and 620 and of B at $\theta/°C$ = 200, 340, 530, and 655. Individual products were cooled to room temperature and identified by chemical analysis, IR and EPR spectra, and X-ray phase analysis.

Tripropylammonium Decavanadates

The compounds mentioned above were prepared by dissolving V_2O_5 in the solution of tripropylamine (TPA) in water. The reaction mixtures were kept in dark and stirred at room temperature until all amount of V_2O_5 was dissolved (t_R — reaction time). For preparing of $[TPAH]_4H_2V_{10}O_{28} \cdot nH_2O$ (A) V_2O_5 (1.7 g; 9.35 mmol), TPA (4 cm³, 21 mmol), and H_2O (80 cm³) were used. The mole ratio of TPA to vanadium n(TPA) : n(V) = 1.15; t_R = 24 h. After dissolving of V_2O_5, the pH of the solution was adjusted to 6.0 by hydrochloric acid (c = 2 mol dm^{-3}). The orange solution was allowed to stand for 18 d at room temperature in dark. The lustrous orange crystals were

isolated. The pH_{obs} values of mother solution were in the range 4.5—4.6. The crystals were washed with ethanol and air-dried in dark.

For $[TPAH]_4H_2V_{10}O_{28} \cdot 2H_2O$ w_i(calc.): 32.39 % V, 27.49 % C, 3.56 % N, 6.03 % H; w_i(found): 32.36 % V, 27.67 % C, 3,46 % N, 5,99 % H. The interplanar distances and relative intensities for ten of the most intensive diffractions $(d/nm)/(I_{rel}/\%)$: 0.867/100, 0.737/42, 0.686/35, 0.608/35, 0.593/26, 0.540/16, 0.3917/24, 0.3278/16, 0.3078/31, 0.2066/16. IR spectrum, $\tilde{v}/cm^{-1}$ $(\Delta\tilde{v} = 400—1000\ cm^{-1})$: 985 vs, 970 vs, 950 vs, 870 sh, 825 vs, 760 vs, 725 vs, 670 sh, 590 s, 555 sh, 520 m, 500 w, 455 m, 440 m.

For preparing of $[TPAH]_3H_3V_{10}O_{28}$ (B) V_2O_5 (0.96 g; 5.28 mmol), TPA (1.5 cm³, 7.88 mmol), and H_2O (50 cm³) were used; n(TPA) : n(V) = 0.75; t_R = 30 h. During adjusting the pH of the solution to 2.2 by hydrochloric acid $(c = 2\ mol\ dm^{-3})$, yellow orange precipitate of B was formed. The precipitate was washed with ethanol and air-dried in dark.

For $[TPAH]_3H_3V_{10}O_{28}$ w_i(calc.): 36.56 % V, 23.27 % C, 3.01 % N, 4.99 % H; w_i(found): 36.50 % V, 23.11 % C, 3.01 % N, 4.94 % H. $(d/nm)/(I_{rel}/\%)$: 0.807/85, 0.787/86, 0.725/100, 0.661/63, 0.602/58, 0.591/45, 0.3232/28, 0.3052/27, 0.3022/27, 0.2990/ 33. IR spectrum, $\tilde{v}/cm^{-1}$ $(\Delta\tilde{v} = 400—1000\ cm^{-1})$: 990 vs, 977 vs, 940 s, 840 s, 807 s, 770 s, 723 m, 605 s, 555 m, 508 m, 492 sh, 470 sh, 448 m, 430 sh.

RESULTS AND DISCUSSION

The resonance signals in ^{51}V NMR spectra were unambiguously assigned to polyvanadates according to published chemical shift data of similar polyvanadate solutions [6, 7]. The composition of the $TPA—V_2O_5—H_2O$ system is predominantly influenced by the pH of the solution and total vanadium concentration $[c(V)]$, which is in accordance with the previous results [6, 7]. The presence of $TPAH^+$ cation does not influence the composition of polyvanadate solution. Chemical shifts of particular polyvanadate anions are pH-dependent only if the protonation of the anion takes place. Small change in pH from 6.5 to 6.8 brings about the significant change in the composition of polyvanadate solution. Concentration dependences of the relative amount of individual polyvanadate anions in solution are shown in Fig. 1. With the increase of $c(V)$ the content of $V_4O_{12}^{4-}$ and $V_5O_{15}^{5-}$ is increasing and the content of $H_nV_2O_7^{(4-n)-}$ and $H_nVO_4^{(3-n)-}$ is decreasing. The content of $H_nV_{10}O_{28}^{(6-n)-}$ does not depend on $c(V)$, but is pH-dependent.

It follows from the distribution diagram of polyvanadate ions in the $TPA—V_2O_5—H_2O$ system (Fig. 2) that pH ranging from 2 to 6 is most suitable for the preparation of TPA decavanadate compounds.

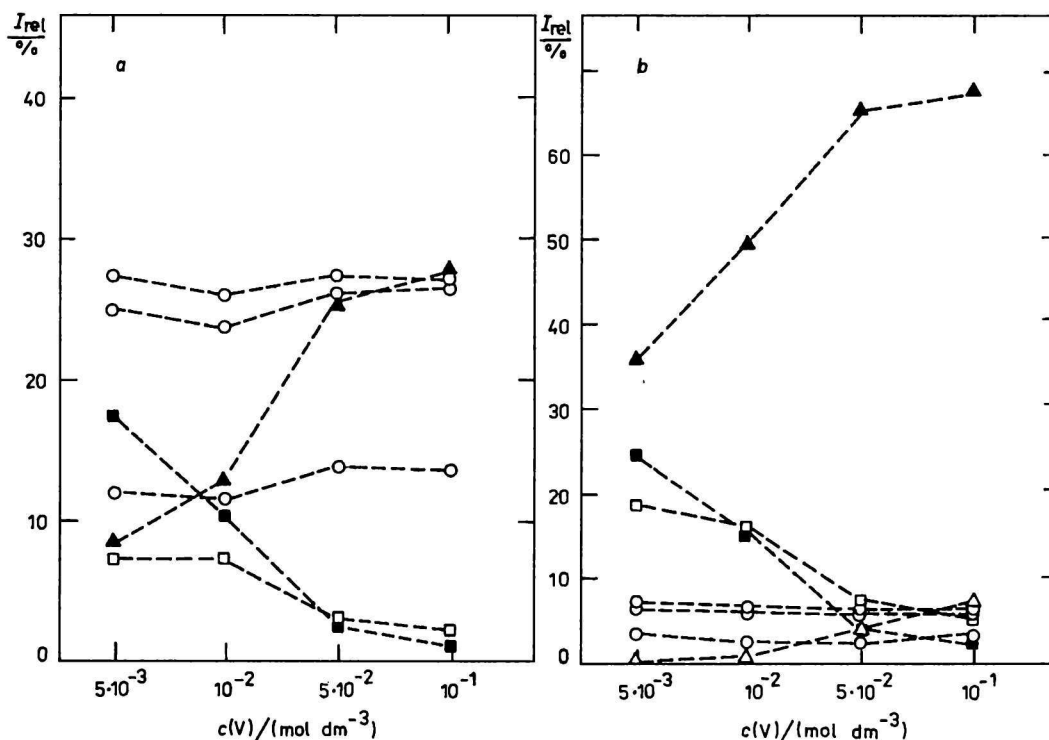Decavanadates prepared exhibit characteristic IR

Fig. 1. Dependence of I_{rel} on $c(V)$ in the $TPA—V_2O_5—H_2O$ system at various pH. I_{rel} is defined as the ratio between vanadium in species $c(V,\ species)$ and total vanadium $c(V)$. ○ $H_nV_{10}O_{28}^{(6-n)-}$, △ $V_5O_{15}^{5-}$, ▲ $V_4O_{12}^{4-}$, □ $H_2V_2O_7^{2-}$, ■ $H_2VO_4^-$. a) pH 6.5; b) pH 6.8; pH was adjusted by hydrochloric acid, $c = 4\ mol\ dm^{-3}$.

spectra in the $\tilde{\nu}$ region of 450—1000 cm^{-1}. The bands above 900 cm^{-1} can be assigned to the stretching of the terminal V—O bonds. The bands in the $\tilde{\nu}$ region of 450—900 cm^{-1} correspond to bridge vibrations $\tilde{\nu}$(V—O—V) and/or to deformation vibrations δ(V—OH) [8, 9]. As follows from comparison of the IR spectra of the TPA, di- and tri-hydrogendecavanadates (Figs. 3a and 4a), band positions and their intensities are slightly different. Thus the number of protons in the $H_nV_{10}O_{28}^{(6-n)-}$ ion influenced the structure of the anion. A certain deformation of the vanadium-oxygen framework is affected not only by protonation of $V_{10}O_{28}^{6-}$ but by the number of hydrogen bonds formed between polyanion and the crystal water molecules or cations, as well.

At the heating rate 5 K min^{-1}, the thermal decomposition of A and B is a more-step process (Fig. 5). The first step of the mass loss in the temperature interval 50—100 °C is connected with dehydration, the anhydrous dihydrogendecavanadate [TPAH]$_4$H$_2$V$_{10}$O$_{28}$ is formed. Compound B is thermally stable up to 120 °C. From the IR spectra of the products obtained at 200 °C and 210 °C (Figs. 3 and 4) it follows that the starting hydrogendecavanadates are decomposed. However, the resulting compounds have the similar V—O framework. The different H : C : N mole ratios of the starting compounds and the intermediates serve as an evidence of bond cleavage of TPAH$^+$
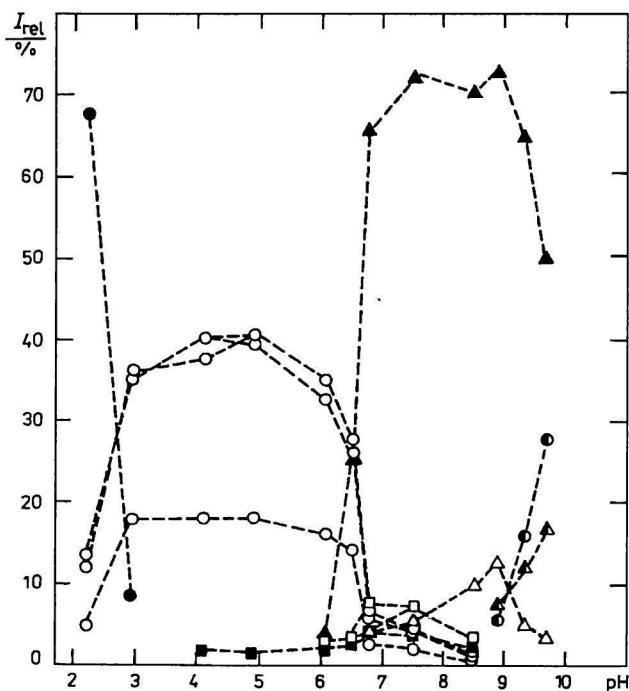

Fig. 3. IR spectra of [TPAH]$_4$H$_2$V$_{10}$O$_{28}$ · nH$_2$O (a) and of the decomposition products obtained at θ/°C: b) 100, c) 210, d) 340, e) 545, f) 620.

cation in course of heating (Table 1). This is in agreement with their IR spectra (Figs. 3 and 4) which exhibit new absorption bands in the 1500—1700 cm^{-1} $\tilde{\nu}$ region. We can assign these bands to deformation vibrations δ(N—H) in residual organic particles or to δ(N—H··O—V), which could be caused by hydrogen bonds formation between V—O framework and the organic particles. According to the IR spectra, the V—O framework structures in the product obtained at 340 °C and in V$_2$O$_5$ are similar. V$_2$O$_5$ exhibits a layered structure and it is the origin of a family of nonstoichiometric insertion compounds $M_x^{n+}V_{2-nx}^VV_{nx}^{IV}O_5$ (M = alkaline metals or organic molecules) [10]. Therefore we suppose that the products obtained at 340 °C could belong to insertion compounds mentioned above. The temperature corresponding to the maximum mass loss for A is 545 °C and for B 530 °C. As follows from X-ray phase analysis, the decomposition products obtained at 545 °C and 530 °C are V$_2$O$_5$—VO$_2$ mixtures with the

Fig. 2. Distribution diagrams I_{rel}—pH. I_{rel} is defined as the ratio between c(V, species) and c(V). ● VO$_2^+$, ○ H$_n$V$_{10}$O$_{28}^{(6-n)-}$, △ V$_5$O$_{15}^{5-}$, ▲ V$_4$O$_{12}^{4-}$, ▲ HV$_2$O$_7^{3-}$, □ H$_2$V$_2$O$_7^{2-}$, ◐ HVO$_4^{2-}$, ■ H$_2$VO$_4^-$. c(V) = 50 mmol dm^{-3}.
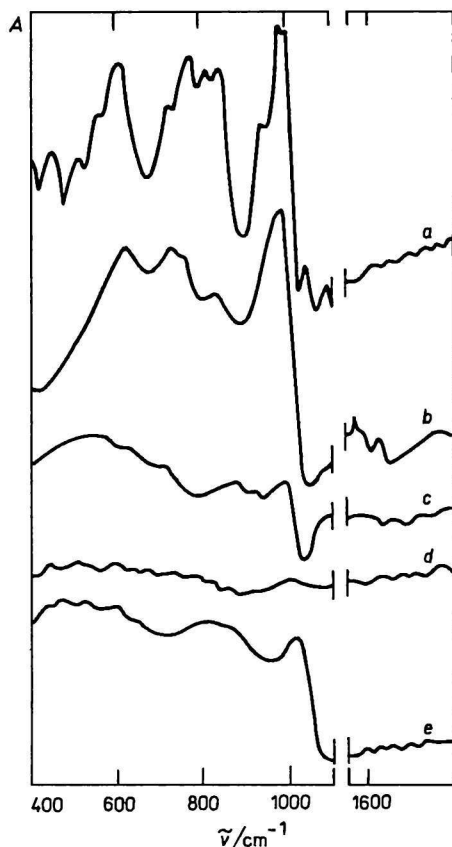
Fig. 4. IR spectra of [TPAH]$_3$H$_3$V$_{10}$O$_{28}$ (a) and of the decomposition products obtained at θ/°C: b) 200, c) 340, d) 530, e) 655.

traces of organic particles. $(d/nm)/(I_{rel}/\%)$, B, θ = 530 °C: 0.575/16, 0.437/43, 0.340/38, 0.330/5[a], 0.319/100[a], 0.288/43, 0.276/20, 0.2682/5, 0.2610/20, 0.2427/56[a], 0.2186/15, 0.2143/32, 0.1991/13, 0.1919/16, 0.1899/16, 0.1865/13, 0.1841/13[a], 0.1783/5, 0.1652/80, 0.1603/19[a], 0.1596/19[a], 0.1567/5. The oxides were identified according to Refs. [11, 12] (a — interplanar distances of VO$_2$). At higher tem-

peratures up to 620 °C and 655 °C, respectively, mass increase was observed in both decomposition products, which is caused by oxidation of vanadium(IV) to vanadium(V). V$_2$O$_5$ is the final decomposition product formed from B and the corresponding mass loss up to 655 °C, 34.95 % is in a good agreement with the theoretical value, 34.90 %. The final product of A is a mixture of V$_2$O$_5$ and small amount of VO$_2$. $(d/nm)/(I_{rel}/\%)$, A, θ = 620 °C: 0.575/23, 0.436/100, 0.409/29, 0.340/71, 0.331/5[a], 0.319/7[a], 0.288/71, 0.276/32, 0.2681/12, 0.2611/29, 0.2490/6[a], 0.2423/5[a], 0.2276/4[a], 0.2255/4[a], 0.2185/21, 0.2146/60, 0.1991/22, 0.1918/32, 0.1900/23, 0.1865/19, 0.1782/10, 0.1741/31, 0.1650/15, 0.1631/9, 0.1574/10. If the heating rate is slowed down (2 K min^{-1}), V$_2$O$_5$ was formed as the final decomposition product. Then also the experimental (41.76 %) and calculated (42.17 %) mass losses are in agreement (Table 1). The reason of this phenomenon is a greater content of TPAH$^+$ in A in comparison with B.

The EPR spectrum of the intermediate product obtained at 200 °C shows a presence of a broad line ($B \approx 40$ mT) with g = 1.96. It indicates that a part of vanadium was reduced to V(IV) in inner redox processes during the thermal decomposition. In the intermediates obtained at higher temperatures (340 °C, 530 °C) the intensity strongly decreases. This can be explained by broadening of EPR lines in consequence of the formation of —V—O—V— bridges in the layered structure. However, an oxidation of V(IV) to V(V) cannot be excluded. A participation of both processes is also possible.

The thermal decomposition of TPA hydrogendecavanadates prepared is a complicated process consisting of simultaneous redox processes involving also vanadium. In course of heating, also dehydration, decomposition of the decavanadate structures, and crystallization of VO$_2$ and V$_2$O$_5$ take place. The
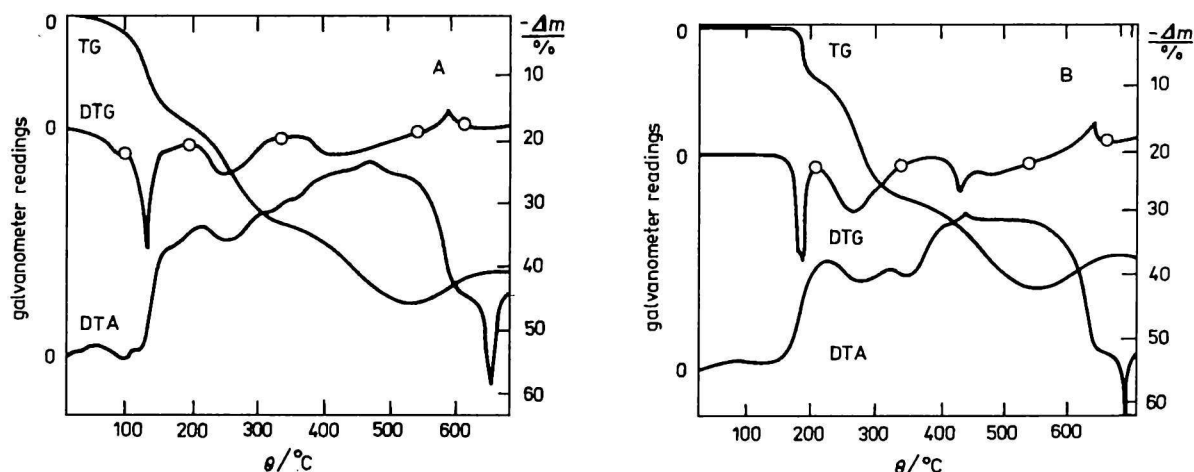

Fig. 5. Thermoanalytical curves of [TPAH]$_4$H$_2$V$_{10}$O$_{28}$ · nH$_2$O (A) and [TPAH]$_3$H$_3$V$_{10}$O$_{28}$ (B) (○ interruption of heating).

Table 1. Characterization of the Decomposition Products

Species	θ/°C	Δm/%	w_i(found)/% H	C	N	V_T	nH	:	nC	:	nN	Colour
A	–	–	5.99	27.66	3.46	32.36	23.5	:	9	:	1	Orange
	100	2.68	5.76	27.57	3.56	32.72	22.5	:	9	:	1	Yellow-orange
	210	17.61	3.62	20.77	3.23	38.83	11.5	:	7.5	:	1	Black
	340	31.92	1.40	17.39	3.48	49.91	5.5	:	6	:	1	Black
	545	44.25	–	1.84	0.28	53.63						Brown
	620	40.25	–	–	–	56.59						Dark orange
	620*	41.76	–	–	–	56.72						Orange
B		–	4.94	23.11	3.01	36.50	23		9		1	Yellow-orange
	200	10.00	3.82	20.19	2.98	40.56	18		9		1	Black
	340	27.40	1.43	14.42	2.41	48.02	8		7		1	Black
	530	40.00	–	1.60	0.32	54.31						Brown
	655	34.95	–	–	–	56.78						Orange

*Heating rate 2 K min^{-1}.

endothermic effects with minimum at 675 °C (A) and at 680 °C (B) represent the melting of V_2O_5.

The thermal decompositions of A and B exhibit only small differences. We suppose that they are caused mainly by mole ratios n(TPAH$^+$) : n(V) and by the presence of the crystal water molecules in the structures of hydrogendecavanadates prepared. The various degree of the V—O framework deformation in polyanion (according to IR spectra) plays only a negligible role.

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Translated by Ľ. Žúrková and I. Tkáč