Monatshefte für Chemie 124, 619–625 (1993)

Monatshefte für Chemie
Chemical Monthly

Synthesis and Properties of Propylammonium Polyvanadates

Ľudmila Žúrková and **Robert Vávra**

Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University,
Mlynská dolina CH-2, 842 15 Bratislava, Slovak Republic

Summary. Propylammonium (*n-Pa*) and isopropylammonium (*i-Pa*) meta- and decavanadates, $(n\text{-}Pa)VO_3$, $(i\text{-}Pa)VO_3$, $(n\text{-}Pa)_5HV_{10}O_{28}\cdot H_2O$, $(n\text{-}Pa)_4H_2V_{10}O_{28}$, $(i\text{-}Pa)_6V_{10}O_{28}\cdot 4H_2O$, and $(i\text{-}Pa)_4H_2V_{10}O_{28}$, were prepared. The physico-chemical properties of the compounds prepared with polyanion of the same composition depend mainly on the cation-anion interaction.

Keywords. Polyvanadates (V); Propylammonium.

Synthese und Eigenschaften von Propylammoniumpolyvanadaten

Zusammenfassung. Es wurden Propylammonium- (*n-Pa*) und Isopropylammonium- (*i-Pa*)-meta- und -decavanadate $(n\text{-}Pa)VO_3$, $(i\text{-}Pa)VO_3$, $(n\text{-}Pa)_5HV_{10}O_{28}\cdot H_2O$, $(n\text{-}Pa)_4H_2V_{10}O_{28}$, $(i\text{-}Pa)_6V_{10}O_{28}\cdot 4H_2O$ und $(i\text{-}Pa)_4H_2V_{10}O_{28}$ hergestellt. Die physikalisch-chemischen Eigenschaften der Verbindungen mit gleichem Polyanion hängen hauptsächlich von der Kation-Anion-Wechselwirkung ab.

Introduction

The study of polyvanadates with organic cations resulted either in synthesis of new types of polyvanadates, which were not observed with inorganic cations, or in isolation of known types of polyvanadates, however, with a different structure of the polyanion [1–3]. In the metavanadates, except $[n\text{-}(C_4H_9)_4N]HV_4O_{12}$ [1], the $(VO_3)_n^{n-}$ polyanion has the same chain structure [4–5] as found in metavanadates with inorganic cations [6–9] and, in all decavanadates, the isolated $V_{10}O_{28}^{6-}$ ion has also the same structure [10–13].

The data obtained so far indicate a possible influence of cation properties on the structure of polyanions, mainly on those with layer or chain structure. A systematic study on the relation between properties of organic cation and structure of polyvanadate ion was not yet performed. From this view point we have studied the synthesis and properties of different types of *n-Pa* and *i-Pa* polyvanadates.

Experimental Part

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

pH was measured on a TTT-2 *pH*-meter (Radiometer) using a GK 2401 C combined electrode. The elemental analysis was performed on CHN-Analyzer 1106 (Carlo Erba). Vanadium (V) was estimated by titration with $FeSO_4$ using diphenylamine as indicator. The IR spectra in nujol mulls, resp. KBr pellets, were measured on a Specord M 80 Spectrophotometer (Zeiss, Jena). The powder diffraction patterns were registered on a Philips PW 1050 diffractometer using CuK_α radiation. The thermal analysis was performed on a Q 1500 D Derivatograph (MOM Budapest), conditions: Pt-crucible, air atmosphere, heating rate 5 °C/min, sample weight 100 mg, Al_2O_3 internal standard.

The *n-Pa* and *i-Pa* metavanadates were prepared by dissolving V_2O_5 in a solution of the amine in 95% ethanol. The optimum mass amount ratio of the amine to vanadium, $n_A{:}n_V$ was 6:1. The pale yellow polycrystalline metavanadates, isolated after 4 hours from the reaction mixture being kept in dark, stirred and heated to 40 °C, were washed with ethanol and dried at room temperature in the dark. The pH_{obs} values of mother solutions for $(n\text{-}Pa)VO_3$ and $(i\text{-}Pa)VO_3$ were in the ranges 10.10–10.25 and 10.50–10.57, respectively. Analyses: calc. for $(Pa)VO_3$: V 32.03, H 6.34, C 22.65, N 8.81; found for $(n\text{-}Pa)VO_3$: V 31.78, H 6.41, C 22.48, N 8.66 and for $(i\text{-}Pa)VO_3$: V 31.69, H 6.33, C 22.27, N 8.65.

The decavanadates were prepared by crystallization from solutions obtained by dissolving V_2O_5 in aqueous solution of the amine. The n_A/n_V ratio, i.e. also the *pH* was changed. The reaction mixture was shortly heated to 80 °C, intensively stirred, kept in dark and filtered after 24 hours. The orange crystalline products formed at room temperature were washed by a small amount of ice-cold water and dried to constant weight above silica gel.

$(n\text{-}Pa)_4H_2V_{10}O_{28}$ crystallized at *pH* 3.70–3.80 and n_A/n_V ratio 4:10. $(n\text{-}Pa)_5HV_{10}O_{28}\cdot H_2O$ was precipitated by acetone from a solution with a n_A/n_V ratio 6:10 and *pH* 6.30–6.38. $(i\text{-}Pa)_4H_2V_{10}O_{28}$ crystallized at *pH* 3.75–6.01 and $n_A/n_V = 4{:}10$, resp. 5.5:10. $(i\text{-}Pa)_6V_{10}O_{28}\cdot 4H_2O$ was obtained at $n_A/n_V = 6{:}10$, resp. 6.5:10 and *pH* 6.49–7.65. Analyses: calc. for $(Pa)_4H_2V_{10}O_{28}$: V 42.46, H 3.53, C 12.01, N 4.67; found for $(n\text{-}Pa)_4H_2V_{10}O_{28}$: V 42.35, H 3.49, C 11.89, N 4.35 and for $(i\text{-}Pa)_4H_2V_{10}O_{28}$: V 42.53, H 3.48, C 11.69, N 4.54. Calc. for $(Pa)_5HV_{10}O_{28}\cdot H_2O$: V 39.90, H 4.18, C 14.11, N 5.48; found for $(n\text{-}Pa)_5HV_{10}O_{28}\cdot H_2O$: V 39.41, H 4.08, C 13.82, N 5.31. Calc. for $(Pa)_6V_{10}O_{28}\cdot 4H_2O$: V 36.65, H 4.93, C 15.55, N 6.04; found for $(i\text{-}Pa)_6V_{10}O_{28}\cdot 4H_2O$: V 36.30, H 4.94, C 15.46, N 5.91. Some hydrogendecavanadates were also prepared from D_2O according to procedures described.

Results and Discussion

In solid compounds the metavanadate ion has a chain structure formed by joined VO_x polyhedra ($x = 4, 5$) [4–9]. The VO_4 tetrahedra are characteristic for anhydrous alkali metal metavanadates, however, they have been found also in the structures of $(enH_2)(VO_3)_2$ [4] and $Ba(VO_3)_2\cdot H_2O$ [9]. Apart from barium salt consisting of spiral chains of V–O polyhedra, all other metavanadates can be regarded as variants of the pyroxene structure. The anion in hydrates metavanadates is mostly built up from VO_5 polyhedra. The IR spectra allow to distinguish between the structures built up from VO_4 or VO_5 polyhedra.

According to the characteristic IR spectra (Table 1), the structure unit in both metavanadates prepared is the VO_4 tetrahedron, and the structures of the metavanadate ions are very similar. In accordance with [14, 15], the absorption bands at 800–1000 cm^{-1} can be assigned to V–O (end-bonded) and at 500–700 cm^{-1} to V–O–V stretchings. The marked absorption band at about 750 cm^{-1} observed in Pa-metavanadates does not occur in the spectra of metavanadates with pyroxene structure. The IR spectra of $Ba(VO_3)_2\cdot H_2O$ and $Ba(VO_3)_2\cdot 1/2H_2O$ exhibit bands at 790 resp. 740 cm^{-1} [16]. Thus, the absorption band discussed can be assigned to V–O stretchings in VO_4 polyhedra forming a spiral chain as found in the structure

Table 1. Observed wave numbers and intensities in the IR spectra of metavanadates in the region of V–O stretchings

$(n\text{-}Pa)VO_3$ $\tilde{\nu}/cm^{-1}$	I	$(i\text{-}Pa)VO_3$ $\tilde{\nu}/cm^{-1}$	I	Assignment
991[a]	w	–		
943	vs	950	vs	$\nu_s(VO_2) + \nu_{as}(VO_2)$
–		935[a]	s	
915	vs	917	vs	
885	vs	890	vs	
860[a]	s	–		
823	vs	827	vs	
–		805	sh	
749[a]	s	744	s	?
640	vs	642	vs	$\nu_s(VOV) + \nu_{as}(VOV)$
567	s	575	s	
502	sh	497	vw	
–		470[a]	m	
452[a]	m	–		
–		407[a]	s	

[a] Absorption band assigned to organic cation

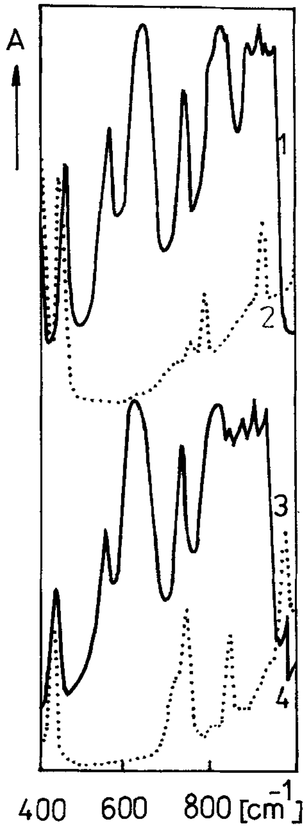

Fig. 1. IR spectra of metavanadates (——) and amine hydrochlorides (...): $(i\text{-}Pa)VO_3$ (1), $(n\text{-}Pa)VO_3$ (3), $(i\text{-}Pa)HCl$ (2), $(n\text{-}Pa)HCl$ (4)

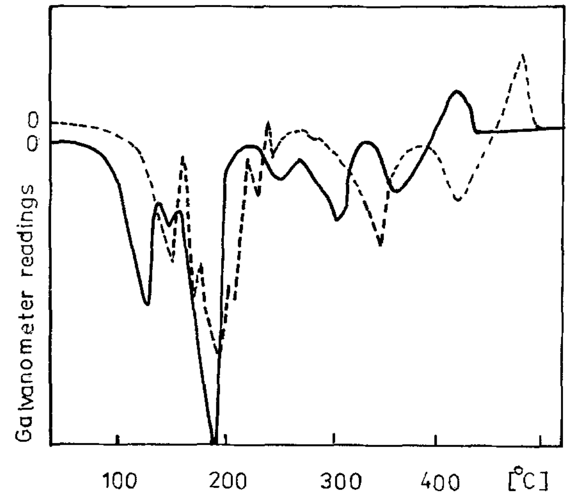

Fig. 2. DTG curves of metavanadates: (*n-Pa*)VO_3 (- - -) and (*i-Pa*)VO_3 (——)

of $Ba(VO_3)_2 \cdot H_2O$ [9]. Nevertheless, these band can be assigned also to strechings in VO_4 polyhedra being deformed by O···H–N hydrogen bonds between cation and anion.

The thermal decomposition of Pa metavanadates points to different interactions between the organic cation and the $(VO_3)_n^{n-}$ ion. The *n-Pa* metavanadate is more stable than the *i-Pa* metavanadate. The observed weight loss is in temperature intervals 80–460 °C and 60–395 °C, respectively (Fig. 2). At higher temperatures, a weight increae was observed in both decomposition products which is caused by oxidation of vanadium(IV) to vanadium(V). V_2O_5 is the final decomposition product formed from both metavanadates. In both compounds, the total weight loss is 43.5% (calc. 42.8%). The thermal decomposition of metavanadates prepared is a complicated process consisting of simultaneous redox processes involving also vanadium. Vanadium(IV) was detected even in decomposition products obtained by interruption of heating at 150 °C.

The powder diffraction patterns indicate some differences in the crystal structures of Pa metavanadates (Table 2).

The structures of anions, both in *n-Pa* and *i-Pa* metavanadates, are expected to be very similar. The compounds, however, exhibit certain differences in their thermal and diffraction properties. The differences are caused by those cation properties which influence their interaction with the $(VO_3)_n^{n-}$ anion.

The *n-Pa* and *i-Pa* decavanadates exhibit characteristic IR spectra in the region of V–O stretching vibrations, with band position only slightly influenced by the cation (Table 3). This is in agreement with crystal structures of some decavanadates known [10–13] in which the cation does not influence essentially the structure of the voluminous, highly condensated $V_{10}O_{28}^{6-}$ ion. A greater deformation of its structure can be expected on protonation of bridging oxygen atoms in $H_nV_{10}O_{28}^{(6-n)-}$ ($n = 1$–3). All protons in $H_nV_{10}O_{28}^{(6-n)-}$ ions are supposed to be bonded to bridging oxygen atoms [17, 18]. The hydrogen bond formation between crystal water molecules and bulky anion have a stabilizing effect on the structure of hydrates of decavanadates

Table 2. Interplanar distances in nm

$(n\text{-}Pa)VO_3$		$(i\text{-}Pa)VO_3$	
d_{hkl}/I_{rel}	d_{hkl}/I_{rel}	d_{hkl}/I_{rel}	d_{hkl}/I_{rel}
1.12/100	0.3657/25	1.04/100	0.2861/<5
0.783/13	0.3520/21	0.774/<5	0.2819/<5
0.669/13	0.3448/23	0.673/6	0.2797/6
0.663/33	0.3326/27	0.641/6	
0.576/15	0.3169/23	0.583/<5	
0.557/22	0.3102/13	0.568/<5	
0.504/18	0.3073/47	0.4439/8	
0.4676/18	0.3050/16	0.4183/13	
0.4336/48	0.3028/17	0.4040/5	
0.4152/26	0.2940/11	0.3883/11	
0.4088/35	0.2876/17	0.3723/5	
0.3986/27	0.2805/15	0.3607/6	
0.3900/17	0.2686/11	0.3570/5	
0.3818/34	0.2675/11	0.3498/9	
0.3792/31	0.2622/20	0.3326/12	
0.3723/34	0.1852/11	0.2971/5	

Table 3. Observed wave numbers and intensities in the IR spectra of decavanadates in the region of V–O stretchings (T – terminal, B – bridging)

$(n\text{-}Pa)_5HV_{10}O_{28}\cdot H_2O$		$(n\text{-}Pa)_4H_2V_{10}O_{28}$		$(i\text{-}Pa)_6V_{10}O_{28}\cdot 4H_2O$		$(i\text{-}Pa)_4H_2V_{10}O_{28}$		Assignment
$\tilde{\nu}$/cm^{-1}	I	$\tilde{\nu}$/cm^{-1}	I	$\tilde{\nu}$/cm^{-1}	I	$\tilde{\nu}$/cm^{-1}	I	
975[a]	sh	993[a]	vs	985	s	990	vs	$\gamma(VO_T)$
–		960	vs	–		976	sh	
945	vs	944	vs	944	vs	945	vs	
–		–		925	vs	–		
–		902	m	–		899	m	δ(V–OH)
–		840	vs	835	vs	842	vs	$\nu_{as}(VO_B)$
820	vs	814	vs	800	vs	815	vs	
–		765[a]	vs	–		768	vs	
740	vs	740	vs	740	vs	740	vs	
–		630	m	–		634	m	δ(V–OH)
595	s	585	s	590	s	582	s	$\gamma_s(VO_B)$
552	s	550	sh	550	s	552	sh	
534	s	528	s	523	s	527	s	
500	sh	–		–		–		
453[a]	s	446[a]	m	465[a]	sh	462[a]	m	
–		–		446	m	441	m	
–		–		–		425	sh	
–		–		405[a]	s	–		

[a] Together with absorption band assigned to organic cation

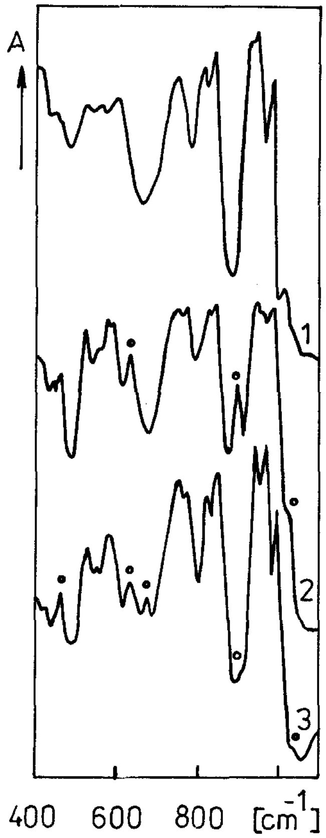

Fig. 3. IR spectra of *i-Pa* decavanadates: $(i\text{-}Pa)_6V_{10}O_{28}\cdot 4H_2O$ (1), $(i\text{-}Pa)_4H_2V_{10}O_{28}$ (2), *i-Pa* dihydrogendecavanadate prepared from D_2O (3); ° indicates bands discussed in the text

with inorganic cations [19], whereas in decavanadates with organic cations, known also in form of anhydrous compounds, such hydrogen bonds can be formed directly between cation and anion. It means that in all decavanadates there are V–O···H bonds. Therefore, the assignment of bands corresponding to $\underset{\mathrm{H}}{\underset{|}{\mathrm{V{-}O{-}V}}}$ vibrations in the IR spectra of hydrogendecavanadates will be very difficult. The study of tetraalkylammonium polyvanadates showed [20] that their IR spectra exhibit strong absorption bands at about 620 cm^{-1} which cannot be observed in spectra of unprotonated decavanadates. However, it was reported [21] that absorption bands at 600–640 cm^{-1} occur in spectra of a great number of crystallohydrates of unprotonated decavanadates with inorganic cations. Based on the crystal structure of $Cs_4H_2V_{10}O_{28}\cdot 4H_2O$, the bands at 560 and 275 cm^{-1} were assigned to asymmetric, resp. symmetric V–OH–V vibrations [21].

As follows from comparison of the IR spectra of $(i\text{-}Pa)_6V_{10}O_{28}\cdot 4H_2O$ (Fig. 3-1) with $(i\text{-}Pa)_4H_2V_{10}O_{28}$ (Fig. 3-2), the latter one exhibits additionally two strong bands at 899 and 634 cm^{-1}. In the spectrum of dihydrogendecavanadate prepared from D_2O (Fig. 3-3), the intensities of these bands are markedly diminished and two new bands at 670 and 456 cm^{-1} occur. Therefore we assign the bands at 899 and 634 cm^{-1} to deformation vibrations of two structurally nonequivalent V–OH groups. As the *i-Pa* dihydrogendecavanadate is an anhydrous compound and the V–OH groups in the $H_2V_{10}O_{28}^{4-}$ ion should be equivalent [18], one of the bands discussed may result from N–H···O–V hydrogen bond formation between cation and anion.

In the IR spectrum of $(n\text{-}Pa)_5HV_{10}O_{28}\cdot H_2O$ prepared from D_2O, no changes allowing the assignment of absorption bands corresponding to V–OH vibrations were observed.

Although the IR spectra of decavanadates and mainly those of *Pa*- dihydrogendecavanadates indicate a great similarity in structures of the polyanions, the properties of these compounds are also affected by properties of the cation. This conclusion is supported also by the fact that *i-Pa* hydrogendecavanadate and *n-Pa* decavanadate could not be prepared.

Acknowledgement

This work was supported by the Department for Education and Science of the Slovak Republic (Grant No. 1/109/92).

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Received April 9, 1992. Revised October 31, 1992. Accepted November 3, 1992