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Preparation, chemical characterization and thermal behaviour of some alkyldiammonium polyoxovanadates(V)

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Abstract

The thermal behavior of 1,3-propanediammonium (*Pda*) polyvanadates: $[Pda\mathrm{H_2}](\mathrm{VO_3})_2$ (**1**), $[Pda\mathrm{H_2}]_3\mathrm{V_{10}O_{28}}\cdot5\mathrm{H_2O}$ (**2**), $[Pda\mathrm{H_2}]_2\mathrm{H_2V_{10}O_{28}}$ (**3**), and 1,6-hexanediammonium (*Hda*) polyvanadates: $[Hda\mathrm{H_2}](\mathrm{VO_3})_2$ (**4**), $[Hda\mathrm{H_2}]_3\mathrm{V_{10}O_{28}}\cdot2\mathrm{H_2O}$ (**5**), $[Hda\mathrm{H_2}]_2\mathrm{H_2V_{10}O_{28}}\cdot2\mathrm{H_2O}$ (**6**) was studied in air atmosphere. The thermal decomposition of polyvanadates is a more-steps process consisting of simultaneous processes involving also vanadium. V_2O_5 is the final decomposition product formed from all polyvanadates studied.

The new compounds, hexanediammonium decavanadates **5** and **6** were prepared by the reaction V_2O_5 with 1,6-hexanediammine in aqueous solution. The IR spectra confirmed the presence of the decavanadate anion in these compounds.

Keywords: 1,3-Propanediammonium polyvanadates; 1,6-Hexanediammonium polyvanadates; IR spectra

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1. Introduction

Interest of polyoxometalates has received increasing attention in recent years because of their participation in some industrial processes and their use in biomedical field [1]. Organoammonium isopolyvanadates are used as precursors for preparation of vanadium oxides which play an important role in catalysis. These oxides are prepared by thermal decomposition of the precursors [2]. The nature of organic cation, stoichiometric composition of the compound, the surrounding atmosphere and experimental conditions play an important role in course of the thermal decomposition of polyvanadates as well as in formation of the final products [3].

This paper deals with thermal properties of 1,3-propanediammonium (*Pda*) polyvanadates: $[Pda\mathrm{H_2}](\mathrm{VO_3})_2$ (**1**), $[Pda\mathrm{H_2}]_3\mathrm{V_{10}O_{28}}\cdot5\mathrm{H_2O}$ (**2**), $[Pda\mathrm{H_2}]_2\mathrm{H_2V_{10}O_{28}}$ (**3**) 1,6-hexanediammonium metavanadate $[Hda\mathrm{H_2}](\mathrm{VO_3})_2$ (**4**) and synthesis, chemical characterization and thermal properties of two new 1,6-hexanediammonium (*Hda*) decavanadates: $[Hda\mathrm{H_2}]_3\mathrm{V_{10}O_{28}}\cdot2\mathrm{H_2O}$ (**5**), $[Hda\mathrm{H_2}]_2\mathrm{H_2V_{10}O_{28}}\cdot2\mathrm{H_2O}$ (**6**).

2. Experimental

2.1. Methods

V_2O_5 was prepared by thermal decomposition of NH_4VO_3. The other chemicals used were of analytical grade. Vanadium (V) was determined by titration with $FeSO_4$, using diphenylamine as indicator. The total

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vanadium content, V_{tot}, was determined gravimetrically as V_2O_5. V(IV) was calculated from the $V_{tot}-V(V)$ difference. Carbon, hydrogen and nitrogen contents were determined on a 1106 CHN-analyzer (Carlo Erba). The IR-spectra in Nujol mulls were recorded on a spectrometer FTIR Nicolet, Magna 750. The X-ray powder diffraction measurements were performed on a Philips PW 1050 diffractometer using Cu K_α radiation.

2.2. Synthesis and chemical and IR spectroscopic characterization of compounds

1,3-Propanediammonium polyvanadates: $[PdaH_2](VO_3)_2$. $[PdaH_2]_3V_{10}O_{28}\cdot5H_2O$, $[PdaH_2]_2H_2V_{10}O_{28}$ were prepared according to Ref. [4] and 1,6-hexanediammonium metavanadate $[HdaH_2](VO_3)_2$ according to Ref. [5].

1,6-Hexanediammonium decavanadate dihydrate. $[HdaH_2]_3V_{10}O_{28}\cdot2H_2O$ V_2O_5 (0.45 g, 2.5 mmol) was added to a stirred aqueous solution (80 ml) of 1,6-hexanediammine (0.30 g, 2.5 mmol). The reaction mixture kept in dark was stirred at room temperature until complete dissolution of V_2O_5 (about 1 h). After filtration, the pH of solution was adjusted by $HClO_4$ (1 mol dm^{-3}) to 6.0. Orange crystals were formed within seven days from the solution kept in refrigerator. They were filtered off, washed with cold water, and then dried in air. Calculated values (%) for $C_{18}H_{58}N_6V_{10}O_{30}$ (**5**): C, 16.03; H, 4.34; N, 6.23; V, 37.79; Analytical results (%): C, 15.88; H, 4.30; N, 6.18; V, 37.64. IR spectrum (1650–1550, 1000–400 regions, in cm^{-1}): 1630 w, 1617 w, 1603 w, 971 s, 960 sh, 945 vs, 919 vs, 835 sh, 826 s, 811 m, 791 w, 736 m, 733 m, 594 w, 545 vw, 525 w, 477 vw, 458 vw.

1,6-Hexanediammonium dihydrogendecavanadate dihydrate: $[HdaH_2]_2H_2V_{10}O_{28}\cdot2H_2O$.

This compound was prepared by similar method as for (**5**). The starting compounds were V_2O_5 (0.45 g, 2.5 mmol) and 1,6-hexanediammine (0.30 g, 2.5 mmol). After dissolution of V_2O_5 the resulting solution was diluted by water to 100 ml. The pH was then adjusted to 3.5 by HCl (4 mol dm^{-3}). After six days, orange crystals were obtained. Calculated values (%) for $C_{12}H_{42}N_4V_{10}O_{30}$ (**6**): C, 11.70; H, 3.38; N, 4.55; V, 41.35. Analytical results (%): C, 11.62; H, 3.38; N, 4.49; V, 41.37. IR spectrum (1650–1550, 1000–400 regions, in cm^{-1}): 1625 w, 1593 m, 1572 sh, 1553 sh, 986 vs, 926 s, 825 s, 776 sh, 767 m, 747 m, 720 sh, 609 m, 558 w, 519 w, 450 w, 431 vw.

2.3. Thermal studies

Thermal analysis was performed on a Derivatograph Q-1500 (MOM Budapest) at following conditions: air atmosphere, sample mass 100–200 mg, heating rates 2.5°C min^{-1} or 5°C min^{-1}, Pt-crucible, Al_2O_3 as reference material, temperature interval 20–700°C. KNO_3, $KClO_4$ and K_2SO_4 (Chemcomex) as reference standards for temperature calibration of DTA were used. The thermal analysis of the polyvanadates was interrupted at chosen temperatures. The products thus obtained were cooled to room temperature and identified by chemical analysis, IR spectroscopy and X-ray phase analysis.

3. Results and discussion

3.1. Infrared spectra

The IR spectroscopy is a good method of identification of the type of polyvanadate anion as the structures of these anions are relatively rigid. They are only slightly influenced by the nature of cation and by hydrogen bonds between cation and anion or between crystal water and anion, respectively. Therefore, the compounds **5** and **6** could be identified based on their IR spectra (Fig. 1) and chemical analysis as decavanadates. Some authors believe that IR spectra allow to distinguish the protonated and nonprotonated decavanadates. According to Ref. [6], the IR spectra of compounds with $H_nV_{10}O_{28}^{(6-n)-}$ anion, exhibit two characteristic bands at 995 cm^{-1} [$\nu(V–O_t)$] and 630 cm^{-1} [$\delta(V–O_b–H)$]. In the IR spectrum of hexanediammonium dihydrogendecavanadate dihydrate **6** (Fig. 1(b)) there are two bands at 986 and 609 cm^{-1} which could be characteristic of protonated decavanadate anions [6]. However, some of the dihydrogendecavanadates prepared in our laboratory do not exhibit these bands [7].

In the 450–1000 cm^{-1} region the IR spectra of the compounds **5** and **6** (Fig. 1) exhibit bands corresponding to $V–O_t$ stretchings at 900–1000 cm^{-1} and to $V–O_b$ stretchings at 450–900 cm^{-1}, all of them with

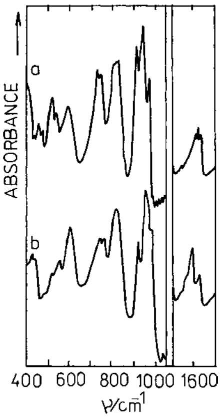

Fig. 1. IR spectra of $[HdaH_2]_3V_{10}O_{28}\cdot 2H_2O$ (a) and $[HdaH_2]_2H_2V_{10}O_{28}\cdot 2H_2O$ (b).

positions characteristic for decavanadates [8]. The band at 431 cm^{-1} in IR spectrum of **6**, can be associated with the deformation mode of the $V–O_b$ groups.

3.2. Thermal behaviour

The thermo-analytical curves of anhydrous *metavanadates* **1** and **4** are in their main features quite similar (Fig. 2). The thermal decomposition starts approximately at 165°C (**1**) and 180°C (**4**), respectively (Table 1), and proceeds as a more-step process. All endo- and exothermic effects are connected with weight changes, except the endothermic one with minimum at 680°C (Fig. 2) which corresponds to the melting of V_2O_5.

The thermal analysis of **1** was interrupted at 220°C, 330°C, 400°C and 500°C, and of **4** at 230°C, 360°C and 610°C. The intermediates obtained at 220°C and 230°C, respectively, are black products containing vanadium (IV). The different H:C:N molar ratios of the starting compounds and intermediates provide an evidence of bond cleavage of the cation in course of heating. As follows from the IR-spectra and X-ray diffraction patterns, the structures of both metavanadates decomposed. The intermediates obtained at 330°C, 400°C and 360°C are black amorphous products. The maximum mass loss is reached at 500°C and 610°C, respectively (Table 1). These products are $V_2O_5–VO_2$ mixtures with traces of organic particles;

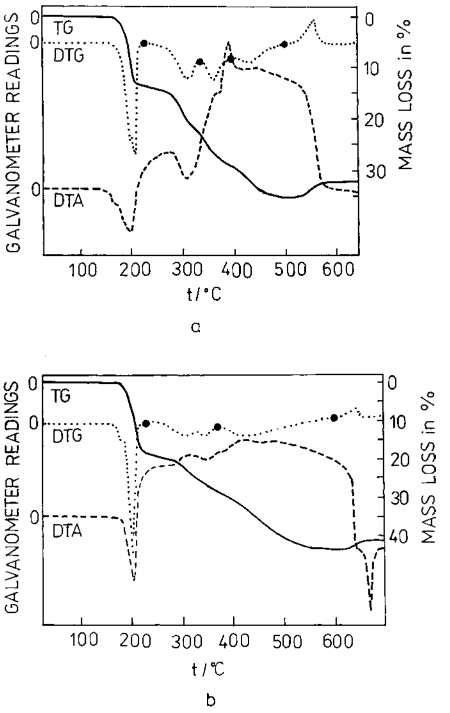

Fig. 2. Thermo-analytical curves of metavanadates: $[PdaH_2](VO_3)_2$ (a) and $[HdaH_2](VO_3)_2$ (b); (●) interruption of heating.

Table 1
Basic thermo-analytical data

Species	t_i (°C)	t_m (°C)	Δm_m (%)	t_f (°C)	Δm_f (%)	Δm_c (%)	$\Delta m_m-\Delta m_f$ (%)
$[PdaH_2](VO_3)_2$	165	500	35.5	570	32.8	33.62	2.7
$[HdaH_2](VO_3)_2$	180	610	43.3 (44.3)	650	41.3 (42.9)	42.46	2 (1.4)
$[PdaH_2]_3V_{10}O_{28}\cdot 5H_2O$	70	420	32.2	440	29.2	28.72	3
$[HdaH_2]_3V_{10}O_{28}\cdot 2H_2O$	75	505	36.8	555	34.0	33.44	2.8
$[PdaH_2]_2H_2V_{10}O_{28}$	160	420	22.5	500	17.8	18.19	5
$[HdaH_2]_2H_2V_{10}O_{28}\cdot 2H_2O$	70	500	30.0	575	26.2	26.18	3.8

t_i: start of decomposition; t_m: maximum mass loss; t_f: final mass loss; Δm_m: mass loss at t_m; Δm_f: mass loss at t_f; Δm_c: calculated mass loss; ( ) obtained at heating rate 2.5°C min.

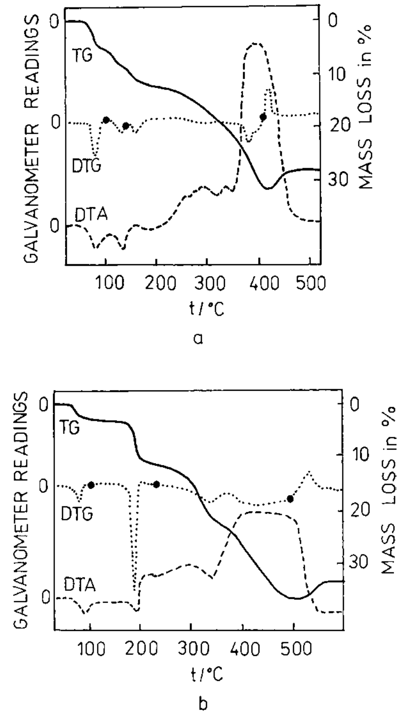

Fig. 3. Thermo-analytical curves of decavanadates: $[Pda\mathrm{H}_2]_3\mathrm{V}_{10}\mathrm{O}_{28}\cdot5\mathrm{H}_2\mathrm{O}$ (a) and $[Hda\mathrm{H}_2]_3\mathrm{V}_{10}\mathrm{O}_{28}\cdot2\mathrm{H}_2\mathrm{O}$ (b); (●) interruption of heating.

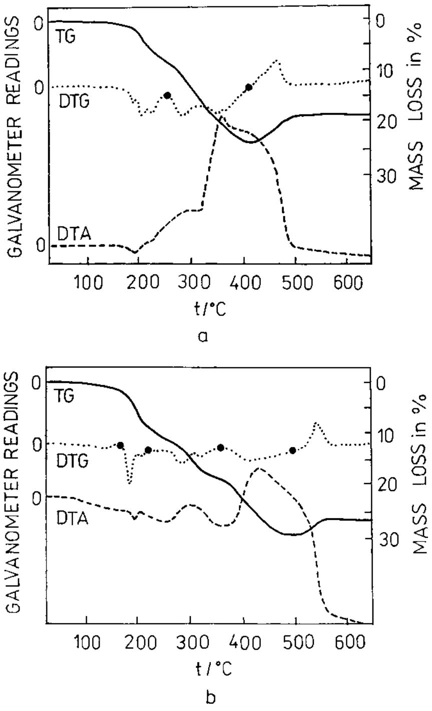

Fig. 4. Thermo-analytical curves of dithydrogendecavanadates $[Pda\mathrm{H}_2]_2\mathrm{H}_2\mathrm{V}_{10}\mathrm{O}_{28}$ (a) and $[Hda\mathrm{H}_2]_2\mathrm{H}_2\mathrm{V}_{10}\mathrm{O}_{28}\cdot2\mathrm{H}_2\mathrm{O}$ (b); (●) interruption of heating.

in product obtained at 500°C (**1**), V_6O_{13} was also detected. At higher temperatures, up to 570°C, respectively, 650°C a mass increase caused by oxidation of vanadium (IV) to vanadium (V) was observed in both decomposition products. Vanadium is quantitatively oxidized in **4** only if the thermal decomposition is performed at a lower heating rate (2.5°C min^{-1}). The end-product of the thermal decomposition of metavanadates is V_2O_5. The observed and the calculated mass losses are in good agreement (Table 1).

The thermal decomposition of crystallohydrates of *decavanadates* starts already at about 70°C (Table 1, Fig. 3). The first endothermic processes (weight loss is 3.9% for **2** and 2.5% for **5**) are accompanied by release of $3H_2O$ and $2H_2O$, respectively: the decavanadate dihydrate, $[Pda\mathrm{H}_2]_3\mathrm{V}_{10}\mathrm{O}_{28}\cdot2\mathrm{H}_2\mathrm{O}$, and the anhydrous $[Hda\mathrm{H}_2]_3\mathrm{V}_{10}\mathrm{O}_{28}$ are formed. Both products, obtained at 105°C and 120°C, respectively, are orange and their IR spectra and chemical analysis are in agreement with formulas mentioned above. The intermediate formed at 150°C (**2**) is not anhydrous decavanadate but as well as the intermediate obtained at 230°C (**5**), it is rtg-amorphous, contains vanadium (IV) and H:C:N molar ratios differing from that of starting compound. Thus, various redox reactions connected with bond cleavage of the cation, reduction of vanadium (V), and structure decomposition take place in the temperature intervals 105–150°C (**2**) and 120–230°C (**5**). The products obtained at temperatures corresponding to the maximum mass loss (Table 1) have the analogical composition as those obtained for metavanadates (**1**,**4**). At higher temperatures, up to 440°C (**2**) and 555°C (**5**), respectively, a mass increase was also registered. V_2O_5 is the final decomposition product of both decavanadates.

The temperatures corresponding to the start of the thermal decomposition of *dihydrogendecavanadate* are in agreement with fact that **3** is anhydrous compound and **6** is a crystallohydrate (Table 1, Fig. 4). Anhydrous hexanediammonium dihydrogendecavanadate could not be prepared because vanadium (V) is reduced just in course of the crystal water release in the interval 70–170°C.

Thermal analysis of **3** was interrupted at 230°C and 420°C, and of **6** at 225°C, 360°C and 500°C. The intermediates obtained at 230°C, 225°C and 360°C are black and rtg-amorphous. The maximum weight loss was reached at 420°C and 500°C, respectively. The products isolated at these temperatures are orange-brown, they contain V_2O_5, V_2O_4 and residues of the organic component. At even higher temperatures, the oxidation of vanadium (IV) to vanadium (V) as well as of the rests of organic particles takes place. The end-product of the decomposition of **3** and **6** is V_2O_5.

4. Conclusions

From the reaction systems *Hda*–V_2O_5–H_2O–HX, at different amounts of reactants and pH, two new decavanadates have been prepared.

Thermal decomposition of the polyvanadates described is a complicated process consisting of simultaneous redox reactions involving also vanadium. In course of heating, dehydration, decomposition of the polyvanadates structures and crystallization of vanadium oxides also take place. The end-product of the decomposition is V_2O_5. Thermal properties of polyvanadates, under same experimental conditions, can be influenced of the cation properties, polyanion structures and the stoichiometry of the polyvanadate.

The thermal properties of polyvanadates studied are mainly influenced by the structure of anion. The t_m and t_f values are markedly higher for metavanadates as for decavanadates or dihydrogendecavanadates. This result is in agreement with Ref. [9], that the isopolyvanadates with chain structure of the polyanion (metavanadate) are thermally more stable than those containing an isolated polyanion in the structure (decavanadate).

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