Synthesis and Properties of 1,4-Butanediammonium Polyvanadates

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Polyvanadates $[BdaH_2](VO_3)_2$ (**A**), $[BdaH_2]_3V_{10}O_{28} \cdot 6H_2O$ (**B**), and $[BdaH_2]_2H_2V_{10}O_{28} \cdot 4H_2O$ (**C**) were synthesized from the system V_2O_5—1,4-butanediammonium (Bda)—H_2O—(HCl). Syntheses variables were: mole ratio $n(V):n(Bda)$, concentration of V, pH of the solution, and reaction temperature. Compounds were characterized by X-ray powder diffraction and IR spectra. The thermal decomposition in air was also studied. As the intermediate reaction product of the compound **C** was determined nonaqueous dihydrogendecavanadate $[BdaH_2]_2H_2V_{10}O_{28}$ (**D**). V_2O_5 was the final reaction product of all compounds.

Chemistry of polyoxovanadates initiates research in solutions as well as in solid state. Large number of various polyoxo anions exist, unique structures contribute to the interesting physicochemical properties of the above compounds. It is a topical area of the chemical research due to possible applications of the compounds in medicine, materials science, and catalysis [1—3].

According to the structure of polyvanadate ions, solid phases can be divided into three groups:

1. Compounds with isolated polyvanadate units ($V_2O_7^{4-}$, $V_4O_{12}^{4-}$, $V_5O_{14}^{3-}$, $V_6O_{19}^{8-}$, $V_{10}O_{28}^{6-}$) [4—8],

2. compounds with chains ($(VO_3^-)_n$) [9],

3. compounds with layers of polyvanadate ions ($(V_5O_{14}^{3-})_n$, $(V_6O_{16}^{2-})_n$) [10, 11].

Important is the influence of properties of cations upon the structure of polyvanadate ions, *i.e.* up-to-date known penta- and hexavanadates with inorganic cations form layer structures [10, 11], whilst organic cations contain the relevant polyvanadate ion as the isolated unit [6, 7]. Depending on the synthesis conditions some organic cations form chain metavanadates – $(VO_3^-)_n$ as well as tetravanadates – $V_4O_{12}^{4-}$ [12], inorganic cations form exclusively metavanadates with the chain structure [13]. Syntheses of polyoxovanadates with organic cations led to the formation of structural types not known with inorganic cations, *i.e.* dodeca-, trideca-, and pentadecavanadates [14—16] and alkoxypolyvanadates [17]. These polyoxovanadate ions form isolated structural units. Thus, organic cations enable the increase of variability of the structure of polyvanadate ions and, consequently, compounds with new properties can be synthesized.

Present paper, as the part of our study of polyoxovanadates, deals with syntheses and characterization of three new compounds with divalent organic cation: 1,4-butanediammonium (Bda) meta-, deca-, and dihydrogendecavanadate.

EXPERIMENTAL

V_2O_5 was prepared by thermal decomposition of a previously purified NH_4VO_3. All other chemicals used were of anal. grade. The elemental analysis was performed on a CHN analyzer 1106 (Erba, Milan). Vanadium(V) was determined by titration with $FeSO_4$, using diphenylamine as indicator. The total vanadium, V_{tot}, was determined gravimetrically as V_2O_5. V(IV) was calculated from the V_{tot} – V(V) difference. pH was measured on a TTT-2 pH-meter (Radiometer, Copenhagen) using a GK 2401C electrode. The IR spectra in Nujol mulls were measured on a Specord M 80 spectrophotometer (Zeiss, Jena) and FTIR Nicolet, Magna 750. The X-ray powder diffraction measurements were performed on a Philips PW 1050 diffractometer using CuK_α radiation ($\lambda = 1.5418 \times 10^{-10}$ m). Thermal analysis was performed on a STD 2960 (T. A. Instruments) enabling simultaneous collection of TG, DTG, and DTA curves. Topical experimental parameters: sample mass 20 mg, heating rate 5 °C min^{-1}, Pt crucibles, air atmosphere. Sequential thermal treatment was accomplished on the Derivatograph Q 1500 D (MOM Budapest), it produced the kinetically frozen probes at given conditions (*cf.* • in Figs. 2—4). Topical experimental parameters: as formerly, with the exception of sample mass – 100 mg.

Syntheses

$[BdaH_2](VO_3)_2$ (**A**) was synthesized by dissolution of V_2O_5 (0.45 g; 2.5 mmol) in the aqueous solution of Bda (0.46 g; 5 mmol in 40 cm^3 of H_2O). When V_2O_5 has been dissolved the volume of reagent solution was completed to 50 cm^3, value of its pH was 9.8. The solution was placed to the refrigerator. After 24 h white microcrystalline compound was formed, washed by ethanol and air-dried in the darkness.

During syntheses of $[BdaH_2]_3V_{10}O_{28} \cdot 6H_2O$ (**B**) and $[BdaH_2]_2H_2V_{10}O_{28} \cdot 4H_2O$ (**C**) aqueous suspension of V_2O_5 (0.23 g; 1.3 mmol in 40 cm^3 of H_2O (**B**), or in 90 cm^3 of H_2O (**C**)) was incubated at 70—80 °C and aqueous solution of Bda (0.09 g; 1 mmol) was continuously added within 30 min of the reaction. Total volume of the Bda solution added was 3 cm^3, the reaction mixture was stirred and incubated at 70—80 °C for this reaction period. The solution of orange colour was cooled, its volume was completed to 50 cm^3 (**B**) giving the value of pH = 6.0, or to 100 cm^3 (**C**) and by addition of HCl (2 mol dm^{-3}) the value of pH was modified to 2.5. The crystallization was performed in the refrigerator for 24 h, solid compounds were air-dried in the darkness. Water-free $[BdaH_2]_2H_2V_{10}O_{28}$ (**D**) was the kinetically frozen reaction product of the compound **C** at 120 °C, the topical conditions are given elsewhere in Experimental.

For $[BdaH_2](VO_3)_2$ (**A**) w_i(calc.): 35.57 % V, 4.89 % H, 16.67 % C, 9.72 % N; w_i(found): 35.20 % V, 4.87 % H, 16.65 % C, 9.66 % N. For $[BdaH_2]_3V_{10}O_{28} \cdot 6H_2O$ (**B**) w_i(calc.): 38.10 % V, 4.07 % H, 10.78 % C, 6.28 % N; w_i(found): 37.99 % V, 4.00 % H, 10.46 % C, 6.19 % N. For $[BdaH_2]_2H_2V_{10}O_{28} \cdot 4H_2O$ (**C**) w_i(calc.): 42.04 % V, 3.16 % H, 7.93 % C, 4.62 % N; w_i(found): 41.91 % V, 3.03 % H, 7.75 % C, 4.44 % N. For $[BdaH_2]_2H_2V_{10}O_{28}$ (**D**) w_i(calc.): 44.68 % V, 2.65 % H, 8.43 % C, 4.94 % N; w_i(found): 43.91 % V, 2.48 % H, 8.09 % C, 4.77 % N.

RESULTS AND DISCUSSION

Butanediammonium metavanadate $[BdaH_2](VO_3)_2$ (**A**) and decavanadate $[BdaH_2]_3V_{10}O_{28} \cdot 6H_2O$ (**B**) were synthesized in the system V_2O_5—Bda—H_2O. When synthesizing butanediammonium dihydrogendecavanadate $[BdaH_2]_2H_2V_{10}O_{28} \cdot 4H_2O$ (**C**) the hydrochloric acid was added with the aim to optimize the pH level during syntheses conditions.

It is well known that in aqueous solutions of polyvanadates complex equilibria exist among the individual polyanions, and these equilibria depend upon the pH, concentration of vanadium (c_V) and temperature. Moreover, syntheses conditions of various types of solid polyvanadates with identical cation depend as well on the solubility of individual compounds. Proper pH level of syntheses of compounds **A** and **B** has been achieved if optimal c_V are 10^{-1} mol dm^{-3} or 5×10^{-2} mol dm^{-3} and mole ratios $n(V):n(Bda)$ are 1 for **A** and 2.6 for **B**. Compound **C** requires the $n(V):n(Bda) = 2.6$ and $c_V = 2.5 \times 10^{-2}$ mol dm^{-3}. Equilibria are in the reaction systems affected by the temperature and by the sequence of the addition of components. Also the reaction solution of compound **A** was produced by dissolution of V_2O_5 in aqueous solution of Bda at ambient conditions, this is not the route for syntheses of decavanadates. When synthesizing these, to the aqueous suspension of V_2O_5 Bda should be added at elevated temperature (70 °C).

Butanediammonium metavanadate (**A**) is white microcrystalline compound soluble in hot water. Butanediammonium decavanadate (**B**) forms dark yellow needle-like crystals, dihydrogendecavanadate (**C**) is orange yellow, and anhydrous dihydrogendecavanadate (**D**) is yellow microcrystalline product. Synthesized compounds are practically insoluble in cold water and in ethanol, exert restricted solubility in acetone. Butanediammonium metavanadate was formerly prepared hydrothermally in form of the yellow crystals, it was a major part (>75 %) of the mixture, from which it was mechanically isolated. Its structure is also reported in the same paper [18]. The synthesis of pure compound was not reported by now. All butanediammonium decavanadates reported in this paper are new phases.

The polyanion $(VO_3^-)_n$ exhibits either chain structure [9, 18] or forms isolated cyclic structural units of $V_4O_{12}^{4-}$ (or $HV_4O_{12}^{3-}$) [5, 19]. In metavanadates of organic cations, tetrahedrons of VO_4 share common oxygens in both types of structures. The structure of polyanion is only weakly affected by properties of the present organocation. Thus, metavanadates are identified and the topical type of structure of the anion is deduced based on ν(V—O) in IR spectra of polyvanadates.

Metavanadate **A** exhibits a characteristic IR spectrum in the 400—1000 cm^{-1} region. The assignments proposed for $\nu_s + \nu_{as}(V—O_t)/cm^{-1}$ are: *946 vs, 931 vs, 912 vs, *883 vw, 865 vw, 815 s; and for $\nu_{as} + \nu_s(V—O_b)/cm^{-1}$:*775 vw, 731 w, *720 vw, 645 vs, 545 w, *506 s, 462 sh, 443 m. The asterisk indicates cationic bands or overlapping bands corresponding to ν(V—O) and vibrations of the cation.

Structure of $V_{10}O_{28}^{6-}$ is formed by ten more or less disordered VO_6 octahedrons linked by joint edges. Basic V—O skeleton remains intact in protonated anions – $H_nV_{10}O_{28}^{(6-n)-}$ (n = 1—4), protons are bonded to bridging oxygens [8, 20]. The majority of reported structures are dihydrogendecavanadates, here protons are almost exclusively bonded with symmetrical double-bonded atoms of oxygen [8, 21], or symmetrical triple-bonded oxygens [22]. Only one paper [23] gives the structure with nonsymmetrical $V—O_b—H$ bonds, where two types of protons exist, entering the interactions either with double- or triple-bonded atoms of oxygen.

Table 1. Observed Wavenumbers and Intensities (I) in IR Spectra of Decavanadates in the Regions of 400—1000 cm^{-1} and 1500—1650 cm^{-1}

$[BdaH_2]_3V_{10}O_{28} \cdot 6H_2O$		$[BdaH_2]_2H_2V_{10}O_{28} \cdot 4H_2O$		$[BdaH_2]_2H_2V_{10}O_{28}$		Assignment
$\tilde{\nu}$/cm^{-1}	I	$\tilde{\nu}$/cm^{-1}	I	$\tilde{\nu}$/cm^{-1}	I	
		991	s	993	s	$\nu(V—O_t)$
968	vs	967	vs	969	vs	
946	vs	947	vs	953	vs	
932	sh	932	sh			
		896	w	906	m	$\delta(V—OH)$?
884	m			889	sh	$\nu_{as}(V—O_b)$
		877	sh			
837	s	839	sh	845	sh	
827	sh	828	vs	824	vs	
811	m					
		766	m			
		752	s			
734	s	731	s	734	vs	
667	vw					
656	vw					
		628	m	626	m	
		605	sh			
591	m			587	s	$\nu_s(V—O_b)$
563	m	578	s	575	sh	
				549	m	
530	m	535	s	532	s	
510	m	511	m			
		495	w	490	w	
		479	vw			
453	m			458	sh	
444	sh	446	m	443	m	$\delta(V—O_b)$
420	m					
408	vw					
1634	m	1631	sh	1635	w	$\delta(H_2O)$
1621	sh	1622	m	1618	w	$\delta(NH_3^+)$
1605	m	1602	s			
1593	m			1593	w	$\delta(C—N^+—H)$
				1558	vw	
1536	m			1541	vw	
1513	s	1523	m	1516	w	
				1506	w	

Structure of this bulky polyanion is relatively rigid and IR spectroscopy is an effective method for identification of decavanadates. Compounds **B**, **C**, **D** were identified as decavanadates based on characteristic absorption bands in the interval of ν(V—O) ranging from 400 to 1000 cm^{-1} (Fig. 1, Table 1). Comparison of the details of IR spectra of three synthesized Bda decavanadates displays different positions as well as intensities of absorption bands, these are connected with the distortions of V—O skeleton of decavanadate ion. IR spectrum of decavanadate **B** is more different from that of dihydrogendecavanadates **C**, **D**, as if comparing IR spectra of tetrahydrate **C** and nonaqueous **D** dihydrogendecavanadates. It is obvious that binding of protons upon oxygens in $H_2V_{10}O_{28}^{4-}$ causes larger deformations of angles and interatomic distances in V—O skeleton, than hydrogen bonds among cation and decavanadate anion or among water molecules and anion. Product **C** was prepared in D_2O with the purpose to identify absorption bands of δ(V—OH). IR spectrum of deuterated dihydrogendecavanadate (**C**) shows no absorption bands in the region 1523—1635 cm^{-1} that are assigned to δ(N—H) in cation and δ(O—H) in crystalline water. Corresponding bands in deuterated probes are in the region 1151—1200 cm^{-1} (Fig. 1). Additional five absorption bands are deuterium-sensitive (Fig. 1), anyway, only band with low intensity at 896 cm^{-1} is not assigned to cation. We suggest that this band would be the δ(V—OH) in $H_2V_{10}O_{28}^{4-}$. Corresponding band in deuterated phase is not visible, probably due to its very low intensity and overlapping with the other absorption bands. Band at 884 cm^{-1} is present also in the spectrum of the compound **B** containing proton-free decavanadate ion. Thus, rigorous assignment of the band corresponding to δ(V—OH) in IR spectrum of compound **C** is not possible.

For identification purposes, new compounds – decavanadates have been characterized by powder diffraction patterns, sets of ten most intensive diffrac-

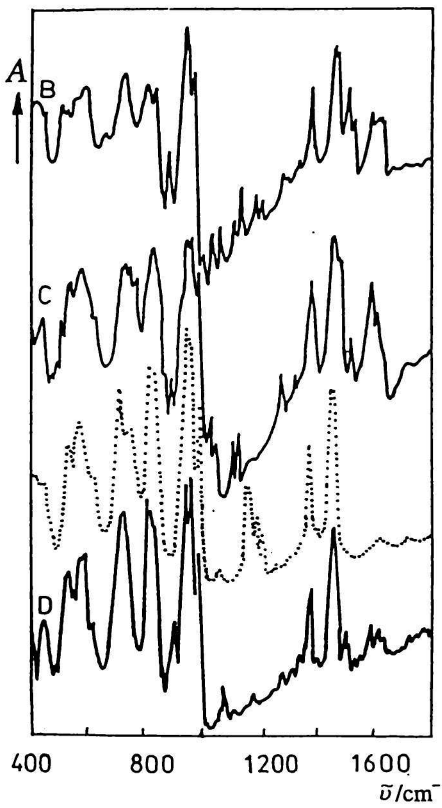

Fig. 1. IR spectra of decavanadates (labeling of compounds matches the summary and main text); ······ IR spectrum of compound **C** prepared from D_2O.

tions of phases **B**, **C**, **D** are present in Table 2.

Thermoanalytical curves and basic thermoanalytical data of synthesized compounds (Figs. 2—4, Table 3) show that the thermally most stable compound is metavanadate **A**, it is in agreement with the fact that the above compound is water-free. Bda decavanadate (**B**) and dihydrogendecavanadate (**C**) are crystallohydrates, so they decompose at substantially lower temperatures. All mass changes are on DTA curves demonstrated by endo- or exoeffects. (The reactions of the thermal decomposition of studied samples are rather explosive at around 400 ℃, *cf.* the DTA exoeffects in Figs. 2—4.)

Deeper understanding of individual thermal events was achieved by sequential thermal treatment producing the kinetically frozen probes at following temperatures: 240 ℃, 338 ℃, 420 ℃, and 560 ℃ for compound **A**, 120 ℃, 160 ℃, 400 ℃, and 550 ℃ for compound **B**, 120 ℃, 240 ℃, 420 ℃, and 545 ℃ for compound **C**. Chemical analysis, IR spectroscopy, and X-ray powder diffractometry were employed to characterize the intermediate reaction products after cooling to ambient temperature. The only intermediate reaction product with defined composition is the phase formed from compound **C** at 120 ℃. Estimated mass loss (6.21 %) displays that this step represents dehydration of tetrahydrate to nonaqueous dihydrogendecavanadate $[BdaH_2]H_2V_{10}O_{28}$. The above knowledge is confirmed by IR spectra and chemical analysis (Fig. 1, Table 1). Compound **B** did not form nonaqueous decavanadate, as seen from the comparison of thermoanalytical curves of compounds **B** and **C** (Figs. 3 and 4). Curves of dihydrogendecavanadate **C** exhibit plateau between 120 ℃ and 180 ℃, but it is not the case of curves of decavanadate **B** where the superposition of dehydration and redox processes occurs and gray kinetically frozen intermediate at 120 ℃ contains vanadium(IV). The other intermediate reaction products are mixtures containing vanadium(V) and vanadium(IV). The different mole ratios $n(H):n(C):n(N)$ of the starting compounds and intermediates provide an evidence of bond cleavage of cation. The content of vanadium(IV) depends on the temperature of decomposition and on the mole ratios of vanadium to cation in the original compound. The maximum content of vanadium(IV) is at around 200 ℃, at higher temperatures it decreases; moreover, at the given temperatures it is directly proportional to the increase of $n([BdaH_2]):n(V)$ ratio. The reaction products with the highest mass loss during thermal

Table 2. Interplanar Distances (d) and the Relative Intensities (I_r) of Ten Most Intensive Diffractions of Butanediammonium Decavanadates

$[BdaH_2]_3V_{10}O_{28}\cdot nH_2O$		$[BdaH_2]_2H_2V_{10}O_{28}\cdot nH_2O$		$[BdaH_2]_2H_2V_{10}O_{28}$	
d/nm	I_r/%	d/nm	I_r/%	d/nm	I_r/%
93.02	63	96.05	96	91.10	82
91.11	60	84.18	72	82.61	38
88.38	42	80.37	57	78.24	100
76.88	100	77.56	82	68.04	18
43.92	31	73.69	40	61.46	23
35.59	54	52.42	43	37.35	36
32.06	42	32.17	100	33.36	23
22.31	51	29.95	73	32.17	17
21.59	37	24.27	52	26.19	22
17.56	32	23.19	40	23.07	19

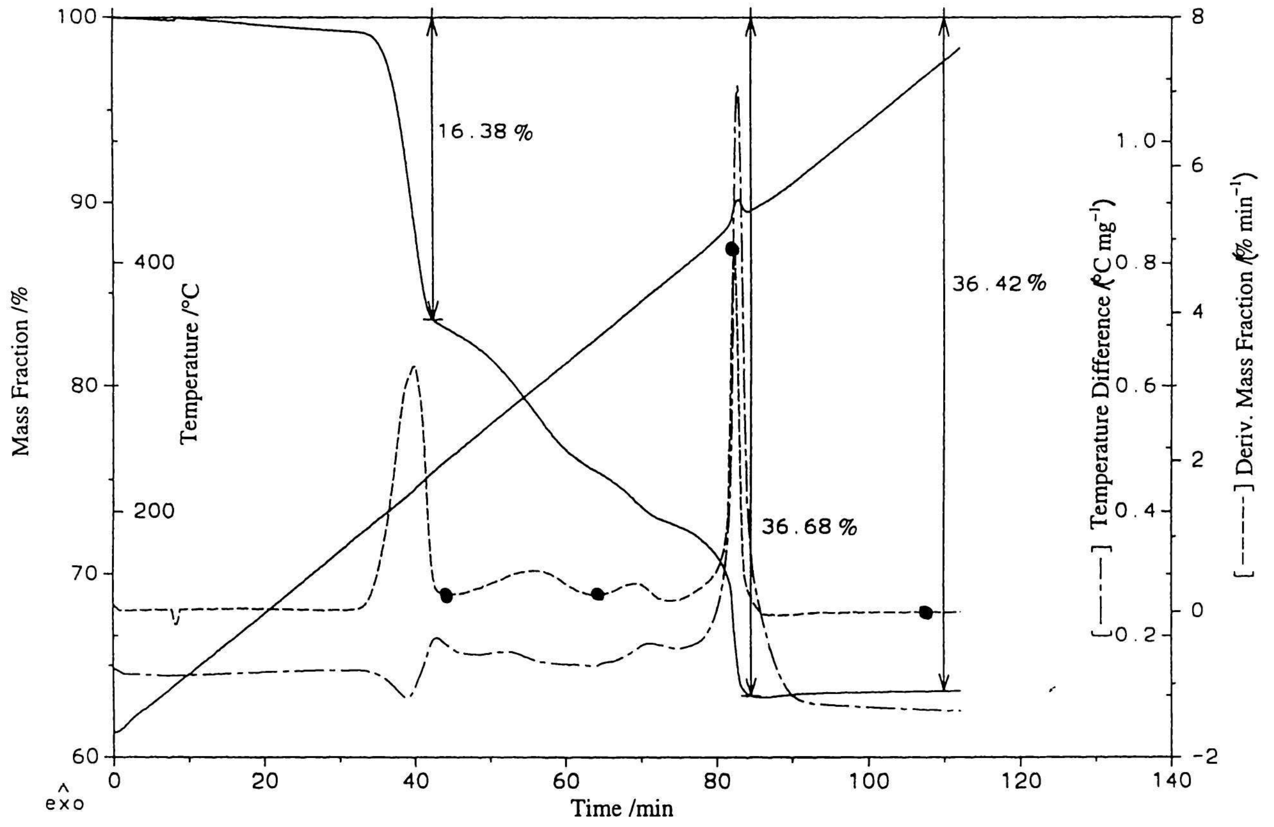

Fig. 2. Thermoanalytical curves of metavanadate **A**; thermal treatment kinetically frozen at ●.

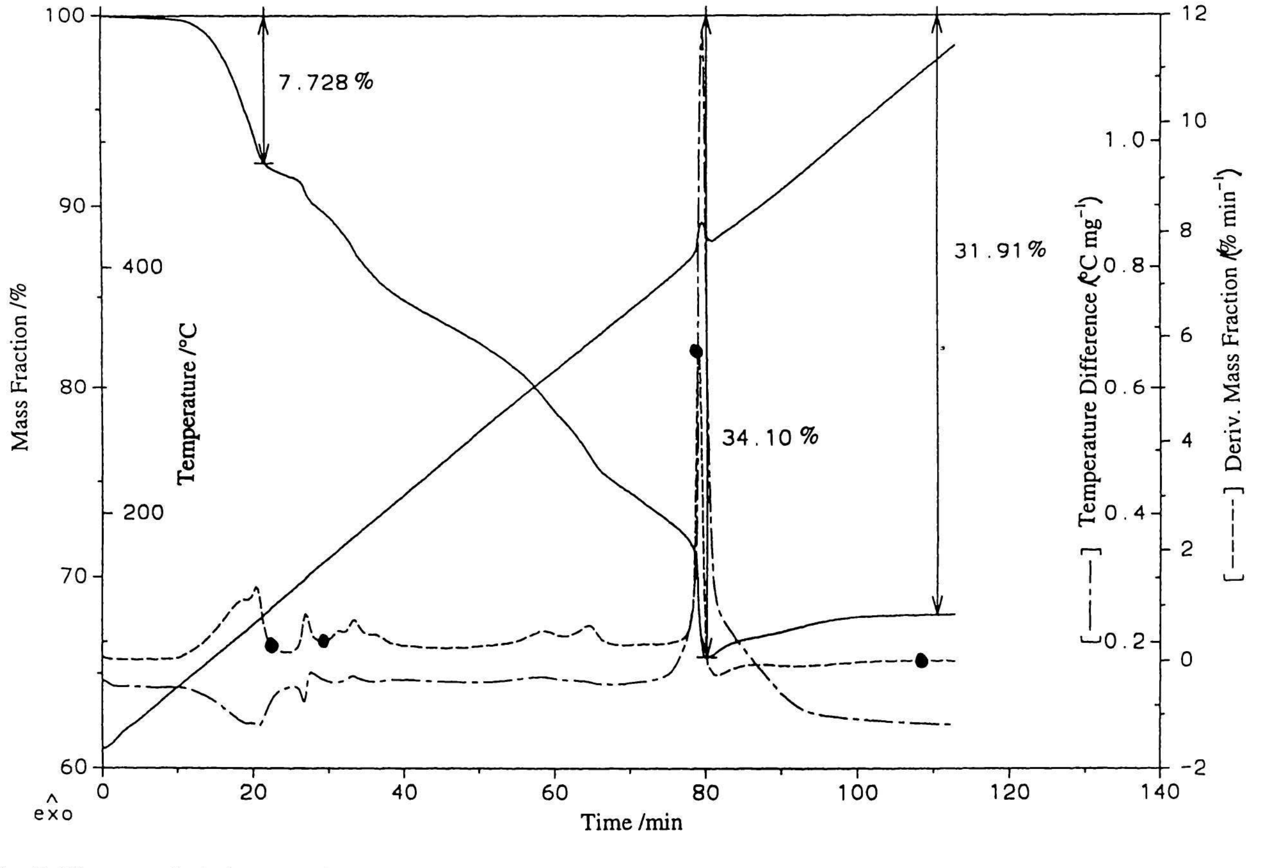

Fig. 3. Thermoanalytical curves of decavanadate **B**; thermal treatment kinetically frozen at ●.

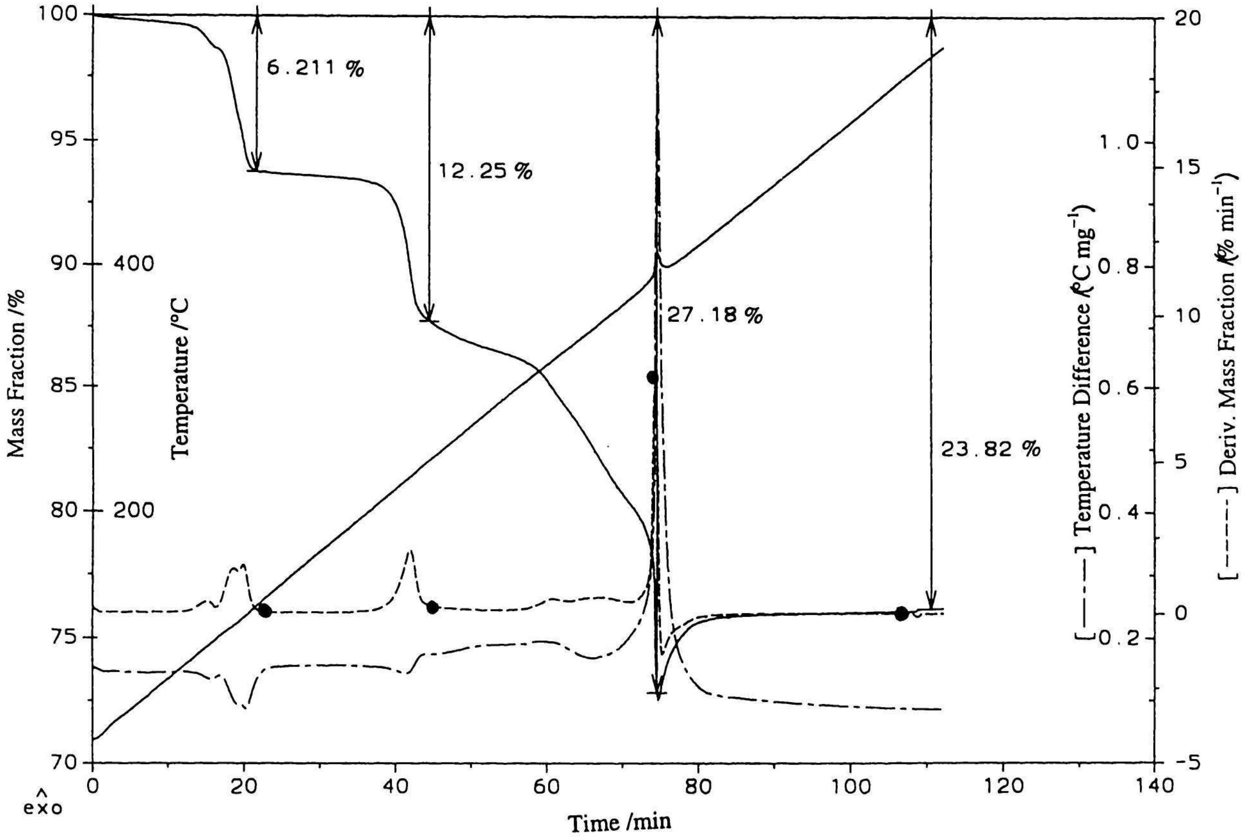

Fig. 4. Thermoanalytical curves of dihydrogendecavanadate **C**; thermal treatment kinetically frozen at ●.

Table 3. Basic Thermoanalytical Data

Compound	t_i/°C	t_m/°C	Δm_m/%	t_f/°C	Δm_f/%	Δm_c/%	(Δm_m − Δm_f)/%
$[BdaH_2](VO_3)_2$	180	453	36.68	560	36.42	36.77	0.26
$[BdaH_2]_3V_{10}O_{28} \cdot 6H_2O$	60	437	34.10	560	31.91	31.93	2.19
$[BdaH_2]_2H_2V_{10}O_{28} \cdot 4H_2O$	70	411	27.18	560	23.82	24.96	3.36

t_i – start of decomposition; t_m – maximum mass fraction loss; t_f – final mass fraction loss; Δm_m – mass fraction loss at t_m; Δm_f – mass fraction loss at t_f; Δm_c – calculated mass fraction loss.

treatment of all compounds are the mixtures where the major component is V_2O_5. The mixtures comprise also vanadium(IV) and traces of carbon (in the case of **A** and **B**). Further temperature increase leads to the increase of mass as a consequence of the oxidation of vanadium(IV) to vanadium(V). Due to the presence of traces of carbon before the discussed change in compounds **A** and **B**, the above phenomenon is a superposition of oxidations of vanadium and carbon. Chemical analysis, IR spectroscopy, and X-ray powder diffractometry confirmed that the final product of thermal decomposition of synthesized Bda polyvanadates was V_2O_5. Thermal decomposition of the studied polyvanadates represents the series of interrelated exo- and endothermal processes, these comprise dehydration, redox processes, collapse of the original structures (including the explosive decomposition of Bda cation) and, finally, formation of V_2O_5.

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