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Preparation, chemical characterization and thermal behaviour of triethylenetetrammonium isopolyoxovanadates

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Abstract

The reaction of V_2O_5 with the triethylenetetramine base (trien) in aqueous solution, using different amounts of reactants and pH conditions, yields three new polyoxovanadates of triethylenetetrammonium: $(H_4trien)(VO_3)_4 \cdot 2H_2O$ (TRIENVA1), $(H_4trien)_3[V_{10}O_{28}]_2 \cdot 7H_2O$ (TRIENVA10-I), and $(H_4trien)[H_2V_{10}O_{28}] \cdot 4H_2O$ (TRIENVA10-II). The compounds were characterized by mean of chemical analysis, IR spectroscopy and thermal analysis (TG, DTA and DTG). The IR spectra indicated the presence of the triethylenetetrammonium cation and the type of polyanion in the compounds. The thermal behaviour of the compounds was studied under argon–oxygen and argon atmospheres. The final products of the thermal decompositions were analysed by elemental analysis and X-ray powder diffraction. In argon–oxygen atmosphere, all decompositions yielded vanadium(V) oxide as the final product. In argon atmosphere, the final mass losses were far higher than those expected for vanadium pentoxide, and the final products were identified as vanadium(IV) oxide for TRIENVA1 compound and a mixture of vanadium(IV) and vanadium(III) oxides for the other compounds.

INTRODUCTION

Interest in polyoxometalates has grown increasingly in recent years because of their participation in important industrial processes [1]. Organoammonium polyoxovanadates have been used extensively as precursors for the preparation of vanadium oxides which play an important role in catalysis [2–5]. In addition, isopolyvanadates are becoming interesting models for the investigation of the interactions between organic substrates and catalytic metal oxide surfaces [3, 4].

The surrounding atmosphere and experimental conditions play an

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important role in the thermal decomposition of some polyoxovanadates as well as determining the final products [6, 7]. Because of this, it is important to emphasize these conditions, not only in the chemical and solid state characterization but also in the study of the thermal stability and behaviour of these compounds under different atmospheres. This paper deals with the syntheses, chemical characterization and thermal properties of three new isopolyoxovanadates compounds: triethylenetetrammonium metavanadate(V) dihydrate, $(H_4trien)(VO_3)_4 \cdot 2H_2O$ (TRIENVA1), bis(triethylenetetrammonium) decavanadate(V) heptahydrate, $(H_4trien)_3[V_{10}O_{28}]_2 \cdot 7H_2O$ (TRIENVA10-I), and triethylenetetrammonium dihydrogendecavanadate(V) tetrahydrate, $(H_4trien)[H_2V_{10}O_{28}] \cdot 4H_2O$ (TRIENVA10-II).

EXPERIMENTAL

Synthesis and chemical and spectroscopic characterization of the compounds

The vanadium pentoxide and triethylenetetramine base ($C_6H_{18}N_4$) were purchased from Merck and were used without further purification. Microanalyses of carbon, nitrogen and hydrogen were performed on a Perkin–Elmer 240 C, H, N analyser and vanadium was determined thermogravimetrically as V_2O_5 after thermal decomposition of the samples in an argon–oxygen atmosphere. The densities were measured by flotation in $CHBr_3/CCl_4$ [8]. Infrared spectra were recorded in the 4000–400 cm^{-1} range on a Nicolet 740 FT-IR spectrometer, and the solid compounds were mixed with fused potassium bromide and pressed into transparent discs.

Scheme 1 summarizes the syntheses of the compounds described in this paper.

$$V_2O_5(s) + \text{trien (aq)} \xrightarrow[\text{pH} = 8.1]{H_2O,\ 100\ ^\circ C} (H_4\text{trien})(VO_3)_4.2H_2O(s) \qquad (1)$$

$$\left.\begin{array}{l} V_2O_5(s) + NaOH(aq) \xrightarrow[\text{HCl, pH} = 3.8]{H_2O,\ 20\ ^\circ C} \text{Solution 1} \\ \text{trien(aq)} + HCl(aq) \xrightarrow[\text{pH} = 3.8]{H_2O,\ 20\ ^\circ C} \text{Solution 2} \end{array}\right\} \xrightarrow[\text{pH} = 3.8]{20\ ^\circ C} (H_4\text{trien})_3[V_{10}O_{28}]_2.7H_2O(s) \qquad (2)$$

$$\left.\begin{array}{r} \text{Solution 1} + HCl(aq) \xrightarrow[\text{pH} = 1.5]{H_2O,\ 20\ ^\circ C} \text{Solution 3} \\ \text{trien(aq)} \end{array}\right\} \xrightarrow[\text{pH} = 1.6]{20\ ^\circ C} (H_4\text{trien})[H_2V_{10}O_{28}].4H_2O(s) \qquad (3)$$

Scheme 1. Reactions of V_2O_5 with the triethylenetetramine base at different pH conditions.

Triethylenetetrammonium metavanadate(V) dihydrate $(H_4trien)(VO_3)_4 \cdot 2H_2O$ *(TRIENVA1)*

To a stirred aqueous suspension (60 ml) of V_2O_5 (1.47 g, 8.1 mmol) was added triethylenetetramine (1.0 ml, 6.7 mmol), and the mixture was heated under reflux for 2 h (reaction 1). The resulting yellow solution was filtered off and then allowed to stand at room temperature (pH = 8.1). Dark orange crystals of TRIENVA1 appeared after two months (yield: 0.23 g, 10%). They were filtered off, washed with water, ethanol and diethyl ether, and then dried in open air for a few hours. Crystals were found to be stable to air, light and X-ray exposure. Calculated values for $C_6H_{26}N_4O_{14}V_4$: C, 12.38; H, 4.50; N, 9.63; V_2O_5, 62.49. Analytical results: C, 11.92; H, 4.50; N, 9.71; V_2O_5, 62.96. $D_0 = 2.097(3)$ g cm^{-3}. IR (KBr, cm^{-1}): 3420 vs, br, 3065 m, 2995 m, 2920 m, 2855 m, 2725 (sh), 2660 (sh), 2495 w, 1740 w, 1600 s, 1555 m, 1510 s, 1490 w, 1470 m, 1455 m, 1400 (sh), 1330 m, 1305 m, 1260 w, 1235 w, 1205 w, 1145 m, 1105 w, 1075 m, 1050 m, 990 m, 935 vs, 910 vs, 895 vs, 830 vs, 785 s, 715 w, 625 (sh), 535 vs, br, 425 w.

Bis(triethylenetetrammonium) decavanadate(V) heptahydrate $(H_4trien)_3[V_{10}O_{28}]_2 \cdot 7H_2O$ *(TRIENVA10-I)*

Vanadium pentoxide (2.60 g, 14.3 mmol) and sodium hydroxide (0.90 g, 22.5 mmol) were dissolved with stirring at room temperature in 1000 ml of water. The resulting solution was acidified with 0.1 N HCl up to pH 3.8 (solution 1). Another solution of 1.0 ml (6.7 mmol) of triethylenetetramine in 250 ml of water was acidified at room temperature to pH 3.8 (solution 2). The resulting solution 2 was added to 100 ml of solution 1. A yellow microcrystalline powder was immediately obtained (reaction 2). This product was filtered off, washed with water, ethanol and diethyl ether, and dried in air (yield: 0.10 g, 60%). Calculated values for $C_{18}H_{80}N_{12}O_{63}V_{20}$: C, 8.68; H, 3.24; N, 6.75; V_2O_5, 72.99. Analytical results: C, 8.70; H, 3.27; N, 6.61; V_2O_5, 72.63. $D_0 = 2.321(3)$ g cm^{-3}. IR (KBr, cm^{-1}): 3440 m, 3235 w, 3015–2470 s, br, 1600 m, 1545 m, 1510 m, 1440 m, 1335 w, 1255 w, 950 vs, 805 s, 730 s, 595 (sh), 540 s, 450 m.

Triethylenetetrammonium dihydrogendecavanadate(V) tetrahydrate $(H_4trien)[H_2V_{10}O_{28}] \cdot 4H_2O$ *(TRIENVA10-II)*

This compound was prepared by a method similar to that for TRIENVA10-I. To 100 ml of the solution 1, acidified with 0.1 N HCl up to pH = 1.5, was added 0.1 ml of triethylenetetramine (0.7 mmol) (reaction 3). An orange-yellow polycrystalline powder was immediately obtained. This product was filtered off, washed with water, ethanol and diethyl ether, and dried in air (yield: 0.20 g, 50%). Calculated values for $C_6H_{32}N_4O_{32}V_{10}$: C, 6.10; H, 2.73; N, 4.74; V_2O_5, 76.95. Analytical results: C, 6.24; H, 2.74; N, 4.65; V_2O_5, 76.86. $D_0 = 2.426(5)$ g cm^{-3}. IR (KBr,

cm^{-1}): 3510 s, 3320 s, br, 3175 m, 3030 s br, 2780 s br, 1615 s, 1525 m, 1470 m, 1385 w, 1330 w, 1265 w, 1180 w, 975 vs, 855 s, 825 s, 750 (sh), 605 s, 550 s, 430 m.

Thermal studies

Thermal studies were carried out under argon–oxygen (4:1, v/v) and argon atmospheres. Thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG) were performed on a Setaram TAG 24 S 16 simultaneous thermal analyser at a heating rate of 5°C min^{-1}. All thermal analysis runs were recorded in a dynamic atmosphere. An amount of sample (23–25 mg) was weighed exactly in the platinum crucible, the thermally inert reference being 20 mg of α-Al_2O_3 previously calcinated at 1300°C for 6 hours. X-ray powder diffraction was used to identify the final products using a Philips PW 1710 instrument with Cu Kα radiation. Diffraction patterns were compared with those obtained from the ASTM powder diffraction files of the Joint Committee on Powder Diffraction Standards.

RESULTS AND DISCUSSION

Infrared spectroscopy

IR spectroscopy is a good technique for identifying the type of polyanion and the presence of protonated organic cations. The three IR spectra are quite similar from 4000 to 1000 cm^{-1}, where we find the bands corresponding to cations and water molecules. The IR spectra display broad bands between 3500 and 3400 cm^{-1} corresponding to water molecules and there are several overlapping bands of strong intensity corresponding to the stretching vibrations of the NH_3^+, NH_2^+ and CH groups between 3060 and 2490 cm^{-1}. The medium bands between 1600 and 1510 cm^{-1} are attributable to the flexion vibrations of the NH_3^+, NH_2^+ and NH groups. As expected from the literature, the bands corresponding to the anions are detectable in the 1000–400 cm^{-1} range [9]. The IR spectrum of TRIENVA1 displays several strong bands between 935 and 895 cm^{-1} associated with the symmetric stretching vibration of the *cis*-[VO_2] group. The bands at 830 and 785 cm^{-1} correspond to the anti-symmetric vibration of this group. The strong band at 535 cm^{-1} can be assigned to the stretching vibrations of the V–O_b–V group. In contrast, the IR spectra of TRIENVA10-I and TRIENVA10-II display a strong band at 950 and 975 cm^{-1}, respectively, that can be assigned to the symmetrical stretching of the terminal V–O bonds, with the corresponding anti-symmetric ones associated with the bands in the 855–730 cm^{-1} region. The anti-symmetric bridge vibrations are found at 595 cm^{-1} for TRIENVA10-I and 605 cm^{-1} for TRIENVA10-II. The symmetric vibrations are probably associated with the bands around 540 and 550 cm^{-1}. The bands in the 450–400 cm^{-1} region are assigned to the deformation modes of the two groups V–O$_t$ and V–O$_b$.

Thermal behaviour

The results of the thermal analyses under argon–oxygen and argon atmospheres are summarized in Table 1. Figure 1 shows the TG–DTG–DTA curves for the thermal decomposition of TRIENVA1 in argon–oxygen atmosphere. The compound has two water molecules which are lost in a first endothermic process. However, the dehydration step overlaps with the subsequent decomposition step and this prevents accurate determination of the final dehydration-step temperature. The

TABLE 1

Thermal analysis data for TRIENVA1, TRIENVA10-I and TRIENVA10-II in argon–oxygen and argon atmospheres

Ar + O_2					Ar				
Step	T_i	T_f	T_m [a]	Δm [b]	Step	T_i	T_f	T_m [a]	Δm [b]
TRIENVA1									
1	29	180	150(−)	12.96	1	30	180	150(−)	11.50
2	180	360	340(+)	11.80	2 [c]	180	315		8.97
3	360	400	384(+)	8.01	3 [c]	315	380		8.00
4	400	490		4.27	4 [c]	380	650		13.30
				(37.04)					(41.77)
TRIENVA10-I									
1 [d]	65	150	130(−)	5.60	1	85	190	134(−)	12.04
	150	180	160(−)	4.40	2 [c]	190	650		22.46
2 [c]	180	360		8.77					(34.50)
3	360	430	390(+)	8.60					
				(27.37)					
TRIENVA10-II									
1	60	110	97(−)	6.62	1	70	124	90(−)	2.70
2	110	220	200(+)	5.23	2	124	235	192(−)	8.48
3	220	285	260(+)	3.55	3 [c]	234	650		21.91
4	285	375	300(+)	7.74					(33.09)
				(23.14)					

[a] Endothermic (−) or exothermic (+) process. [b] Total mass losses are shown in parentheses. [c] Progressive mass loss without clear peaks in DTG and/or DTA curves. [d] Overlapping steps.

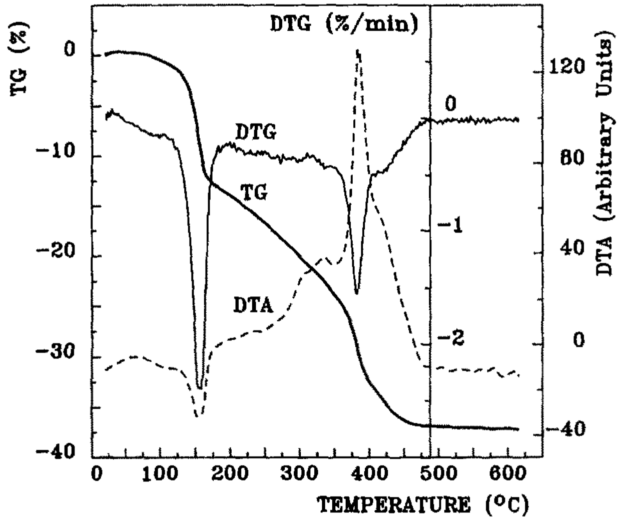

Fig. 1. Thermal decomposition of TRIENVA1 in an argon–oxygen atmosphere.

thermal decomposition is followed by a progressive mass loss with poorly resolved peaks in the DTG curves and no clear peaks in the DTA curve up to 360°C. It finishes with a strong exothermic process which leads to V_2O_5 as the final product above 490°C.

TRIENVA10-I and TRIENVA10-II start their decomposition above 60°C, losing their water molecules in an endothermic process (Fig. 2). For TRIENVA10-I, the dehydration step overlaps with another endothermic process. Its thermal decomposition finishes after a strong exothermic step which yields V_2O_5 above 430°C. Thermal decomposition of TRIENVA10-II follows immediately after the dehydration step with three exothermic processes which lead to V_2O_5 above 375°C.

In order to study possible differences in the thermal behaviour of

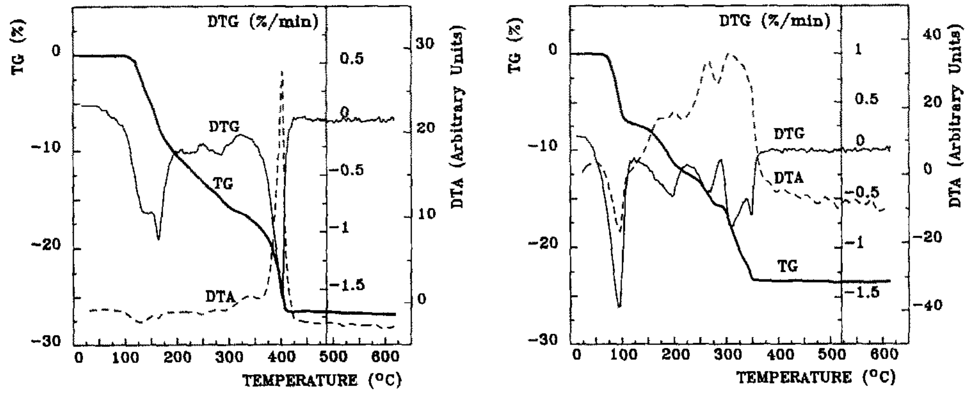

Fig. 2. TG, DTA and DTG curves for the thermal decomposition of TRIENVA10-I (left) and TRIENVA10-II (right) in an argon–oxygen atmosphere.

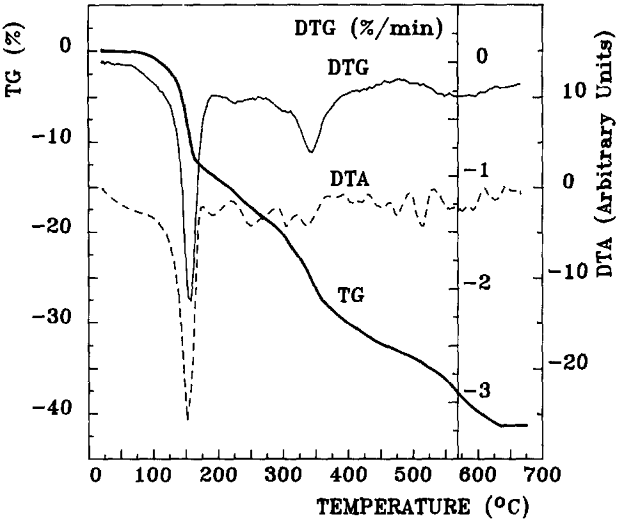

Fig. 3. Thermal decomposition of TRIENVA1 in an argon atmosphere.

alkylpolyammonium isopolyvanadates, decomposition in inert argon atmosphere was performed. Figures 3 and 4 show the thermal decomposition for the compounds in inert atmosphere. The thermal decompositions begin with the dehydration steps which overlap with an endothermic process which is attributed to oxidation, at least partially, of the organic cation by the metalate-oxygen core [5]. This decomposition step is followed by several endothermic processes and a progressive mass loss with poorly resolved peaks in the DTG curve, corresponding to the pyrolysis of the organic cation and the reduction of V_2O_5. At 650°C, the total mass losses are far higher than those expected for vanadium pentoxide as the final product. Chemical analysis and X-ray powder diffractograms show that the final residue is V_2O_4 for TRIENVA1 and a

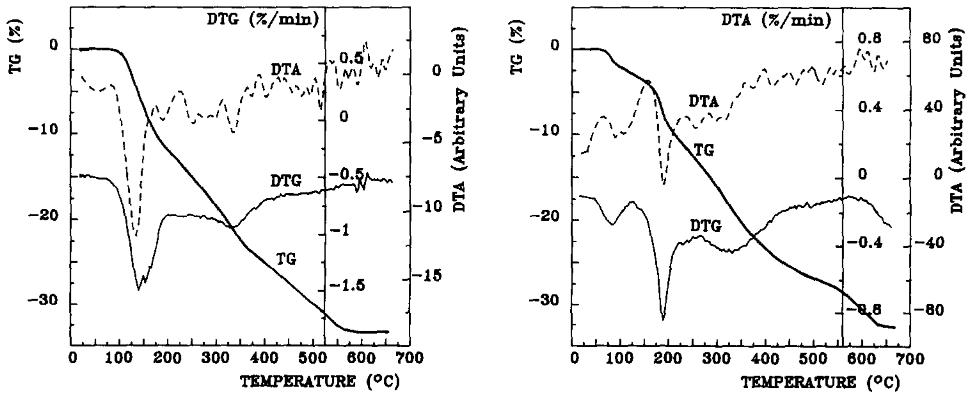

Fig. 4. TG, DTA and DTG curves for the thermal decomposition of TRIENVA10-I (left) and TRIENVA10-II (right) in an argon atmosphere.

mixture of V_2O_4 and V_2O_3 for TRIENVA10-I and TRIENVA10-II. These reduced vanadium oxides are formed during the catalytic decomposition of NH_3 on the surface of V_2O_5 as is suggested in the literature [10, 11].

On cooling the thermobalance down to 100°C and reheating the sample to 650°C in an argon–oxygen atmosphere, there is an increase in mass which is related to the occurrence of a strong exothermic peak in the DTA curve at around 350°C. At 650°C, the weight of the residues in the crucible were in accordance with that calculated for V_2O_5. The exothermic process can be explained by the metal oxidation, which releases a high amount of energy at this temperature [12].

CONCLUSIONS

The reaction of V_2O_5 with triethylenetetramine base in aqueous solution, using different amounts of reactants and pH conditions, yields three new polyoxovanadates salts which have been characterized by elemental analyses and thermal and spectroscopic techniques. The IR spectroscopy not only reveals the presence of cations and water molecules but also identifies the type of anion in the compounds. The results indicate that the thermal decomposition of the triethylenetetrammonium isopolyvanadates, as well as the final products which are formed, are influenced by the surrounding atmosphere and the starting compound. Whereas the thermal decompositions under an excess of oxygen lead to V_2O_5 as the final solid stable product, in an inert atmosphere the organoammonium cation reduces, direct or indirectly, the vanadium atoms of the polyanion, leading to different vanadium oxides which depend on the starting compound.

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