Thermal behaviour and properties of *n*-alkylammonium decavanadates

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Abstract

The thermal behaviour of three *n*-alkylammonium decavanadates with the general formula $[(C_nH_{2n+1})NH_3][V_{10}O_{28}] \cdot 2H_2O$ where $n = 4$–6, has been studied by thermogravimetry (TG and DTG) and differential thermal analysis (DTA) under argon–oxygen and argon atmospheres from room temperature to 600°C. The surrounding atmosphere is an important factor which significantly influences the course of the decomposition reaction and the final products. In an argon–oxygen atmosphere the compounds lose two water molecules during a first endothermic step to give a stable anhydrous compound. A relationship has been found between the density values of the compounds and the dehydration temperature range. The anhydrous compounds decompose via several oxidative exothermic processes to give vanadium(V) oxide. No other stable products were found during the thermal decomposition owing to the overlap of these last oxidative processes. The thermal decompositions in an argon atmosphere begin with a similar dehydration step for the three compounds followed by a progressive weight loss. The final products at 600°C in an inert atmosphere were identified by X-ray powder diffraction data as mixtures of vanadium(IV) and vanadium(III) oxides. The essential thermal features, as well as the influence of the crystal structure of the *n*-alkylammonium decavanadates on their thermal behaviour, are also reviewed and discussed.

INTRODUCTION

Polyoxovanadates may be considered as analogous to metal oxide surfaces, and as such have received considerable attention as catalysts for studying the interactions between organic substrates and catalytic metal oxide surfaces [1]. Isopolyvanadates with protonated cations are used as precursors for the preparation of vanadium oxides, which play an important role in catalysis. These oxides, which are normally prepared by means of thermal decomposition of precursors previously deposited on the catalyst carriers, may be useful to support other metals, to improve the

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efficiency of oxidative processes catalyzed by other metal oxides, and to catalyze oxidative processes involving organic reactions [2–5]. It is interesting to study the thermal properties of polyoxovanadates in different atmospheres and conditions because of the influence of the surrounding atmosphere on the thermal decomposition of polyoxometallates and on the different metallic oxides obtained [5–8].

The influence of water molecules in stabilization of the polyvanadates has been extensively studied. It has been found that most of the voluminous polyoxovanadates, such as $[V_{10}O_{28}]^{6-}$, exist as discrete structural units in the form of crystallohydrates [9]. However, thermal decomposition of some hydrated polyvanadate salts may lead, depending on the counterion, to anhydrous isopolyvanadates which can be isolated and identified. Because of the importance of water molecules in polyvanadate salts, a more extensive study on the dehydration step, and on the stable intermediate solid products resulting from it, needs to be carried out in order to relate water molecules and counterions to crystal structure stabilization in different polyoxovanadates.

In this context, and during the course of our general research programme on synthesis, structural characterization and thermal behaviour of some organoammonium polyoxometallates [6,7,10,11], we decided to study the thermal properties and thermochemistry of some n-alkylammonium decavanadates by means of techniques such as TG, DTG and DTA. Our interest in the thermal behaviour of organoammonium polyvanadates is aimed at revealing the relationship between the nature and size of the cation and the thermal features of the individual salts, and between their hydration condition and their thermal stability. We are also looking for new ways of preparing anhydrous polyvanadates containing such voluminous ions as $[V_{10}O_{28}]^{6-}$, as well as vanadium oxides with catalytic properties.

In this paper we report the essential thermal features and the influence of crystal packing on the thermal behaviour of three alkylammonium decavanadates: hexakis(n-butylammonium) decavanadate(V) dihydrate (BUTVA10), hexakis(n-pentylammonium) decavanadate(V) dihydrate (PENTVA10) and hexakis(n-hexylammonium) decavanadate(V) dihydrate (HEXVA10).

EXPERIMENTAL

Vanadium pentoxide and alkylamine bases were purchased from Merck and were used without further purification. The compounds under investigation were obtained by direct reaction between vanadium pentoxide and the corresponding alkylamine base in aqueous solution as described in a previous paper [11]. The chemical characterization of the three compounds was reported in the same reference, as well as the crystal structure of the

TABLE 1

Crystal data for the compounds BUTVA10, PENTVA10 and HEXVA10

	BUTVA10 [a]	PENTVA10 [a]	HEXVA10 [b]
Formula weight	1438.30	1522.47	1606.63
Space group	$P2_1/m$	$P2_1/m$	$P2_1/a$
a (Å)	16.91(2)	17.18(2)	10.190(5)
b	19.59(1)	20.57(2)	18.206(4)
c	16.29(2)	16.30(5)	19.126(4)
β (deg)	102.7(1)	101.7(2)	105.35(3)
V (Å³)	5269(6)	5645(12)	3447(2)
Z	4	4	2
$F(000)$	2928	3120	1656
D_0 (mg m^{-3})	1.83(1)	1.77(1)	1.57(1)
D_x	1.82	1.77	1.55

[a] X-ray powder diffraction data.
[b] X-ray single crystal data.

n-hexylammonium decavanadate(V) dihydrate. Table 1 shows the crystal data for the three compounds.

Thermal studies were carried out under argon and argon–oxygen (4:1) atmospheres from room temperature to 600°C. Thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG) were performed on a SETARAM TAG 24 S 16 simultaneous thermal analyzer at a heating rate of 5°C min^{-1}. All thermal decompositions were monitored in a dynamic atmosphere with a flow rate of 40 cm^3 min^{-1}. An amount of sample (15–20 mg) was exactly weighed into the platinum crucible. The thermally inert reference was 15 mg of α-Al$_2$O$_3$ previously calcinated at 1300°C for 5 h.

RESULTS AND DISCUSSION

The main features of thermal decomposition for all compounds in an argon–oxygen atmosphere are quite similar, leading to a residual weight equal to that expected for V$_2$O$_5$. Figure 1 gives the TG and DTA curves for the compounds BUTVA10, PENTVA10 and HEXVA10 under an argon–oxygen atmosphere. Table 2 lists the steps, initial and final temperature (°C), partial and total weight loss, enthalpy (endothermic or exothermic) and maximum peak for each step in the thermal decomposition of the compounds in the argon–oxygen atmosphere.

Thermal decomposition starts with an endothermic step due to the loss of the two water molecules. The dehydration process leads to the corresponding anhydrous decavanadate salt for the three compounds BUTVA10, PENTVA10 and HEXVA10 [reaction (1)] but, in contrast to the anhydrous n-butyl- and n-pentylammonium decavanadates, the n-hexylammonium
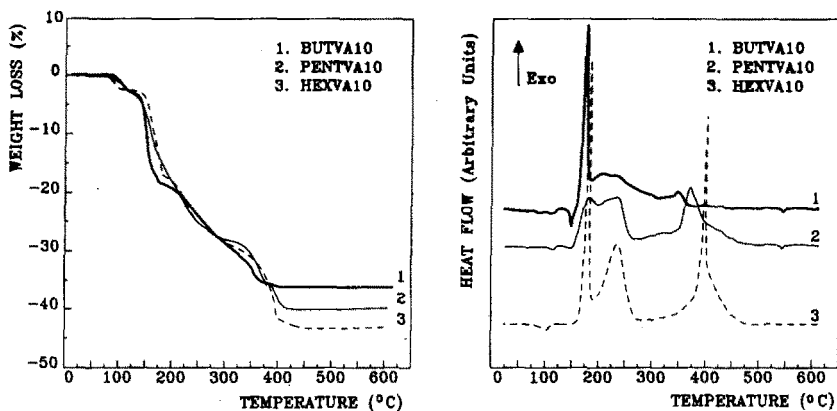
Fig. 1. TG (left) and DTA (right) curves for the thermal decomposition of the compounds BUTVA10, PENTVA10 and HEXVA10 in an argon–oxygen atmosphere.

decavanadate is stable over a wider range of temperatures (115–130°C). This last compound has been identified by elemental analysis and IR spectra.

$$(HB)_6[V_{10}O_{28}] \cdot 2H_2O \xrightarrow{[O],\Delta} (HB)_6[V_{10}O_{28}] + 2H_2O \tag{1}$$
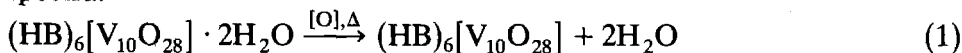
TABLE 2

Steps, initial and final temperature (°C), partial and total weight loss, enthalpy and maximum peak for each step in the thermal decomposition of the three compounds in an argon–oxygen atmosphere

Compound	T_i	T_f	T_m	ΔH	Δm (%)	$\Sigma \Delta m$ (%) [a]
BUTVA10	92	131	114	Endo	2.62	
	131	185	179	Exo	16.51	
	185	315	311	Exo	12.50	
	315	400	383	Exo	4.88	36.51
						(36.76)
PENTVA10	90	126	115	Endo	2.49	
	126	199	183	Exo	14.82	
	199	273	234	Exo	8.80	
	333	408	372	Exo	7.65	
	408	450				39.20
						(40.20)
HEXVA10	68	115	104	Endo	2.32	
	130	188	186	Exo	14.51	
	188	270	235	Exo	9.31	
	372	424	404	Exo	9.79	
	424	500				43.06
						(43.36)

[a] Calculated value for V_2O_5 as final product is shown in parentheses.

Thermoanalytical data indicate that temperature limits for this dehydration step show some dependence on the compound density, and there is a shift towards higher temperature values in the denser crystal structures. For the compounds BUTVA10, PENTVA10 and HEXVA10 the final temperature of the dehydration steps are 131, 126 and 115°C, respectively. It is important to note that the difference between the final temperature of the dehydration step for the compounds BUTVA10 and PENTVA10 is smaller than that for PENTVA10 and HEXVA10. A possible explanation of this shift towards higher temperatures can be ascribed to the different interactions of water molecules in the crystal lattice. Crystal structures of decavanadates are stabilized via hydrogen bonding networks. Water molecules participate in these networks, interacting via hydrogen bonding with oxygen atoms from the polyanions and nitrogen atoms from the cations, and play an important role in the stability of the crystal structure; even more, voluminous polyvanadates such as $[V_{10}O_{28}]^{6-}$ exist as isolated structural units in the form of crystallohydrates.

The BUTVA10 and PENTVA10 compounds are isostructural, but the a and b parameters are slightly different ($a,b_{BUTVA10} < a,b_{PENTVA10}$). This effect leads to smaller density values and a lower thermal stability in compound PENTVA10. The compound HEXVA10 crystallizes in a different space group and has the lowest density value. In the crystal structure the decavanadate anions form layers along the [010] direction. The n-hexylammonium cations occupy the space among these layers, with the nitrogen atoms forming hydrogen bonds with the oxygen atoms of the polyanion and the water molecules [11]. This hydrogen bonding interaction together with the electrostatic interactions stabilize the crystal structure. However, because there are no interactions of the type O_w–H $\cdots$ O_w between water molecules, and the organic chain has at least one methylene group more (leading to lower thermal stability) than n-butyl and n-pentylamine, the crystal packing is less effective and the temperature range of the dehydration step is shifted towards lower temperatures. Similar behaviour has been described for the family of isostructural n-alkylammonium heptamolybdates [7].

The thermal decomposition processes for the three compounds continue essentially with three exothermic steps corresponding to different oxidation processes, where all DTG peaks have their parallel exothermic DTA peaks. Isolation of the intermediate products after the dehydration step was difficult because of the overlap of the oxidation processes. Attempts to correlate the results with the theoretical weight losses were not successful, except for the anhydrous decavanadate salts and the final solid products. The thermal decompositions finish when a constant weight is achieved above 400, 450 and 500°C for the compounds BUTVA10, PENTVA10 and HEXVA10, respectively. The observed final solid product was identified by its X-ray powder diffraction pattern and IR spectra as V_2O_5. It is supposed
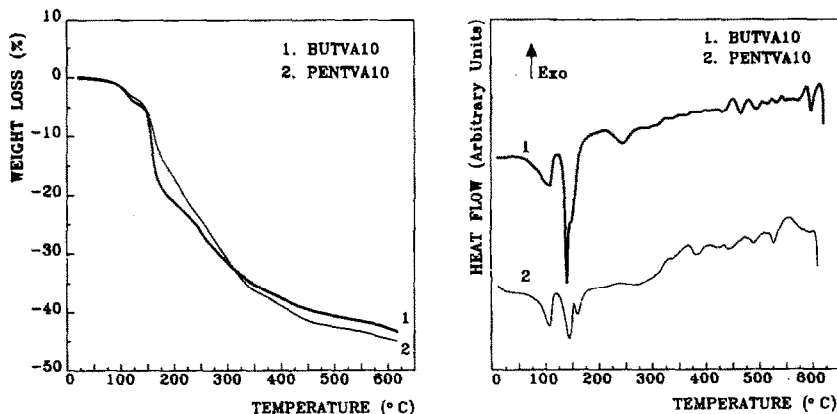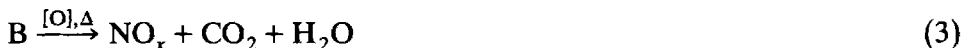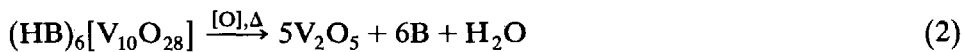
Fig. 2. TG (left) and DTA (right) curves for the thermal decomposition of the compounds BUTVA10 and PENTVA10 in an argon atmosphere.

that anhydrous decavanadates are decomposed as shown by reaction (2) and unidentified organic intermediate compounds are oxidized as shown in (3).

$$(HB)_6[V_{10}O_{28}] \xrightarrow{[O],\Delta} 5V_2O_5 + 6B + H_2O \tag{2}$$

$$B \xrightarrow{[O],\Delta} NO_x + CO_2 + H_2O \tag{3}$$

In order to study possible differences in the thermal behaviour of the alkylammonium decavanadates, thermal decompositions in argon as inert atmosphere were performed. Figure 2 displays the TG and DTA curves for the decomposition of BUTVA10 and PENTVA10 in an argon atmosphere. A comparison of the thermal behaviour of HEXVA10 in the two atmospheres is shown in Fig. 3. Thermoanalytical data are listed in Table 3. The thermal behaviour in an inert atmosphere is quite different from that in an oxidative atmosphere. Whereas the compounds BUTVA10 and PENTVA10 show no exothermic steps during the thermal decomposition, the compound HEXVA10 presents some exothermic peaks.

The loss of water molecules takes place in temperature ranges similar to those in the oxidative atmosphere for the compounds BUTVA10 and PENTVA10, but this range is shifted to higher temperatures for the n-hexylammonium decavanadate dihydrate. Thermal decomposition in an inert atmosphere leads to a lower number of steps, and a progressive weight loss takes place without clear peaks in the DTG and DTA curves. In the argon atmosphere, the decomposition does not lead to a constant weight until 600°C is reached. At this temperature, total weight losses are far higher than those expected for a final product of vanadium pentoxide.
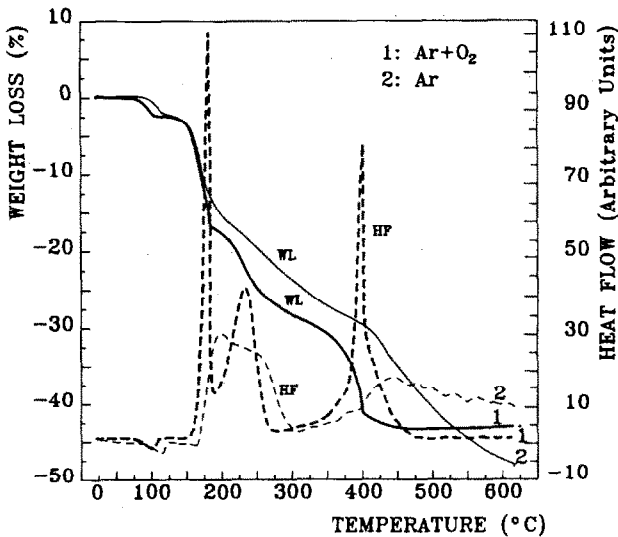
Fig. 3. Thermal decomposition of HEXVA10 in an argon–oxygen and in an argon atmosphere.

The solid final residues have been identified by X-ray powder diffraction patterns as mixtures of vanadium(IV) and vanadium(III) oxides. Some authors have suggested that the catalytic decomposition of NH_3 on the surface of V_2O_5 could cause some degree of reduction of the oxide [12–14] or that it is possible that a product formed during the thermal decomposi-

TABLE 3

Steps, initial and final temperature (°C), partial and total weight loss, enthalpy and maximum peak for each step in the thermal decomposition of the three compounds in an argon atmosphere

Compound	T_i	T_f	T_m	ΔH	Δm (%)	$\Sigma \Delta m$ (%)
BUTVA10	90	130	116	Endo	2.55	
	130	160	150	Endo	5.22	
	155	192	157	Endo	7.25	
	192	600 [a]				43.80
PENTVA10	90	127	116	Endo	2.50	
	127	155	152	Endo	6.51	
	160	191	166	Endo	9.84	
	191	600 [a]				45.00
HEXVA10	84	122	116	Endo	2.28	
	136	220	138	Exo	14.65	
	220	308	223	Exo	7.10	
	308	600 [a]				48.06

[a] Progressive weight loss without clear peaks in the DTG and DTA curves.

tion of the organic base could produce some reduction of the metal atom or react with it to give metal oxocarbides or metal carbides [7]. In our case, elemental analyses of the final black products give no indication of C present in the composition. On cooling the thermobalance down to 400°C and reheating the sample up to 600°C in oxygen, first there is an abrupt increase in mass over a short temperature range, which is related to a strong exothermic peak in the DTA curve. The increase in mass continues without clear peaks in the DTG and DTA curves up to 600°C. At this temperature the weights of the residue in the crucible were in accordance with that calculated for V_2O_5. The exothermic process could be a result of the oxidation of the vanadium(III) and vanadium(IV) oxides.

CONCLUSIONS

The thermal behaviour of the *n*-alkylammonium decavanadates described in this paper under an argon–oxygen atmosphere is quite different from that under an argon atmosphere because of the influence of oxygen on the thermal decomposition processes. Whereas thermal decomposition under an excess of oxygen leads to V_2O_5 as the final stable solid product, in an inert atmosphere the organoammonium cation reduces, direct or indirectly, the vanadium atoms of the polyanion to give a mixture of vanadium(IV) and vanadium(III) oxides at 600°C.

Although several intermediate steps take place in an argon–oxygen atmosphere before the final products are formed, only the *n*-hexylammonium decavanadate anhydrous salt has been identified because of the overlap of the oxidative processes.

It is important to recognize the influence of the crystal packing and of the water molecules on the stability of the compounds, as dehydration temperature ranges are strongly influenced by the crystal packing of the compounds. In general, a gradual shift towards higher temperatures is observed as the density values increase.

ACKNOWLEDGEMENTS

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