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Thermal properties of pyridinium and imidazolium hexavanadates

V. Suchá * and Ľ. Žúrková

Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, 84215 Bratislava (Slovak Republic)

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Abstract

The thermal decomposition of pyridinium (PyH) and imidazolium (ImH) hexavanadates, $(PyH)_2V_6O_{16} \cdot H_2O$ and $(ImH)_2V_6O_{16} \cdot H_2O$, was studied by dynamic methods. The decomposition is influenced by the properties of the cation. PyH, which is thermally more stable, gives rise to the $(PyH)HV_6O_{16}$ intermediate at 275°C which is then decomposed at 420°C to a V_2O_5–V_3O_7 mixture. ImH is successively decomposed from 200°C and urea is formed as one component of the decomposition product. Vanadium pentoxide is the final decomposition product of both hexavanadates.

INTRODUCTION

Studies on the thermal properties of polyvanadates with inorganic cations have shown that the course of the thermal decomposition depends mainly on the cation properties and on the stoichiometry of the compound [1–8].

The $M_2V_6O_{16}$ hexavanadates, where M is K^+, Rb^+, Cs^+, Tl^+ or $NH_4{}^+$, are isostructural layer polymers [9, 10]. Except for the NH_4^+ salt, they are the thermally most stable polyvanadates [3, 4]. Hexavanadates with small mono- or divalent metals exist only as crystallohydrates which are all thermally unstable. Their dehydration is accompanied by structure decomposition and formation of new types of polyvanadates, the "vanadium–oxygen bronzes" and oxides of V(V) and V(IV) [5, 8]. The compounds formulated as $M^I_{2-x}H_xV_6O_{16} \cdot nH_2O$ [6, 8] or $M^I_2V_{12}O_{31} \cdot nH_2O$ [11, 12] have thermal properties that are similar to those of $M^I_2V_6O_{16} \cdot nH_2O$ and $M^{II}V_6O_{16} \cdot nH_2O$.

Very few papers reporting the thermal properties of polyvanadates with organic cations have been published. They deal either with a comparison of the thermal stabilities of compounds having the same stoichiometry or with

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* Corresponding author.

the identification of the final decomposition products [13–17]. In refs. 18 and 19, the thermal properties of V_2O_5 intercalates with organic molecules or with cations also containing V(IV) were described.

We report here a study of the thermal decomposition of PyH and ImH hexavanadates which presents new data on the thermal properties of the polyvanadates with organic cations and is a contribution towards the identification of the relation between the cation properties and the course of the thermal decomposition of a polyvanadate.

METHODS

The hexavanadates, $(PyH)_2V_6O_{16} \cdot H_2O$ **A** and $(ImH)_2V_6O_{16} \cdot H_2O$ **B**, were prepared according to ref. 20 and were identified by chemical analysis, IR spectra and X-ray powder diffraction patterns.

The thermal analysis was performed on a Derivatograph Q-1500 (MOM Budapest), with the following conditions: air atmosphere, sample mass 100 mg, heating rates 10 and 5°C min^{-1}, Pt crucible, Al_2O_3 reference material, and temperature interval 20–700°C. The thermal analysis of **A** was interrupted at 275, 350, 415 and 480°C, and of **B** at 240, 260, 305, 375 and 480°C.

The products at the individual DTA temperatures were cooled to room temperature and then identified by chemical analysis, IR spectroscopy and X-ray phase analysis.

The IR spectra in Nujol mulls or KBr pellets were measured on a Specord M80 spectrophotometer (Zeiss, Jena). The X-ray powder diffraction measurements were performed on a Philips PW 1050 diffractometer using Cu Kα radiation.

Carbon, hydrogen and nitrogen contents were estimated on a 1106 CHN-analyzer (Carlo Erba). V(V) was estimated by titration with $FeSO_4$ and diphenylamine as indicator. The total vanadium content V_{tot} was estimated gravimetrically as V_2O_5. V(IV) was calculated from the $V_{tot} - V(V)$ difference. Pyridine was identified by CGC using a mass detector (Hewlet Packard GC 5890, Series II with MSD 5971A). Urea was estimated after enzymatic hydrolysis by urease and by detection of the released ammonia by Nessler's reagent [21].

RESULTS AND DISCUSSION

The thermal decomposition of **A** (Fig. 1) is a multi-step process. Two exothermic peaks can be observed on the DTA curve: the first in the temperature interval 175–275°C (with maximum at 240°C) and the second in the interval 280–475°C (with a marked maximum at 375°C).

To explain the first process, we interrupted the heating at 275°C and identified the product formed. Based on the results of the chemical analyses (Table 1), the composition of the product can be given by the formula $(PyH)HV^{V}_{6-n}{}^{IV}_{n}O_{16-n/2}$, where $n = 0.18$.

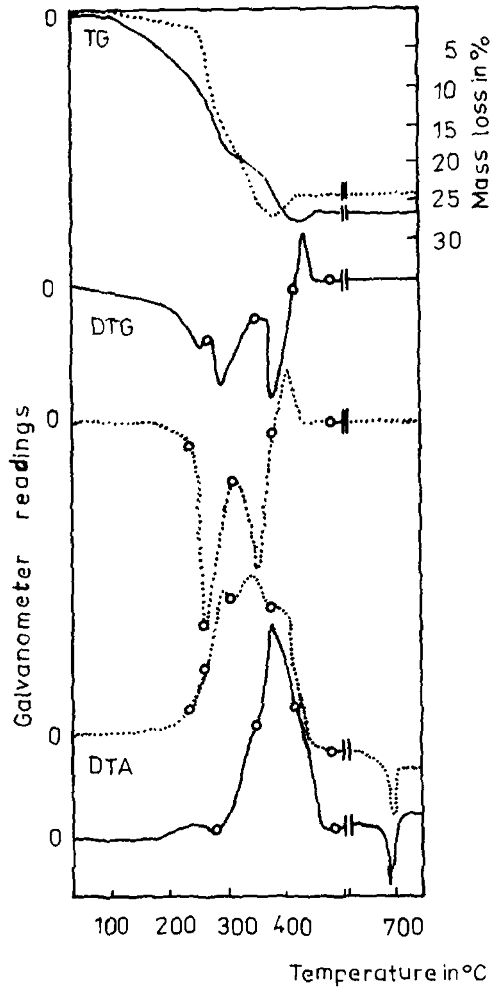

Fig. 1. Thermoanalytical curves of $(PyH)_2V_6O_{16} \cdot H_2O$ (—) and $(ImH)_2V_6O_{16} \cdot H_2O$ (···): O, heating interruption.

The comparison of the IR spectra and X-ray diffraction patterns (Figs. 2 and 3), of both the starting compound and its decomposition products, indicates a certain deformation of the parent structure, without, however, any essential change in the arrangement of the hexavanadate anion. The IR spectrum of the decomposition product exhibits all the bands characteristic for the PyH cation [22, 23]. The exothermic process can be described by

$$(PyH)_2V_6O_{16} \cdot H_2O(s) \rightarrow$$
$$(PyH)HV^{V}_{6-n}V^{IV}_{n}O_{16-n/2}(s) + Py(g) + H_2O(g) + (n/2)O(g) \qquad (1)$$

where $n = 0.18$.

TABLE 1

Chemical analysis of the PyH and ImH hexavanadates and of their decomposition products

Product		%V(V)	%V(IV)	%C	%N	%H
$(PyH)_2V_6O_{16} \cdot H_2O$	Calc.	41.32		16.23	3.78	1.95
	Found	41.40		16.03	3.80	1.64
275°C[a]	Calc.	46.23	1.43	9.36	2.18	1.10
	Found	45.90	1.48	9.18	2.14	1.00
350°C	Found	45.24	4.98	3.98	1.17	0.63
415°C[b]	Calc.	47.37	9.47			
	Found	47.14	9.30			
480–700°C	Calc.	56.10				
	Found	55.90				
$(ImH)_2V_6O_{16} \cdot H_2O$	Calc.	42.58		10.04	7.80	1.68
	Found	42.31		10.34	8.00	1.49
240°C	Found	44.84	3.42	8.55	7.42	1.32
$n_C:n_N = 2.68:2.00$						
260°C	Found	37.56	9.28	6.67	6.05	1.08
$n_C:n_N = 2.56:2.00$						
305°C	Found	35.93	14.58	2.69	4.01	0.98
$n_C:n_H = 2.00:2.56$						
375°C	Found	37.42	15.13	tr.[d]	tr.	tr.
480–700°C	Calc.	56.10				
	Found	55.53				

[a] $(PyH)HV^{V}_{6-n}V^{IV}_{n}O_{16-n/2}$. [b] $V_3O_7 + 1.5V_2O_5$. [c] V_2O_5. [d] tr, traces.

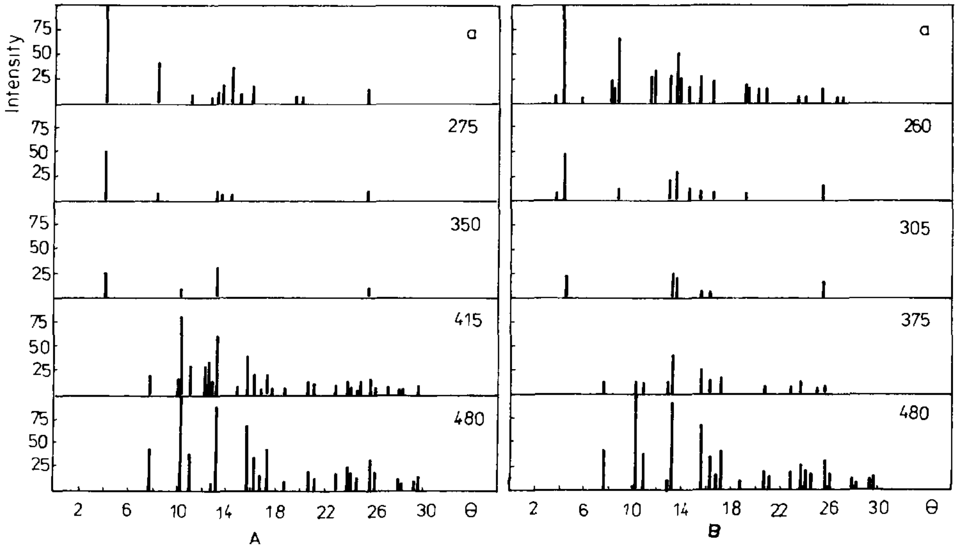

Fig. 2. Powder diffraction patterns of (A) $(PyH)_2V_6O_{16} \cdot H_2O$ **A**, (B) $(ImH)_2V_6O_{16} \cdot H_2O$ **B**, and of their decomposition products.

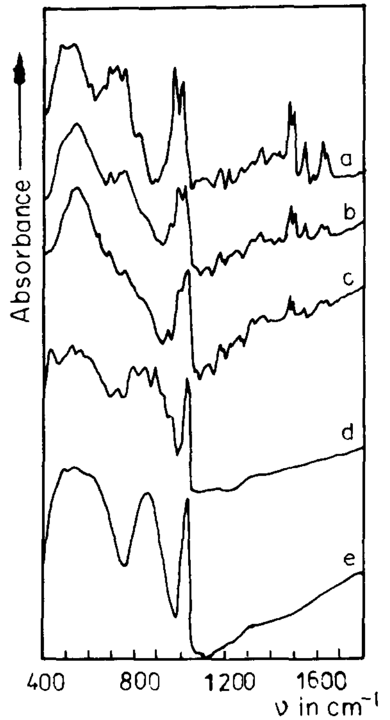

Fig. 3. IR spectra of $(PyH)_2V_6O_{16} \cdot H_2O$ (a) and of the decomposition products obtained at 275°C (b), 350°C (c), 415°C (d) and 480°C (e).

On the TG curve, the corresponding mass loss up to 275°C, 13.20%, is in very good agreement with the value of 13.32% calculated for eqn. (1). The release of molecular pyridine from **A** was confirmed as follows: **A** was heated in a distillation apparatus under the same conditions as used in DTA and the condensate obtained was identified by CGC as pyridine.

The second exothermic process in the temperature interval 280–475°C is manifested on the DTA curve by the very intense peak with a marked maximum at 375°C, and also by weak maxima at 330 and 435°C which indicate that there are more overlapping processes in this interval.

The IR spectrum proves unambiguously that PyH is present in the product obtained at 350°C (Fig. 3). The changes in the positions of the V–O band clearly correspond to a greater decomposition of the anion structure and probably also to the presence of a small amount of V_2O_5 (Figs. 2 and 3). V(IV) in the decomposition product can be caused by presence of further admixture.

From the X-ray analysis (Fig. 2), the decomposition product obtained at 420°C is a V_2O_5–V_3O_7 mixture. The oxides were identified according to refs. 24 and 25; more over, V_2O_5 is also indicated in the IR spectrum (Fig. 3).

The thermal decomposition of the hexavanadate up to 420°C can be described by

$$(PyH)HV^{V}_{6-n}V^{IV}_{n}O_{16-n/2}(s) \rightarrow$$
$$V_3O_7(s) + 1.5V_2O_5(s) + Py(g) + H_2O(g) + (n/2)O(g) \quad (2)$$

where $n = 0.18$.

On the TG curve, the corresponding mass loss up to 415°C, 27.50%, is in good agreement with the value of 27.33% calculated for eqn. (2). In the interval 415–450°C, a mass increase of 1.0% was observed on the TG curve, probably due to the reaction

$$V_3O_7(s) + 1.5V_2O_5(s) + 0.25O_2(g) \rightarrow 3V_2O_5(s) \quad (3)$$

The final decomposition product at 480°C is V_2O_5 (Table 1, Figs. 2 and 3). The endothermic process with a minimum at 685°C corresponds to the melting of V_2O_5.

In the temperature interval 175–466°C, the DTA curve of $(ImH)_2V_6O_{16} \cdot H_2O$ exhibits overlapping exothermic peaks with maxima at 290, 345 and 375°C and an endothermic peak with a minimum at 690°C (Fig. 1). The TG and DTG curves show that the mass loss is moderate up to 240°C and that the rate of decomposition is highest in the interval 240–305°C (maximum 260°C). The maximum mass loss, 27.00%, was reached at 375°C. The final mass loss at 420°C, 24.00%, is in agreement with the value calculated for

$$(ImH)_2V_6O_{16} \cdot H_2O \rightarrow 3V_2O_5 + \text{gaseous products} \quad (4)$$

The thermal decomposition of compound was interrupted at the temperatures shown in Fig. 1. Because the C:N molar ratios for the intermediates formed on thermal decomposition and for **B** are different (Table 1), the heating must cause a bond cleavage in the imidazolium ring such that gas products with higher carbon contents are formed, while organic molecules with higher nitrogen contents, urea, remain in the solid phase. The urea is manifested on the IR spectrum by characteristic bands in the 1700–1400 cm^{-1} region: σ(NH) at 1670 and 1622 cm^{-1}, γ(CO) at 1605 cm^{-1} and γ(CN) at 1468 cm^{-1} [26]. These bands also occur in the spectrum of the decomposition product obtained at 220°C. The maximum urea and minimum ImH contents were observed at 305°C (Fig. 4). Urea was estimated qualitatively according to ref. 21, and also in the aqueous solution obtained by extracting the intermediate formed at 305°C.

The redox reactions of decomposition also involve reduction of V(V) to V(IV) and simultaneous oxygen release from the hexavanadate anion. During heating, in addition to dehydration, decomposition of the hexavanadate structure and crystallization of V_2O_5 take place. The structure of hexavanadate is only deformed up to 260°. Its decomposition is

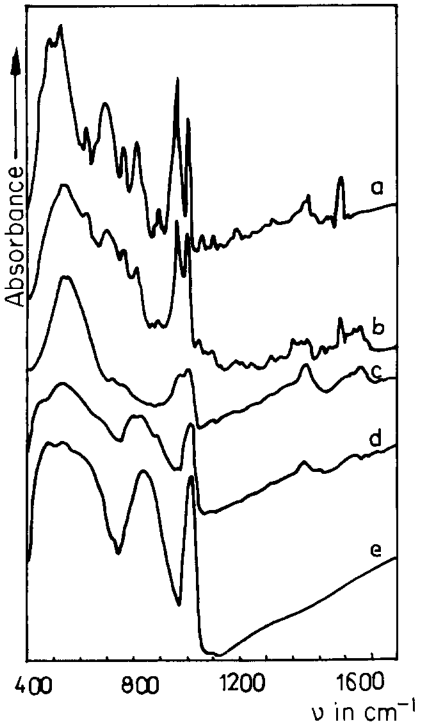

Fig. 4. IR spectra of $(ImH)_2V_6O_{16} \cdot H_2O$ (a) and of the decomposition products obtained at 260°C (b), 305°C (c), 375°C (d) and 480°C (e).

complete at 305°C when V_2O_5 starts to crystallize. The X-ray diffraction pattern and the IR spectrum (Figs. 2 and 4) of the product obtained at 375°C prove the presence of V_2O_5, although, a high content of V(IV), indicating the presence of admixtures, was found in this product (Table 1).

In the temperature interval 375–480°C, the final traces of the organic compound are released and the oxidation of V(IV) to V(V) occurs, accompanied by the bonding of oxygen to vanadium and the corresponding mass increase. The endothermic effect with a minimum at 690°C is the melting of V_2O_5.

The thermal decomposition of the hexavanadates studied, i.e. polyvanadates with the same anion structure and one crystal water molecule, is influenced by the cation properties. PyH (**A**) is thermally more stable than ImH (**B**). This is why crystal water and pyridine molecules are released from **A** and also why an intermediate of composition $(PhY)HV_6O_{16}$ is formed at 275°C. The thermal decomposition of **B** is accompanied by bond cleavage in ImH and formation of urea. The high levels of energy required for initiation of this process may explain the more moderate decomposition of **B** at lower temperatures and the essentially higher V(IV) content in the intermediate decomposition products formed.

The temperature corresponding to the maximum mass loss, as well as the temperature at which the thermal decomposition is complete, are both higher for **A** than for **B**.

In the last decomposition step of **A** and **B**, oxygen is bonded to vanadium in the course of a reversible oxidation of V(IV) to V(V), and the last traces of the organic compound are still being released from the decomposition products of **B**. This indicates the relatively strong bonding of urea or of other small molecules in the interplanar space of the V_2O_5 structure.

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