*Thermochimica Acta*, 237 (1994) 143–146
Elsevier Science B.V., Amsterdam
*SSDI* 0040-6031(93)01604-2

# Evidence for the intermediate generation of hexavanadate during the thermal degradation of $(NH_4)_2V_3O_8$

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(Received 14 June 1993; accepted 12 September 1993)

## Abstract

The thermal behaviour of $(NH_4)_2V_3O_8$ was investigated by TG and DSC measurements in oxygen and nitrogen atmospheres. The pyrolysis is very complex, but the generation of ammonium hexavanadate, $(NH_4)_2V_6O_{16}$, in the first step of the degradation in both atmospheres, was unambiguously established.

## INTRODUCTION

The polyanion $V_3O_8^{2-}$, present in the phase of composition $(NH_4)_2V_3O_8$, is a well-known mixed-valence vanadate. The compound was discovered more than one hundred years ago [1] and rediscovered and investigated intensively in the last thirty years [2–7].

The crystal system and the cell dimensions have been known for a long time [3] and, more recently, a complete structural analysis was performed, together with EPR and magnetic studies [8]. Also, its vibrational and electronic spectra have recently been reported [9].

In order to obtain an insight into the thermal behaviour of this interesting material, we have now investigated its pyrolysis by means of TG and DSC measurements.

## EXPERIMENTAL

$(NH_4)_2V_3O_8$ was obtained by reduction of $V_2O_5$ with zinc powder in a concentrated $NH_4Cl$ solution [7, 9] and characterized by X-ray powder diffractometry, IR spectroscopy and chemical analysis (vanadium content: calc., 48.23%; found, 48.1%).

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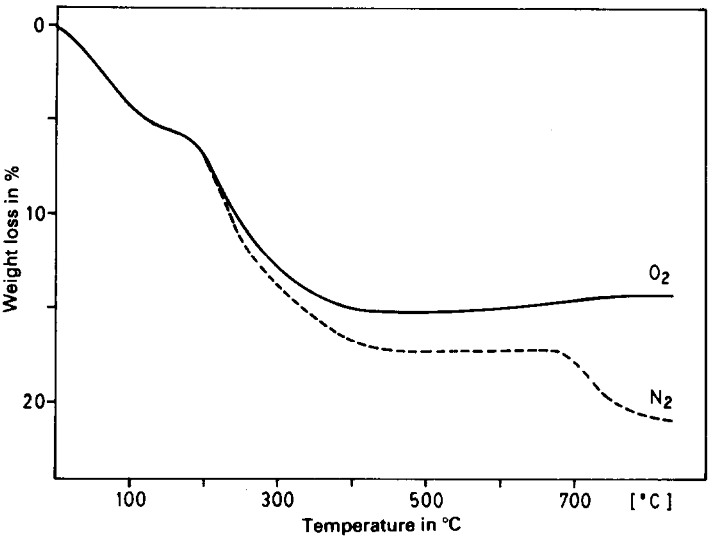

Fig. 1. Typical TG traces for $(NH_4)_2V_3O_8$ in oxygen and nitrogen atmospheres.

$(NH_4)_2V_6O_{16}$ was obtained by heating a saturated aqueous solution of $NH_4Cl$ with $V_2O_5$ at 95°C for approx. 3 h [10] (vanadium content: calc., 51.14%; found, 50.8%).

Infrared spectra were recorded with a Perkin-Elmer 580 B spectrophotometer, using the KBr pellet technique.

Thermogravimetric (TG) measurements were carried out with a Perkin-Elmer TG 2 thermobalance, in flowing $O_2$ or $N_2$ atmospheres. A Mettler TA 4000 instrument was used for differential scanning calorimetry (DSC). The heating rate was 10°C $min^{-1}$ and the sample mass ranged between 1 and 5 mg.

The TG and DSC experiments were complemented with studies in a crucible furnace in air, using greater sample weights.

## RESULTS AND DISCUSSION

Figure 1 shows the TG traces of the pyrolysis of $(NH_4)_2V_3O_8$ in $O_2$ and $N_2$ atmospheres. The corresponding DSC traces show no defined signals.

As can be seen from Fig. 1, the behaviour of the compound in both atmospheres is practically identical up to 250°C. At higher temperatures, the mass loss is slightly higher in $N_2$. At the end of the process, the mass is stable in $O_2$, whereas in $N_2$, another clearly defined mass loss can be observed.

In agreement with these observations, the following decomposition scheme, also supported by IR measurements and some additional investigations, can be proposed. In both atmospheres, the first step may be

$$(NH_4)_2V_3O_8 \rightarrow (NH_4)_2V_6O_{16} + 3VO_2 + 4NH_3 + 2H_2O \tag{1}$$

which gives a mass loss of 10.94% and occurs in the temperature range up to 250°C.

We have heated $(NH_4)_2V_3O_8$ samples up to this temperature in a crucible furnace in air, until a mass loss of between 11% and 25% was attained. The IR spectra of the obtained residues were practically identical to those obtained from a $(NH_4)_2V_6O_{16}/VO_2$ mixture in a 1:3 molar ratio, clearly supporting the stoichiometry proposed in eqn. (1) and showing, without doubt, the generation of hexavandate in this first step of the pyrolysis.

The formation of $(NH_4)_2V_6O_{16}$ is followed practically immediately by its degradation to the well-known "vanadium-bronze" of composition $NH_4V_4O_{10}$, according to

$$(NH_4)_2V_6O_{16} \rightarrow 1.5NH_4V_4O_{10} + H_2O + 0.25N_2 \tag{2}$$

with a total mass loss (steps 1 + 2) equal to 13.56%.

It is known that in vacuum this transformation occurs at around 230°C [11].

Residues collected after crucible furnace experiments, conducted with pure $(NH_4)_2V_6O_{16}$ samples at different temperatures and up to the mass loss defined by eqn. (2), gave IR spectra which are similar to those of the hexavanadate, suggesting a close structural relationship between the hexavanadate and the "bronze". In some cases, weak absorptions corresponding to $V_2O_5$ also became evident, indicating that a further degradation had taken place.

In the next step, some differences in the two atmospheres employed are evident. In $O_2$ atmosphere, the total oxidation of the "bronze" probably takes place

$$1.5NH_4V_4O_{10} \xrightarrow{O_2} 3V_2O_5 + 1.5NH_3 + 0.75H_2O \tag{3}$$

producing a total mass loss for the three consecutive steps of 16.40%. Another possible alternative is the generation of $3H_2O + 0.75N_2$ as the volatile products in this step (see also ref. 12).

The fact that the value of 16.40% was not observed in the thermogravimetric experiments is most probably due to the fact that the $VO_2$ generated in step (1) is slowly oxidized to $V_2O_5$ with increasing temperatures in the $O_2$ atmosphere, and the concomitant mass increase is in competition with the losses depicted in eqns. (2) and (3). Therefore, the final step in this case is

$$3VO_2 + O_2 \rightarrow 1.5V_2O_5 \tag{4}$$

However, in $N_2$ atmosphere, the degradation of the "bronze" may occur in a different way

$$1.5NH_4V_4O_{10} \rightarrow 2.25V_2O_5 + 1.5VO_2 + 0.75H_2O + 1.5NH_3 \tag{3a}$$

now with a total mass loss for the three consecutive steps, (1) + (2) + (3a), of 17.66%, followed at higher temperatures by the well-known degradation of $V_2O_5$ [13]

$$2.25V_2O_5 \rightarrow 4.5VO_2 + 0.125O_2 \tag{4a}$$

Nevertheless, a total degradation such as depicted by the preceding equation, it not possible at the temperature of our experiments; moreover, this oxygen loss is reversible. However, part of the $VO_2$ generated in process (3a) may be present in a hydrated form, $VO_2 \cdot xH_2O$ [11]. The residual water would also be released in the last part of the degradation.

The fact that the IR spectra of all the phases involved in the processes described, i.e. $(NH_4)_2V_3O_8$, $(NH_4)_2V_6O_{16}$, $NH_4V_4O_{10}$ and $V_2O_5$, show some similarities, supports the existence of strong structural relations between all the phases and suggests that the analysed transformations may be topotactic.

In conclusion, the very complex thermal degradation of the mixed-valence vanadate $(NH_4)_2V_3O_8$ provides a new example of the intermediate generation of hexavanadate, a phase which also plays a key role during the pyrolysis of $NH_4VO_3$ [11, 14–16].

## ACKNOWLEDGEMENTS

This work was supported by CONICET-República Argentina. MBV is a research fellow from CIC-PBA (Argentina).

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