Thermochimica Acta, 81 (1984) 23–27
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MODE OF THERMAL DEGRADATION OF $(NH_4)_3VO_2F_4 \cdot \frac{1}{2}H_2O$

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(Received 11 May 1984)

ABSTRACT

Evidence in favour of the path of thermal degradation of $(NH_4)_3VO_2F_4 \cdot \frac{1}{2}H_2O$, previously proposed involving three intermediate compounds, is presented by way of the thermal degradation of the intermediates themselves.

INTRODUCTION

In earlier communications [1,2] the thermal stability, the occurrence of a reversible first-order phase transition and the presence of discrete ions of $[VO_2F_4]^{3-}$ with a D_{4h} symmetry in $(NH_4)_3VO_2F_4 \cdot \frac{1}{2}H_2O$ (I) were reported. While DSC and EPR gave evidence for the existence of a phase transition at 135 °C in this compound, TG indicated the onset of decomposition at temperatures very close to the temperature of transition. The TG curve showed a single step in weight loss between 170 and 450 °C while the corresponding DTA curve exhibited several endotherms in addition to a high-temperature exotherm. Based on these and other related data, a scheme was proposed for the thermal degradation of this compound to V_2O_5, as represented by eqns. (1)–(5) given later in this communication.

EXPERIMENTAL

The materials used were V_2O_5, NH_4VO_3, NH_4F (all Baker's AR grade) and NH_4HF_2 (BDH LR grade). The instruments employed were a Stanton TG thermobalance, a Perkin-Elmer DSC-1B differential scanning calorimeter and a home-made DTA set-up described elsewhere [3]. The starting materials were mixed in stoichiometric proportions according to eqns. (6)–(8) on a polythene sheet and ground well. Neither the X-ray powder pattern nor the IR scan of the product at room temperature showed the presence of the reactants. Without heating, intimate grinding brought about the reaction in all three cases, just as in the formation of $(NH_4)_3VO_2F_4 \cdot \frac{1}{2}H_2O$ and $Na(NH_4)_2VO_2F_4 \cdot H_2O$ reported earlier [1].

0040-6031/84/$03.00

RESULTS AND DISCUSSION

The thermal degradation behaviour of the title compound, proposed earlier [1] is as follows

$$(NH_4)_3VO_2F_4\cdot\tfrac{1}{2}H_2O \rightarrow \underset{\textbf{(I)}}{(NH_4)_3VO_2F_4\cdot\tfrac{1}{2}H_2O} \tag{1}$$

$$(NH_4)_3VO_2F_4\cdot\tfrac{1}{2}H_2O \rightarrow \underset{\textbf{(II)}}{(NH_4)_2VO_2F_3\cdot\tfrac{1}{2}H_2O} + NH_4F \tag{2}$$

$$2(NH_4)_2VO_2F_3\cdot\tfrac{1}{2}H_2O \rightarrow \underset{\textbf{(III)}}{(NH_4)_3V_2O_4F_5\cdot H_2O} + NH_4F \tag{3}$$

$$(NH_4)_3V_2O_4F_5\cdot H_2O \rightarrow \underset{\textbf{(IV)}}{2NH_4VO_2F_2\cdot\tfrac{1}{2}H_2O} + NH_4F \tag{4}$$

$$2NH_4VO_2F_2\cdot\tfrac{1}{2}H_2O \rightarrow 2NH_4F + V_2O_5 + 2HF \tag{5}$$

The above intermediates **II**–**IV** were prepared as described above according to the following reactions

$$2NH_4F + 2NH_4HF_2 + V_2O_5 \rightarrow 2(NH_4)_2VO_2F_3\cdot\tfrac{1}{2}H_2O \tag{6}$$

$$NH_4F + 2NH_4HF_2 + V_2O_5 \rightarrow (NH_4)_3V_2O_4F_5\cdot H_2O \tag{7}$$

$$2NH_4HF_2 + V_2O_5 \rightarrow 2NH_4VO_2F_2\cdot\tfrac{1}{2}H_2O \tag{8}$$

The room temperature X-ray powder patterns of the intermediates are given in Table 1. The patterns of intermediates **II**–**IV** are in variance with those reported by Rakhov et al. [4]. These authors recorded the patterns while heating compound **I** assuming that they represent single components. This is far from true, as indicated by the present TG curve of the same

TABLE 1

X-ray powder patterns of the compounds studied

$(NH_4)_3VO_2F_4\cdot\frac{1}{2}H_2O$		$(NH_4)_2VO_2F_3\cdot\frac{1}{2}H_2O$		$(NH_4)_3V_2O_4F_5\cdot H_2O$		$NH_4VO_2F_2\cdot\frac{1}{2}H_2O$	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
5.21	100	5.15	100	5.27	100	5.82	100
4.46	17	4.53	15	4.31	15	5.71	70
3.20	10	4.44	17	3.72	15	4.44	15
3.16	67	4.23	10	3.07	44	4.23	15
2.61	13	3.18	17	2.47	10	3.56	20
—	—	3.14	11	2.33	44	3.40	12
—	—	2.98	26	2.12	10	3.30	17
—	—	2.28	28	1.78	15	3.18	13
—	—	2.20	10	1.74	10	2.93	25
—	—	1.77	10	—	—	2.32	17
—	—	—	—	—	—	2.05	20

compound which shows a single-step loss with no plateau region in between except at $T > 450\,^\circ$C, where V_2O_5 is formed in all cases. From the nature of preparation, it is presumed that the samples used here are single components. The TG patterns are given in Fig. 1.

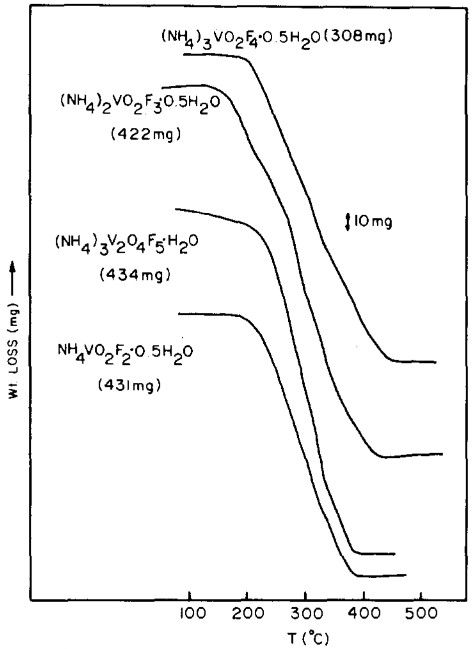

Fig. 1. TG curves of compound **I** and of the intermediates. Rate of heating = 6° min^{-1} in static air.

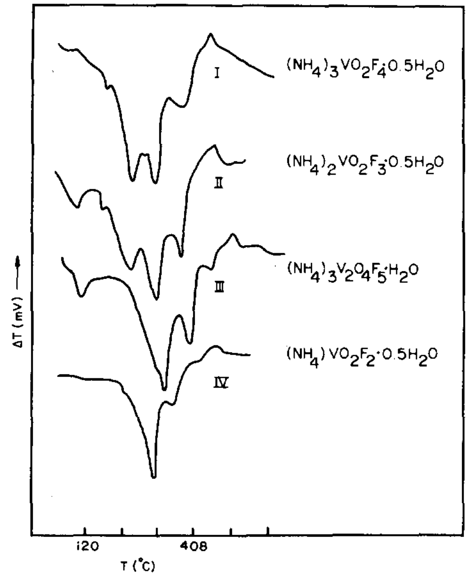

Fig. 2. DTA curves of compound **I** and of the intermediates. Heating rate = 8° min^{-1} in static air.

TABLE 2

DTA data of the compounds studied

Compound	Endotherm temp. (°C)	Exotherm temp. (°C)
$(NH_4)_3VO_2F_4 \cdot \frac{1}{2}H_2O$	110^{π}, 172^{+}, 252^{A}, 285^{s}, 302^{B} 365^{C}	452
$(NH_4)_2VO_2F_3 \cdot \frac{1}{2}H_2O$	90^{π}, 172^{+}, 241^{A}, 302^{s}, 320^{B} 372^{C}	460
$(NH_4)_3V_2O_4F_5 \cdot H_2O$	95^{π}, 307^{s}, 330^{B} 380^{C}	484
$NH_4VO_2F_2 \cdot \frac{1}{2}H_2O$	137^{π}, 313^{B} 363^{C}	465

$^{\pi}$ Occluded water removal; $^{+}$ phase transition; ^{s} shoulder; ^{A,B,C} three sets of endotherms.

Figure 2 shows the DTA curves of compound **I** and of the intermediates. The residue in all cases at $T > 450\,°C$ is V_2O_5, as is clear from the exotherm at $460 \pm 10\,°C$ characteristic of the oxide [1]. Table 2 lists the peak temperatures of the DTA runs of these compounds. All compounds exhibit three endotherms, designated A, B and C, at 240 ± 10, 320 ± 10 and $370 \pm 10\,°C$, respectively, but with different relative intensities. In $NH_4VO_2F_2 \cdot \frac{1}{2}H_2O$ peak C is attributed to the loss of one molecule of HF, while B is attributed to the loss of one molecule of NH_4F. This peak B has a higher intensity in the compound $(NH_4)_3V_2O_4F_5 \cdot H_2O$ because it represents the loss of 1.5 molecules of NH_4F according to the scheme given above. Similarly, peak A in the other two compounds (**I** and **II**) represents the loss of 1.5 molecules and 1 molecule of NH_4F, respectively. This peak A is conspicuously absent in compounds **III** and **IV**.

Thus, chemically, all the three ammonium ions in the compound $(NH_4)_3VO_2F_4 \cdot \frac{1}{2}H_2O$ are not equivalent. Half of these (1.5 ions) are crystallographically different from the other half, and thus on heating, the two sets are lost at different temperatures as fluoride. The steps, however, are overlapping as seen by the DTA. This aspect cannot be resolved in our TG. However, an inspection of our micro-TG/DTG of compound **I** [1] shows three points of inflexion suggesting correspondence with the DTA peaks reported here.

PHASE TRANSITION

As was pointed out earlier [1] compound **I** exhibits a reversible phase transition at 135 °C with a temperature hysteresis of 12 °C and a ΔH value of 2.5 ± 0.4 kJ mol^{-1}. In the present study the compound $(NH_4)_2VO_2F_3 \cdot \frac{1}{2}H_2O$ also exhibits a transition at 149 °C with a hysteresis of 21 °C and a ΔH value 0.9 ± 0.2 kJ mol^{-1}. From the fact that the other two intermediates do not exhibit this phase transition, it is clear that it is caused by the 1.5 molecules of NH_4F lost in the first two steps of degradation of compound **I** attributed to the DTA peak at 240 °C. An EPR study [2] gave evidence for the existence of two kinds of anion, $[VO_2F_4]^{3-}$, in compound **I** one set of anions being rigid and the other set being in free rotation. The proportion of the latter increases at the expense of the former as the temperature is increased. From the present study it is concluded that there are two kinds of $[NH_4]^+$ ions in the same compound of equal number, one set of which is lost at 240 °C. It is probable that these more thermally labile cations are weakly hydrogen bonded to the oxygens of the anions, while the other anions are not bound to the rest of the cations. As the temperature is increased, the hydrogen bonds break, progressively increasing the proportion of the freely rotating anions, as indicated by the EPR experiment. Beyond the phase transition, all the anions are free to rotate. Even $Na(NH_4)_2VO_2F_4 \cdot H_2O$ shows the transition, since it has 0.5 molecules of the H-bonded cations.

CONCLUSION

Evidence for the support of the thermal degration of $(NH_4)_3VO_2F_4 \cdot \frac{1}{2}H_2O$, proposed earlier, has been obtained. The possible origin of the phase transition exhibited by this compound and the first intermediate of decomposition is discussed.

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