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THERMAL BEHAVIOUR OF $(NH_4)_3VO_2F_4$ and $Na(NH_4)_2VO_2F_4$

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ABSTRACT

The thermal behaviour of $(NH_4)_3VO_2F_4$ and $Na(NH_4)_2VO_2F_4$ was investigated using TG, DTA and DSC techniques. The occurrence of a first order phase transition with the onset of decomposition in both the compounds is confirmed. The temperature, energetics and hysteresis of the transition are obtained. A possible path for the thermal degradation is given for both the compounds, and the residues are identified.

INTRODUCTION

Sengupta and Bhaumik [1] reported the preparation of $(NH_4)_3VO_2F_4$ as a pale yellow solid by evaporating to dryness a mixture of aqueous solutions of NH_4VO_3 and NH_4HF_2 in 1:2 proportion, and reported the X-ray powder pattern for the solid. The authors concluded that on heating to 700 K, this material leaves a residue of V_2O_5 with no fluorine content. Rakov et al. [2] studied the TG, DTG and DTA of (i) a mechanical mixture of V_2O_5 and NH_4HF_2, (ii) a mechanical mixture of NH_4VO_3 and NH_4HF_2, and (iii) $(NH_4)_3VO_2F_4$ made from HF solution. Their findings may be summarized as follows. The reaction in mixture (i) gave $(NH_4)_3VO_2F_4$ as one of the products but the reaction is incomplete. The TG/DTG and DTA of mixture (ii) and the solid in (iii) gave almost identical results. The DTA exhibits endotherms at 383, 433, 483 and 513 K in addition to two strong exotherms at 633 and 653 K. The endotherm at 383 K, corresponding to a DTG peak at 368 K, was attributed to a combined effect arising from the melting of NH_4HF_2 (actual m.p. 399 K) and reaction between NH_4HF_2 and NH_4VO_3. This is not correct because this 383 K endotherm is also shown by $(NH_4)_3VO_2F_4$ of (iii) which does not contain the free NH_4HF_2 or NH_4VO_3. All other endotherms were attributed to decomposition steps while the exotherms were attributed to oxidation and hydrolysis. However, the samples were not subjected to thermal cycling.

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In our recent EPR study [3] of γ-irradiated $(NH_4)_3VO_2F_4$, we showed that the $[VO_2F_4]^{3-}$ anion of the compound is in C_{4v} symmetry in the solid state at room temperature and there exists a reversible phase transition around 418 K. This transformation manifests itself in interconversion of two types of EPR spectra. One type has two octets representing a rigid form of $[VO_2F_4]^{3-}$ units, while the other has one octet representing a dynamic form of the same ion. From 273 to 418 K both forms of the ions coexist, while above 418 K only the dynamic form exists. In the present communication, we present fresh DTA and DSC evidence for the existence of a reversible first order phase transition not only in $(NH_4)_3VO_2F_4$ but also in a related compound, $Na(NH_4)_2VO_2F_4$, besides the absence of such a transition in $Na_3VO_2F_4$, and we also attempt to rationalize the observed differences.

EXPERIMENTAL

The instruments used in this study are a Stanton TG thermobalance, a Perkin-Elmer DSC-1B differential scanning calorimeter, and a home-made DTA apparatus described elsewhere [4].

The IR spectra in the region 400–3500 cm^{-1} of the starting materials, viz. NH_4VO_3 and NH_4HF_2 in the case of $(NH_4)_3VO_2F_4$, and $NaVO_3$ and NH_4HF_2 in the case of $Na(NH_4)_2VO_2F_4$, were recorded prior to mixing and they agree with literature data [5]. The solids were mixed and ground well after wrapping them in a polyethylene sheet. The IR spectra of the mixture at room temperature did not show the presence of strong peaks at 1200 cm^{-1}

TABLE 1

X-Ray powder pattern of $Na(NH_4)_2VO_2F_4$ at 298 K

Serial No.	*d* (Å)	Relative intensity (%)
1	4.87	80
2	4.34	100
3	2.94	65
4	2.44	20
5	2.11	60
6	1.88	20
7	1.73	8
8	1.63	8
9	1.50	16
10	1.41	8
11	1.34	5

and 2100 cm^{-1} of NH_4HF_2, indicating reaction without heating. The heat generated in mechanical grinding was sufficient to bring about the reaction between the two solids. The formation of the product at room temperature was further confirmed by powder X-ray pattern. Since the X-ray pattern for $Na(NH_4)_2VO_2F_4$ is not available in the literature, it is given in Table 1.

RESULTS AND DISCUSSION

Figure 1 shows the results of various thermal studies on $(NH_4)_3VO_2F_4$: (a) TG run, (b) DTA complete run from 300 to 1000 K, (c) DTA run on a fresh sample thermally cycled through the 445 K peak (endotherm), and (d) DSC

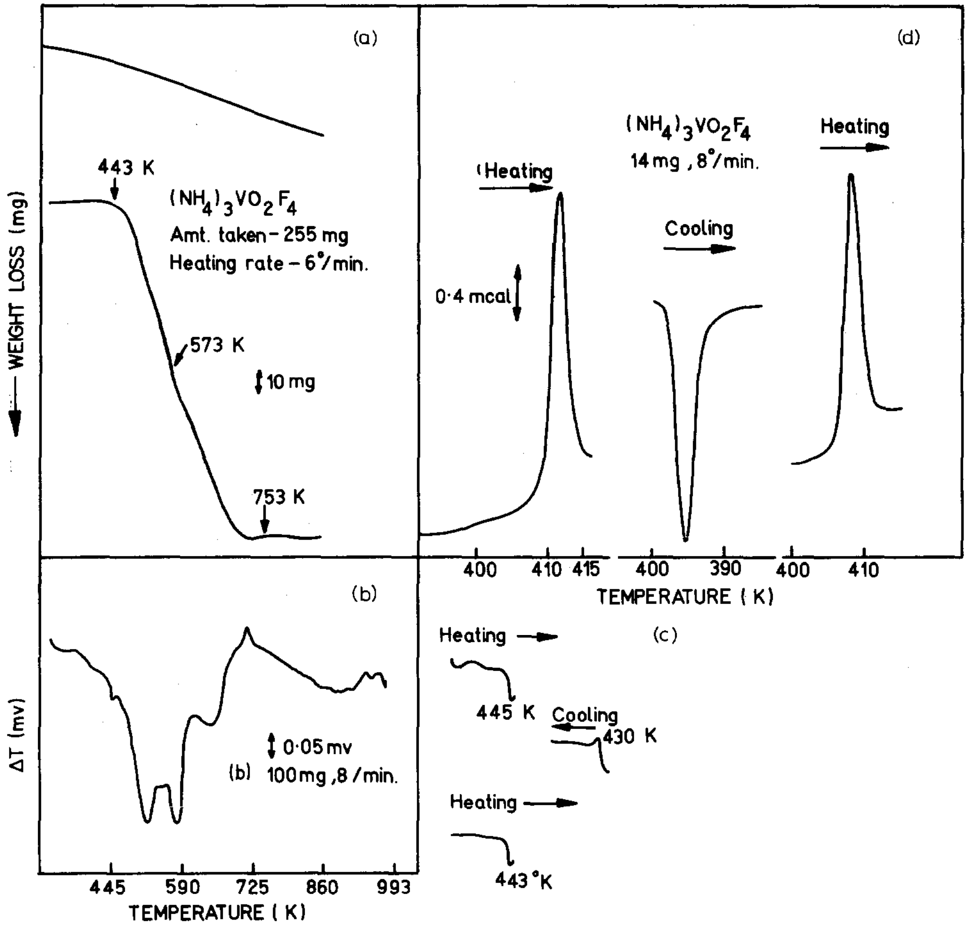

Fig. 1. Thermal studies on $(NH_4)_3VO_2F_4$: (a) TG, (b) DTA, (c) DTA thermal cycling, and (d) DSC thermal cycling.

scans of a fresh sample thermally cycled through the 412 K endotherm. The sample starts to lose weight from 446 K onwards and shows a change of slope around 573 K in the TG run. The DTA run in (b) is in qualitative agreement with that given by Rakov et al. [2]. However, from Fig. 1 (c) the reversibility of the 445 K peak with a temperature hysteresis of 15 K confirms a first-order phase transition in $(NH_4)_3VO_2F_4$. This is reminiscent of what was reported for CsH_2PO_4 [6] where, concomitant with dehydration, CsH_2PO_4 undergoes a first-order phase transition at 508 K. Considered together with TG [Fig. 1(a)], the DTA [Fig. 1(c)] indicates similar happening in $(NH_4)_3VO_2F_4$. As expected, the intensity of this peak in DTA decreases progressively with each thermal cycling through the transition due to increased decomposition. The same effect is better demonstrated in the DSC scans [Fig. 1(d)]. Due to its enhanced resolution and sensitivity, DSC scans were employed to obtain temperature and energetics of the transition. Using first heating we obtained $\Delta H^{\text{heating}} = 2.5 \pm 0.4$ kJ mole^{-1}, the cooling peak was obtained at 396 K. Parallel to DTA, in DSC scans also the area under the peak decreases with each thermal cycling through the transition.

$Na(NH_4)_2VO_2F_4$, prepared according to the procedure outlined in ref. [1], gave the thermal analysis data shown in Fig. 2; TG [Fig. 2(a)] shows the

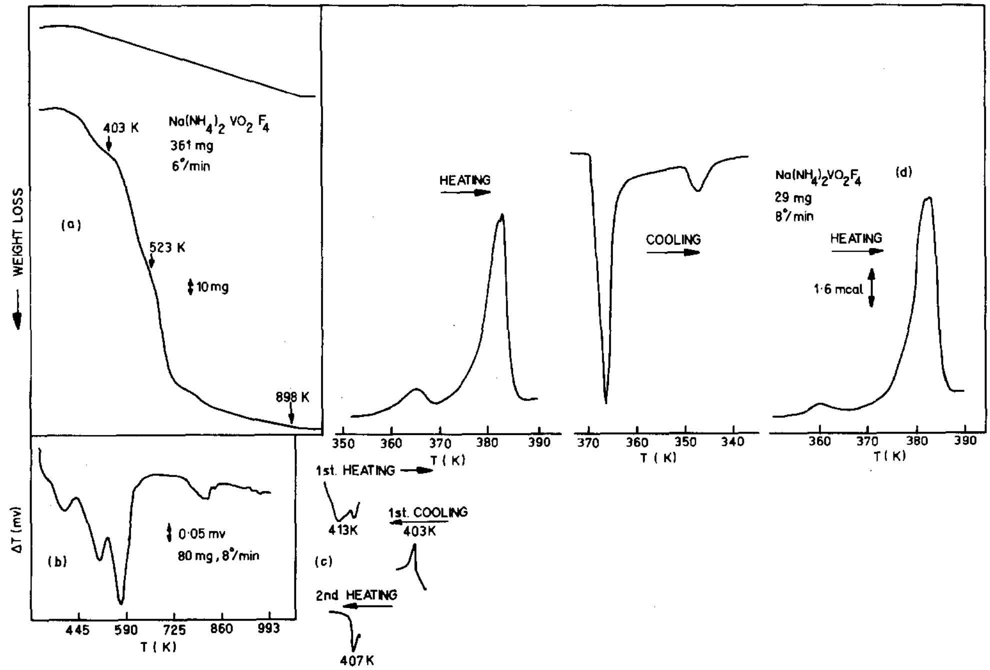

Fig. 2. Thermal studies on $Na(NH_4)_2VO_2F_4$: (a) TG, (b) DTA, (c) DTA thermal cycling, and (d) DSC thermal cycling.

onset of decomposition at 333 K and gives three steps. DTA [Fig. 2(b)] exhibits five endotherms at 393, 419 (shoulder), 519, 591 and 814 K and no exotherm, in contrast to $(NH_4)_3VO_2F_4$, which shows two exotherms. The 393 K endotherm, possibly arising from occluded H_2O removal, disappears after first heating. However, the transition at 419 K, on cooling immediately from 425 K, gives an exotherm at 403 K with a hysteresis of 16 K. On reheating, the peak is obtained at 408 K, albeit with reduced intensity as in the case of the triammonium salt. The thermal cycling behaviour is shown in Fig. 2(c) and the DSC scans are shown in Fig. 2(d). The temperatures and energetics of this reversible transition are obtained from our DSC scans as follows. $\Delta H_{383K}^{\text{heating}} = 11 \pm 1$ kJ mole^{-1} and the transition was observed at 366 K during cooling with a hysteresis of 17 K. The DSC scans show the existence of a second reversible but weak transition at 366 K while heating and at 346 K during cooling.

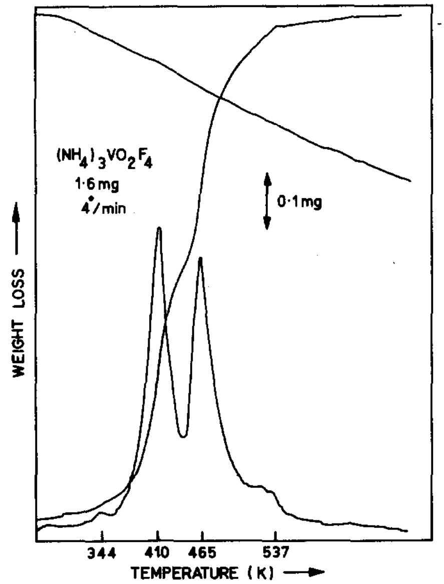

Fig. 3. Micro TG and DTG of $(NH_4)_3VO_2F_4$.

Micro TG as well as the corresponding DTG of the triammonium salt are given in Fig. 3. The composition of the residue from micro TG fits closer to V_2O_5 than that from TG.

Thermal degradation course and residue

It is pertinent at this stage to discuss the thermal degradation of the two compounds. In the triammonium salt, our DTA/DSC results show beyond doubt the nature of the 445 K peak as due to a reversible phase transition in the compound. Other endotherms can be attributed to loss of NH_4F either as such or as NH_3 and HF together, according to the suggestion of Russian workers. Although our TG shows a continuous weight loss with no steps, several steps could be seen in our micro TG/DTG, DTA and DSC. Thus, the inference of Rakov et al. [2] of the sequential formation of intermediates, $(NH_4)_2VO_2F_3$, $(NH_4)_3V_2O_4F_5$ and $NH_4VO_2F_2$, appears to be logical. The only difficulty is the identity of the end product. Sengupta and Bhaumik [1] suggest V_2O_5 as the end product while Rakov et al. [2] proposed VO_2F as the residue. The identity of the latter lacks confirmation as yet. From weight loss considerations, the triammonium salt is expected to give V_2O_5 (beyond 700 K) and no further weight changes are observed up to 900 K in our TG study. The issue, in our opinion, is clinched by the 716 K exotherm present in the DTA of $(NH_4)_3VO_2F_4$ [Fig. 1(b)] and its absence in the DTA of Na salt [Fig. 2(b)]. The suggestion of Rakov et al. [2] that the 716 K exotherm in the DTA of $(NH_4)_3VO_2F_4$ is due to oxidation and hydrolysis is not favoured by us since this would have been reflected in weight changes in the sample, conspicuously absent in the TG. Therefore this exotherm must have something to do with what V_2O_5 experiences at 716 K. To further confirm this, pure NH_4VO_3, free from V^{4+}, as checked by EPR, was subjected to TG and DTA runs under identical conditions. The weight loss ends at 550 K and the residual weight remains the same up to 830 K. The corresponding DTA shows endotherms for a two-step decomposition to form V_2O_5 at 525 K, in agreement with literature [7]. However, on further heating the residue in our DTA, an exotherm at 694 K, characteristic of V_2O_5, is seen. This lends strong support to our earlier contention that the residue at 700 K in $(NH_4)_3VO_2F_4$ is V_2O_5 and not VO_2F as was concluded by Rakov et al. [2]. The X-ray powder pattern and IR of the residue of $(NH_4)_3VO_2F_4$ heated to 700 K indicate V_2O_5 as the material. It is, however, very uncertain as to how $NH_4VO_2F_2$ can pass to V_2O_5 in the last stage of decomposition. To rationalize this one has to bring in the presence of water of hydration in the lattice of the starting material. It is thus gratifying to note that in spite of similarities in DTA between $(NH_4)_3VO_2F_4$ and $Na(NH_4)_2VO_2F_4$, the 716 K exotherm present in the former is absent in the latter, where at no stage of decomposition could V_2O_5 be an intermediate.

From its X-ray powder pattern, the final product of $Na(NH_4)_2VO_2F_4$ heated to 1000 K and cooled back to room temperature was identified as α-$NaVO_3$ [8]. From weight loss considerations, the parent compound yields $NaVO_3$ at about 725 K and its weight remains unchanged between 725 and 1000 K. The endotherms below 800 K are attributed to decomposition while that at 815 K is ascribed to a phase transition of $NaVO_3$ to α-$NaVO_3$. This α-$NaVO_3$, once heated beyond its m.p. of 925 K and cooled back to room temperature, retains its high temperature structure down to room temperature without reverting back to $NaVO_3$. However, if α-$NaVO_3$ is heated up to 880 K, i.e., below its melting point and cooled, it reverts back to $NaVO_3$ at room temperature. An independent check of this was made starting from pure $NaVO_3$ and running its DTA. Pure $NaVO_3$ gave an endotherm at 840 K due to its transformation into α-$NaVO_3$. From the results described so far, the scheme of thermal behaviour of the two compounds is given as

triammonium compound

$$(NH_4)_3VO_2F_4 \cdot 0.5\,H_2O \rightarrow (NH_4)_2VO_2F_3 \cdot 0.5\,H_2O + NH_4F$$

$$2(NH_4)_2VO_2F_3 \cdot 0.5\,H_2O \rightarrow (NH_4)_3V_2O_4F_5 \cdot H_2O + NH_4F$$

$$(NH_4)_3V_2O_4F_5 \cdot H_2O \rightarrow 2\,NH_4VO_2F_2 \cdot 0.5\,H_2O + NH_4F$$

$$NH_4VO_2F_2 \cdot 0.5\,H_2O \rightarrow NH_4F + VO_{2.5} + HF$$

From micro TG, an overall loss of 57.5% is observed against a calculated loss of 59%.

sodium diammonium compound

$$Na(NH_4)_2VO_2F_4 \cdot H_2O \rightarrow NaNH_4VO_2F_3 \cdot H_2O + NH_4F$$

$$2\,Na(NH_4)VO_2F_3 \cdot H_2O \rightarrow Na_2(NH_4)V_2O_4F_5 \cdot 2\,H_2O + NH_4F$$

$$Na_2(NH_4)V_2O_4F_5 \cdot 2\,H_2O \rightarrow 2\,NaVO_2F_2 \cdot H_2O + NH_4F$$

$$NaVO_2F_2 \cdot H_2O \rightarrow NaVO_3 + 2\,HF$$

$$NaVO_3 \xrightarrow{T>850\,K} \underset{\text{residue}}{\alpha\text{-}NaVO_3}$$

In all the thermal degradation steps given above the TG does not necessarily show the losses exactly as expected for the decomposition. In this context the following remarks are relevant. Although the starting materials NH_4HF_2 and NH_4VO_3 did not show any EPR signals prior to mixing, their mechanical mixture which contains $(NH_4)_3VO_2F_4$ did show the presence of V^{4+} by EPR [3] prior to heating or γ-irradiation. It was mentioned that during preparation of V^{5+} compounds, V^{4+} is invariably formed [9]. This is due to the relative ease of formation of V^{4+} ($V^{5+} + e \rightarrow V^{4+} \sim 1$ eV). On thermal decomposition, it is logical to expect that, more and more V^{4+} will be formed. Thus the starting materials, which to start with contain some V^{4+}, on going through several steps of decomposition become contaminated with larger amounts of V^{4+}, thereby vitiating a good fit for weight loss at any intermediate step and much worse in the residue.

Nature of phase transition

Lastly, it is worthwhile to ponder over the nature of phase transition in the compounds. As already mentioned, from our EPR study [3] on γ-irradiated $(NH_4)_3VO_2F_4$ we concluded that the anions are in both dynamic and static forms at room temperature, the proportion of the former increasing at the expense of the latter as the temperature is increased, and finally at $T > 418$ K only the dynamic units exist. Our present DSC data confirm the presence of a reversible first order phase transition in $(NH_4)_3VO_2F_4$ at 408 K and in $Na(NH_4)_2VO_2F_4$ at 382 K. Thus it appears that the anions at room temperature are not free to rotate, probably due to H-bonding in the room temperature phase of both the compounds. The oxygen atoms of the anion take part in H-bonding with protons of the NH_4^+ group. However, due to the favourable Boltzman distribution at room temperature, some of the ions have energies sufficient to overcome this binding and rotate, their fraction increasing with increase in temperature. In the high temperature phase, the H-bonds are completely broken and all the anions are free to rotate. In the case of the monosodium compound the temperature of transition of 382 K is lower compared to that of 408 K in the triammonium salt, possibly due to a lesser number of NH_4^+ groups participating in H-bonding in the former. This belief is further borne out by our preliminary finding [10] that in $Na_3VO_2F_4$, which has no NH_4^+ groups for H-bonding, the phase transition could not be observed from room temperature down to 185 K, which indicates that the anions of this compound are in dynamic form down to $T = 185$ K, the lowest temperature checked by us using DSC.

CONCLUSION

From our TG/DTA/DSC observations on $(NH_4)_3VO_2F_4$ and $Na(NH_4)_2VO_2F_4$ we obtained unequivocal evidence for the existence of a reversible first-order phase transition concomitant with the onset of thermal decomposition of the compounds. By all indications, the end product of decomposition of the triammonium salt is V_2O_5 while in the monosodium salt, if heated beyond 950 K and cooled back to room temperature, it is α-$NaVO_3$.

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