

## MODE OF THERMAL DECOMPOSITION OF $(\text{NH}_4)_3\text{NbOF}_6 \cdot 1.5\text{H}_2\text{O}$

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### ABSTRACT

In spite of its TG curve exhibiting a single step,  $(\text{NH}_4)_3\text{NbOF}_6 \cdot 1.5\text{H}_2\text{O}$  was shown to decompose in three steps by a DTA study of this compound as well as the probable intermediates formed during its decomposition.

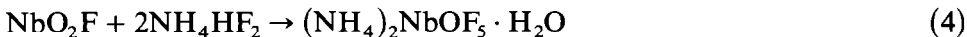
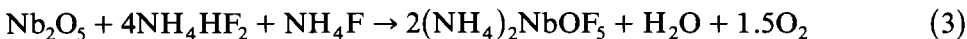
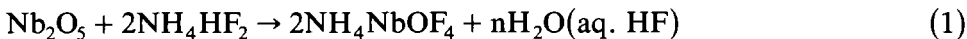
### INTRODUCTION

In our earlier communication on the thermal decomposition of  $(\text{NH}_4)_3\text{VO}_2\text{F}_4 \cdot 0.5\text{H}_2\text{O}$ , the formation of various intermediates was suggested [1]. This was found to be the case despite the fact that the thermogram of the compound showed a single step weight loss in the temperature range 110–400 °C with one point of inflexion at 170 °C. As the TG scan did not show any plateau, isothermal heating for obtaining different intermediates, as proposed by Rakov et al. [2], was not feasible. Subsequently, all the intermediates were prepared independently by us by solid state synthesis, their TG/DTA scans were recorded [3] and from the data the stepwise degradation of  $(\text{NH}_4)_3\text{VO}_2\text{F}_4 \cdot 0.5\text{H}_2\text{O}$  was inferred. The thermal stability of the title compound,  $(\text{NH}_4)_3\text{NbOF}_6 \cdot 1.5\text{H}_2\text{O}$ , was studied earlier [4] along with that of  $(\text{NH}_4)_3\text{VOF}_6 \cdot 1.5\text{H}_2\text{O}$ . In the case of thermal degradation of the niobium compound, the intermediates postulated by us were  $(\text{NH}_4)_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  and  $\text{NH}_4\text{NbOF}_4 \cdot \text{H}_2\text{O}$  with no supporting evidence. In this communication we report on the preparation of these intermediates by solid state synthesis as well as by the solution route, and their thermal stability using TG and DTA, on the basis of which the thermal degradation path of the title compound has been delineated.

### EXPERIMENTAL

The compound  $(\text{NH}_4)_3\text{NbOF}_6 \cdot \text{H}_2\text{O}$  was prepared as reported earlier [4]. Preparation of  $(\text{NH}_4)_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  and  $\text{NH}_4\text{NbOF}_4 \cdot \text{H}_2\text{O}$  was attempted

by solid state synthesis, as per the following scheme



There was no reaction between  $\text{Nb}_2\text{O}_5$  and ammonium hydrogen fluoride at room temperature. However, there was evidence of partial reaction at  $126^\circ\text{C}$ , giving  $(\text{NH}_4)_3\text{NbOF}_6$  but not the products expected from eqns. (2) and (3). The diammonium compound was previously prepared by Buslaev et al. [5] by reacting  $\text{NH}_4\text{F}/\text{NH}_4\text{HF}_2$  and  $\text{NbO}_2\text{F}$  in aqueous solution. Hence  $\text{Nb}_2\text{O}_5$ , the starting material, was replaced by  $\text{NbO}_2\text{F}$  and the diammonium compound was obtained at room temperature as per eqn. 4. Also  $\text{NH}_4\text{NbOF}_4$  was prepared following the recipe of Pakhomov et al. [6]. In this method  $\text{NH}_4\text{F}$  was added to a solution of  $\text{Nb}_2\text{O}_5$  in 48% HF. The X-ray diffraction patterns of all three compounds matched well with those reported in the literature.

The instruments used in studying these compounds were a Stanton TG thermobalance and a home made DTA apparatus described elsewhere [7]. The rate of heating was  $8^\circ\text{C min}^{-1}$ , sample size was a few hundred milligrams and the atmosphere was static air.

## RESULTS AND DISCUSSION

Figure 1 shows the TG scans of  $(\text{NH}_4)_3\text{NbOF}_6 \cdot \text{H}_2\text{O}$  and of the postulated intermediates. All the compounds exhibit single step decomposition. Figure 2 shows the DTA scans of  $(\text{NH}_4)_3\text{NbOF}_6 \cdot \text{H}_2\text{O}$  and of the postulated intermediates of its thermal decomposition. The thermal analysis data are given in Table 1. All three compounds gave  $\text{NbO}_2\text{F}$  as residue at  $400^\circ\text{C}$ . The parent compound showed a first order reversible crystallographic phase transition at  $146^\circ\text{C}$ , as confirmed by thermal cycling around this transition. The other two compounds did not exhibit any phase transition. The triammonium compound showed four endotherms and two exotherms, out of which the first endotherm is attributed to a phase transition. The other three endotherms, designated as A, B and C, overlap with each other. The DTA scan of  $(\text{NH}_4)_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  showed two endotherms and two exotherms: i.e. in  $(\text{NH}_4)_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$  the first two endotherms of the triammonium compound are missing. The difference between these two compounds is only one ammonium fluoride molecule. Thus one can conclude that this endotherm (A) is due to loss of the first of the three ammonium fluoride molecules. This particular  $\text{NH}_4\text{F}$  molecule is responsible for the occurrence of the phase transition. Similarly, on comparing the

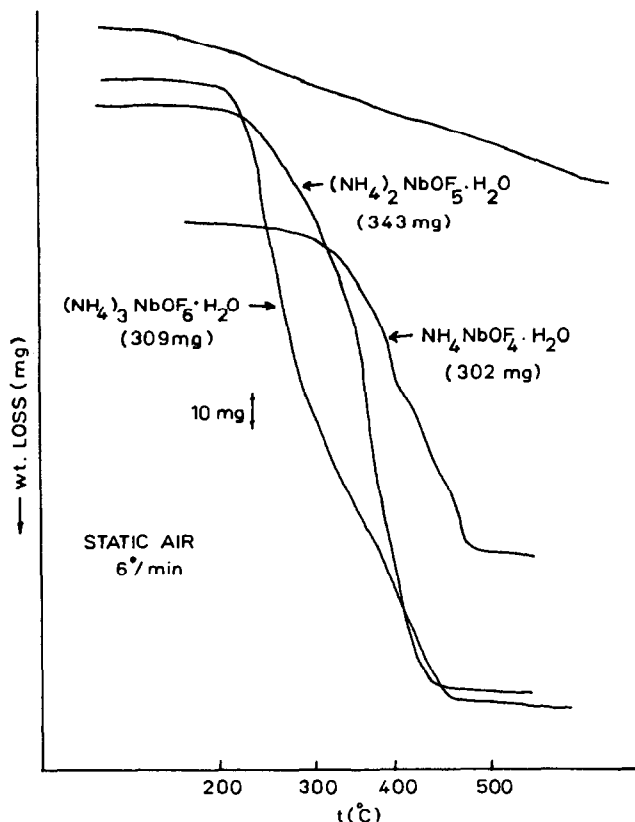
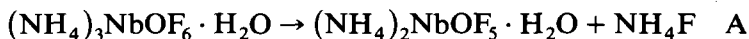
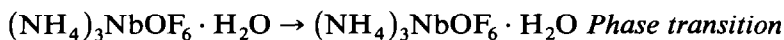
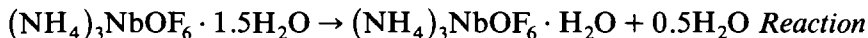


Fig. 1. TG scans of  $(\text{NH}_4)_3\text{NbOF}_6 \cdot \text{H}_2\text{O}$  and of the postulated intermediates of its thermal decomposition.

DTA scans of  $(\text{NH}_4)_2\text{NbOF}_5$  and  $\text{NH}_4\text{NbOF}_4$ , even endotherm B was absent in the latter. Endotherm C showed different steps representing an overall loss of one ammonium fluoride molecule and two HF molecules. In this case, as there is no overlap, one can see the different steps clearly, whereas they could not be discerned in the former two cases. Thus, clear evidence was obtained for the path by which the thermal decomposition of the parent compound occurs. The stepwise decomposition can be written as follows



Thus, in the case of a single step thermogram of  $(\text{NH}_4)_3\text{NbOF}_6 \cdot 1.5\text{H}_2\text{O}$ , the nature of the intermediates could be established in an indirect way using

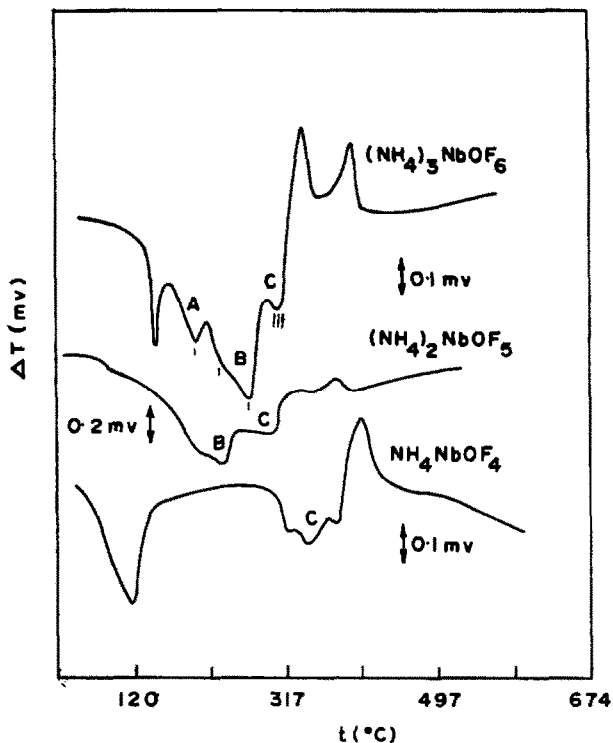


Fig. 2. DTA scans of  $(\text{NH}_4)_3\text{NbOF}_6 \cdot \text{H}_2\text{O}$  and of the postulated intermediates of its thermal decomposition.

TABLE 1

Thermal analysis of niobium compounds

Compound	TG Temp. range (°C)	Weight loss (%)		DTA Peak temp. (°C)	
		obs.	calc.	Endo.	Exo.
$(\text{NH}_4)_3\text{NbOF}_6 \cdot \text{H}_2\text{O}$	150–440	46.9	51.0	146, 200, 232, 270	303, 390
$(\text{NH}_4)_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$	180–440	42.3	44.1	–, –, 240, 280	320, 396
$\text{NH}_4\text{NbOF}_4 \cdot \text{H}_2\text{O}$	280–480	31.0	34.8	–, –, –, 316 346 378	–, 408

TG and DTA techniques as was done earlier by us in the case of  $(\text{NH}_4)_3\text{VO}_2\text{F}_4 \cdot 0.5\text{H}_2\text{O}$ .

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