Thermochimica Acta, 125 (1988) 229–235
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PYROLYSIS OF SODIUM ANALOGS OF $(NH_4)_3VO_2F_4$

U.R.K. RAO, B.N. WANI and K.S. VENKATESWARLU

Water Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085 (India)

(Received 4 June 1987)

ABSTRACT

Three sodium analogs of $(NH_4)_3VO_2F_4$, viz., $Na(NH_4)_2VO_2F_4$ (**I**), $Na_2(NH_4)VO_2F_4$ (**II**) and $Na_3VO_2F_4$ (**III**) were prepared by solid state synthesis and were subjected to thermal degradation. The nature of the residue was established and the possible course of thermal decomposition given in each case. It was inferred that as one goes from **I** to **III**, the Na^+ ions substitute the NH_4^+ ions in an ordered fashion.

INTRODUCTION

In earlier communications [1,2] a detailed study regarding the thermal stability, occurrence of reversible phase transitions and presence of discrete $(VO_2F_4)^{3-}$ with a C_{4v} symmetry in $(NH_4)_3VO_2F_4$ were reported. This compound degrades to give various intermediates such as $(NH_4)_3V_2O_4F_5$, finally giving vanadium pentoxide as residue beyond 700 K. From a TG/DTA study, it was inferred that two kinds of equally populated cations exist in the triammonium compound. The EPR study gave evidence for the existence of two kinds of anion, one rigid and the other fast reorienting. In order to delineate the role of hydrogen bonding in the occurrence of phase transitions in the triammonium compound, sodium analogs of the triammonium compound having the general formula $Na_{(3-x)}(NH_4)_x(VO_2F_4)$ were prepared and their thermal stability studied. The results are presented in this communication.

EXPERIMENTAL

The equipment used in this study was a Stanton thermobalance, a Perkin–Elmer DSC-1B and a home-made DTA set-up [3]. The X-ray powder patterns and IR spectra of the starting materials, viz., $NaVO_3$ and NH_4HF_2 in the case of the monosodium compound, and NH_4VO_3 and $NaHF_2$ in the case of the disodium compound, were recorded prior to mixing. The solids

0040-6031/88/$03.50

TABLE 1

$Na(NH_4)_2VO_2F_4$			$Na_2(NH_4)VO_2F_4$			$Na_3VO_2F_4$		
d	I/I_0	hkl	d	I/I_0	hkl	d	I/I_0	hkl
4.87	80	111	5.70	16	401	5.70	37	010
4.17	100	200	5.19	40	530	4.70	79	011
2.97	64	220	4.93	10	431	4.55	12	101
2.43	22	222	4.67	16	521	4.42	26	101
2.10	62	400	4.53	33	441	3.50	16	111
1.88	23	420	4.43	16	531	3.30	10	012
1.72	8	422	3.14	15	841	3.19	6	102
1.62	8	511	2.73	100	1110	2.89	8	020
1.49	16	440	2.27	16	743	2.79	13	112
1.40	9	442	2.02	16	504	2.73	100	200
			1.73	25	954	2.65	9	003
Cubic			1.64	18	525	2.43	24	121
$a = 8.409$ Å			Tetragonal			2.27	9	202
			$a = 30.14$ Å			1.79	6	301
			$c = 8.57$ Å			1.73	18	032
						1.59	12	223
						1.58	6	005
						1.56	8	124
						Monoclinic		
						$a = 5.51$ Å		
						$b = 5.69$ Å		
						$c = 7.91$ Å		

were mixed in the appropriate ratio and ground together on a polythene sheet. The absence of reflections due to starting materials in the X-ray patterns as well as the absence of IR absorption due to reactants is taken as an indication of completion of reaction at room temperature without heating. The trisodium salt was made using the aqueous HF route as follows:

$$6NaF + V_2O_5 \rightarrow 2Na_3VO_2F_4$$

The X-ray powder pattern of the trisodium compound agrees with that generated using a monoclinic unit cell (Table 1).

$Na(NH_4)_2VO_2F_4 \cdot H_2O$

Figures 1a and 1b show the results of thermal studies of this compound. The TG indicates a single-step decomposition with two points of inflexion just as in the case [1] of the triammonium salt. The points of inflexion are at 403 and 623 K. The X-ray powder pattern of the residue obtained by heating the compound to 1000 K and cooling back to room temperature was

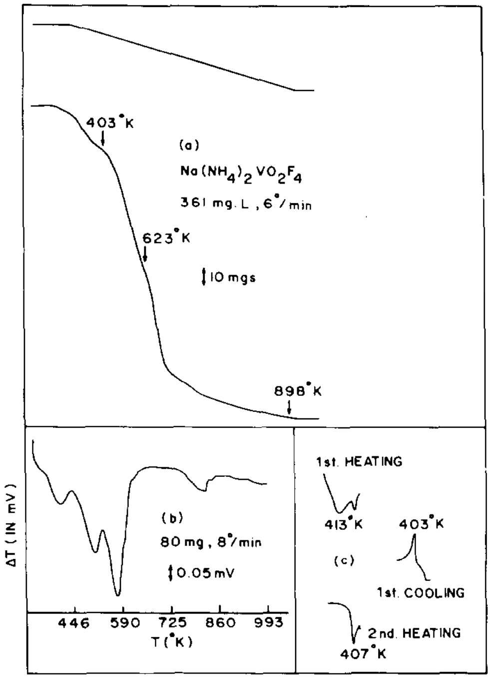

Fig. 1. (a) TG; (b) DTA; (c) DTA thermal cycling around 413 K peak of $Na(NH_4)_2VO_2F_4$.

identified as that of α-$NaVO_3$. Also, an overall weight loss of 48.8% is observed compared with a calculated one of 51.6% (Table 2) as per the following scheme:

$$Na(NH_4)_2VO_2F_4 \cdot H_2O \rightarrow NaVO_3 + 2NH_4F + 2HF$$

The corresponding DTA run (Fig. 1b) exhibits six endotherms at 393, 413, 519, 571, shoulder at 610 and 814 K. This DTA curve resembles that of the triammonium compound reported by us [1] earlier. By comparing the two runs, the first endotherm may be attributed to the removal of occluded

TABLE 2

Thermogravimetric results

S. No.	Compound	Temperature interval (K)	Weight loss percent	
			Observed	Calc
1	$Na(NH_4)_2VO_2F_4$	333–725	48.8	51.6 [a]
2	$Na_2(NH_4)VO_2F_4$	333–993	31.9	30.0 [b]
3	$Na_3VO_2F_4$	373–433	7.0	7.8 [c]
		453–553	10.7	8.5 [c]
		603–923	8.5	9.3 [c]

Assuming the residues to be: [a] $NaVO_3$; [b] $NaVO_3$ and NaF; [c] NaF and $Na_4V_2O_7$.

water. The second one can be attributed to a reversible crystallographic phase transition as is clear from its reversibility on thermal cycling at lower rates of heating/cooling shown in Fig. 1c. The third one is due to loss of a half molecule of NH_4F. The next, stronger endotherm is due to loss of 1.5 molecules of NH_4F. The HF loss is indicated in the shoulder at 610 K. The last one is due to a phase transition of this compound into an alpha polymorph. This path of thermal degradation is in complete conformity with that shown to be the one for the triammonium compound. In this monosodium compound, the relative abundances of the two kinds of NH_4^+ are 0.5 and 1.5 as seen from the DTA. It is clear that the Na^+ replaced 2/3 of the first kind of NH_4^+ ions in the parent compound.

$Na_2(NH_4)VO_2F_4 \cdot H_2O$

Figures 2a and 2b show the TG and DTA runs of this compound. The TG shows onset of decomposition at 333 K with two-step loss in weight. The X-ray pattern of the residue at 1300 K cooled to room temperature showed it to be a mixture of NaF and α-$NaVO_3$. The TG showed an overall loss in weight of 30% compared with the calculated one of 32% (Table 2). The DTA exhibits seven endotherms at 353, 473, 773, 963 (shoulder), 1180, 1245 and

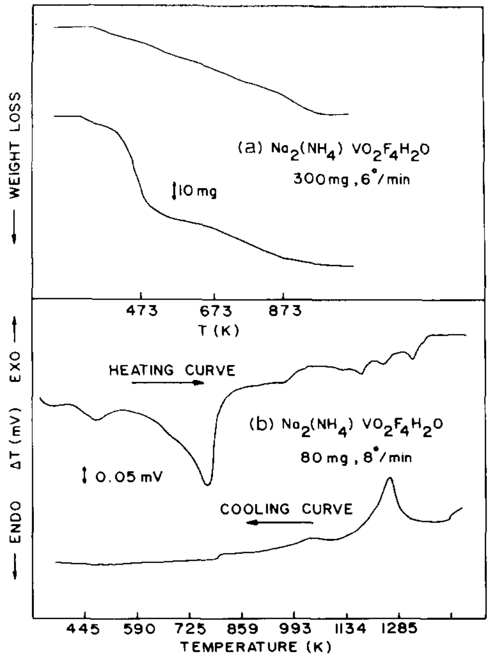

Fig. 2. TG/DTA of $Na_2(NH_4)VO_2F_4$.

1280 K. All are broad and slightly overlapping. On cooling back from 1300 K, the DTA shows only three exotherms at 1260, 1058 and 1033 K. The TG indicates that the overall decomposition, represented by four endotherms, is over by 990 K. The last three endotherms are then due to the products of decomposition, namely NaF and $NaVO_3$. As was shown earlier [4], pure $NaVO_3$ converts itself into α-$NaVO_3$ at 815 K which on further heating melts at 925 K. The finite solubility of one in the other of the two compounds in the residue might explain the enhanced temperature of phase transformation of $NaVO_3$ into its alpha form and also the enhanced melting points of the two compounds, NaF and $NaVO_3$ at 1180 and 1245 K, respectively. The first endotherm again may be attributed to loss of occluded water while the second and the third are due to decomposition, losing NH_4F and HF, respectively. From these results, the following scheme of decomposition may be given for this compound:

$$Na_2(NH_4)VO_2F_4 \cdot H_2O \rightarrow Na_2VO_2F_3 \cdot H_2O + NH_4F$$

$$Na_2VO_2F_3 \cdot H_2O \rightarrow NaVO_3 + NaF + 2HF$$

$$NaVO_3 \rightarrow \alpha - NaVO_3$$

Thus in this compound also only the second kind of ammonium ions are present. It implies that of the two sodium ions 1.5 ions replace completely the first kind of ammonium ions while the other 0.5 sodium ions replace 1/3 of the ammonium ions of the second kind, leaving the remaining 2/3.

$Na_3VO_2F_4 \cdot 1.5H_2O$

TG and DTA scans of the trisodium compound are shown in Figs. 3a and 3b. Weight loss takes place in three distinct steps unlike in all the previous cases. Table 2 summarizes all the thermal data. The DTA exhibits four endotherms, three relatively sharp ones at 336, 438, 557 K, and a broad one in the temperature range 795–950 K. The first weak endotherm is attributed to loss of occluded moisture. The relative areas of the three others are the same. The loss in weight in each step is attributed to loss of one molecule of HF and the postulated intermediates are included in the table. The residue at 1000 K cooled back to room temperature is shown by X-ray to be a mixture of NaF and $Na_4V_2O_7$. Thus the path of degradation of this compound is consistent with the following scheme:

$$2Na_3VO_2F_4 \cdot 1.5H_2O \rightarrow Na_6V_2O_5F_6 \cdot 2H_2O + 2HF$$

$$Na_6V_2O_5F_6 \cdot 2H_2O \rightarrow 2Na_3VO_3F_2 \cdot 0.5H_2O + 2HF$$

$$2Na_3VO_3F_2 \cdot 0.5H_2O \rightarrow 2NaF + Na_4V_2O_7 + 2HF$$

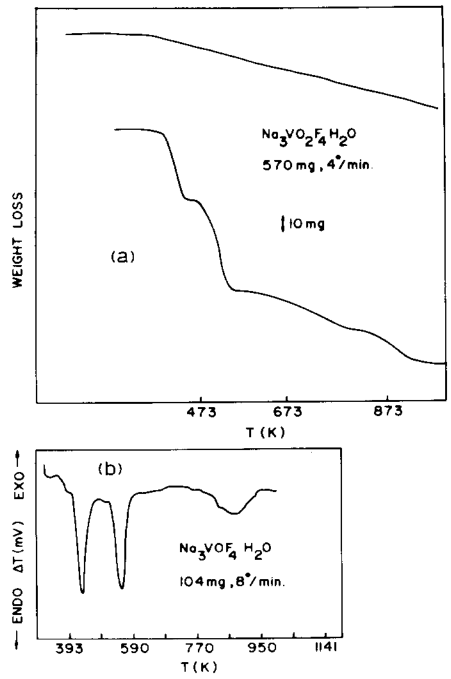

Fig. 3. TG/DTA of $Na_3VO_2F_4$.

PHASE TRANSITIONS

Of the three compounds reported here only the monosodium one shows a crystallographic phase transition [7]. In the triammonium parent compound $(NH_4)_3VO_2F_4$, it was argued earlier [7] that there are two kinds of ammonium ions and the first kind is responsible for the occurrence of phase transition. In the monosodium salt one ammonium ion is replaced in the parent compound while in the disodium salt two are replaced. The monosodium compound shows phase transition while the disodium one does not. Thus the first kind of ammonium ion (0.5 ions per formula) is still present in the monosodium compound while it is totally absent in the disodium. Thus sodium replacement in the analogs is selective, and this is borne out by the similarity of DTA peaks attributable to loss of NH_4F.

CONCLUSIONS

The possible paths of thermal degradation of sodium analogs of $(NH_4)_3VO_2F_4$ are given. Selective replacement of ammonium ions by sodium is inferred. These conclusions are consistent with TG, DTA and X-ray results for these compounds.

REFERENCES

1 U.R.K. Rao, K.S. Venkateswarlu and B.N. Wani, Thermochim. Acta, 81 (1984) 23.
2 U.R.K. Rao, K.S. Venkateswarlu, B.R. Wani, M.D. Sastry, A.G.I. Dalvi and B.D. Joshi, Mol. Phys., 47 (1982) 637.
3 B.N. Wani, Ph.D. Thesis, Bombay University, 1986.
4 B.R. Wani, U.R.K. Rao, K.S. Venkateswarlu and A.S. Gokhale, Thermochim. Acta, 58 (1982) 87.
5 G. Pausewang and K. Dehnike, Z. Anorg. Allg. Chem., 369 (1969) 265.
6 A.K. Sengupta and B.B. Bhaumik, Z. Anorg. Allg. Chem., 390 (1972) 311.
7 U.R.K. Rao, K.S. Venkateswarlu and B.N. Wani, Thermochim. Acta, 98 (1986) 31.