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THERMAL DECOMPOSITION OF AMMONIUM FLUOROOXOVANADATES(IV)

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ABSTRACT

The thermal decomposition of $(NH_4)_2[VOF_4]$, $(NH_4)_2[VOF_4\ H_2O]$ and $(NH_4)_3[VOF_5]$ has been investigated in air and argon by simultaneous TG, DTG and DTA Chemical analysis, X-ray data, and IR spectroscopy have been employed to characterize the intermediate phase for all compounds The complexes start decomposing by giving off NH_4F NH_4VOF_3 has been found as an intermediate phase for all compounds In argon atmosphere NH_4VOF_3 is reduced to a mixture of lower valent compounds, with the main component VF_3 By carrying out the decomposition in air, the oxidation of vanadium to V_2O_5 has been observed

INTRODUCTION

Thermoanalytical techniques are often applied to the chemistry of coordination compounds to elucidate the course of the decomposition as well as to find new possibilities in inorganic synthesis

There are few studies on the thermal decomposition of ammonium fluorometallates reported in the literature For $(NH_4)_3[MF_6]$ (M = Al, Ga, In, Sc, Ti, V) tetrafluorometallates were found as intermediates and trifluorides as final products [1,2] $(NH_4)_3[CrF_6]$ decomposes directly to CrF_3 [2] whilst $(NH_4)_3MnF_6$ decomposes via $(NH_4)_2[MnF_5]$ and NH_4MnF_4 to MnF_2 [3] Four vanadium(IV) ammonium fluorooxo compounds are known ($(NH_4)_2[VOF_4]$, $(NH_4)_2[VOF_4\ H_2O]$, $(NH_4)_3[VOF_5]$ [4] and NH_4VOF_3 [5]) and we now report the thermal decomposition of these compounds

EXPERIMENTAL

The substances studied were prepared in aqueous solution of VOF_2 and NH_4F by using various molar ratios of the fluorides and hydrogen fluoride [4] Their composition was proved by elemental analysis and X-ray powder photographs

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The thermal decomposition was studied by means of a Mettler TA1 thermoanalyzer Experimental conditions TD1 sample holder, platinum crucible, sample mass, 100 mg, atmosphere, dry argon and air with 5 l h^{-1} flow rate, heating rates, 2 or 6 °C min^{-1} Intermediate phases were obtained by heating the initial compound to the desired mass loss and cooling the samples DSC measurements were carried out in a Mettler TA 2000 C thermoanalyzer in dynamic (30 ml min^{-1}) air atmosphere with a sample mass of 50 mg

Isothermal pyrolysis experiments were performed in a tube furnace supplied and regulated by a Mettler TM 16 digital regulator in a dynamic argon and air atmosphere

Infrared spectra were measured using Model 521 Perkin Elmer grating spectrometer (4000–250 cm^{-1}) Crystallographic powder spectra were obtained with a Guinier–de Wolff and high temperature Lenne–de Wolf camera, respectively, using Cu*Kα* radiation

RESULTS

The thermal decomposition of $(NH_4)_2[VOF_4]$ in argon begins at 170 °C as shown in Fig 1 X-ray powder data of intermediate and final steps of decomposition are given in Table 1 In the first step NH_4VOF_3 is formed with the evolution of NH_3 and HF The theoretical mass loss of 20 90% is in good agreement with the observed value of 20 7% (Fig 1) NH_4VOF_3 has been isolated in a separate pyrolysis experiment carried out in an argon atmosphere at 180 °C Data obtained from the X-ray powder photograph of this compound are given in Table 2 The representative part of the IR spectra of NH_4VOF_3 is shown in Fig 2 A 990 and 970 cm^{-1} doublet was observed in the V=O stretching region while synthesized NH_4VOF_3 has a single V=O peak at 975 cm^{-1} [5] The final product of the decomposition is

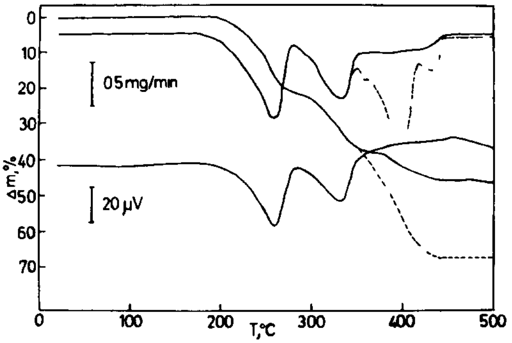


Fig 1 TG, DTG in DTA curves (heating rate 2 °C min^{-1}) of $(NH_4)_2[VOF_4]$ recorded in argon (———) and in air (— — —)

TABLE 1

Intermediate and final products of dynamic and isothermal decomposition of ammonium fluorooxovanadates(IV)

Initial compound [a]	Atmosphere	Mass loss (%)	T (°C)	Time	Mass	X-ray powder pattern [d]
Dynamic thermal decomposition						
III	Ar	46 45				VF_3 + impurities [b]
III	Air	65 80				V_2O_5 [b]
III	Ar, air	21 60				IV
III	Ar, air	30 30				IV
II	Ar	9 20				III
II	Ar	28 9				IV
I	Ar	57 7				VF_3 + impurities [b]
I	Ar, air	16 4				I + III + IV
I	Ar, air	35 5				I + III + IV
I	Air	7 6				I
I	Air	75 9				V_2O_5 [b]
Isothermal decomposition						
III	Ar	22 22	180	15 h	Constant	IV
I	Ar	23 81	120	3 days	Not constant	I + IV
I	Ar	39 29	120	7 days	Constant	IV

[a] I = $(NH_4)_3[VOF_5]$, II = $(NH_4)_2[VOF_4\ H_2O]$, III = $(NH_4)_2[VOF_4]$, IV = NH_4VOF_3 [b] Final product

impure VF_3 as proved by the X-ray powder pattern Chemical analysis of final residue (52 4% V, 29 7% F) gave 1 00 V 1 52 F, while the IR spectrum shows the absence of a strong V=O stretching peak (Fig 2) The most probable admixture is vanadium(III) oxide, which is usually nonstoichiometric The analytical data, as well as the mass loss of 46 45%, are close to the

TABLE 2

Interplanar spacings and intensities of reflections of NH_4VOF_3

d (Å)	I_{rel}	d (Å)	I_{rel}
6 9	9	2 77	6
5 80	10	2 56	6
4 80	5	2 40	5
4 27	5	2 29	7
3 81	9	2 13	4
3 51	3	2 03	7
3 43	9	1 97	6
3 35	2	1 91	8
3 18	9	1 87	2
2 90	3	1 84	3
2 85	8	1 82	5

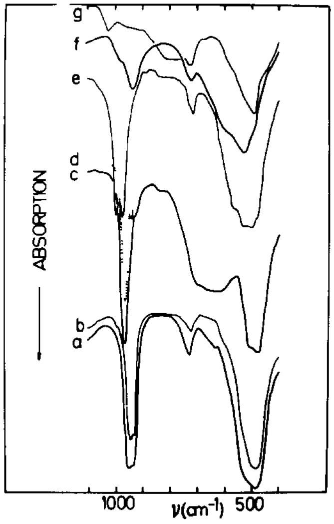


Fig 2 IR spectra of (a) $(NH_4)_3[VOF_5]$, (b) $(NH_4)_8V_3O_3F_{14}$, (c) $(NH_4)_2[VOF_4\ H_2O]$, (d) $(NH_4)_2[VOF_4]$, (e) NH_4VOF_3, and final residue of decomposition of $(NH_4)_2[VOF_4]$ isolated (f) in air and (g) in argon

composition $1\ 03VF_3 + VO_{1\ 79}$ The simultaneously obtained DTA curve is endothermal and runs parallel to the DTG curve The peak temperatures are given in Table 3

The thermal decomposition of $(NH_4)_2[VOF_4]$ in air (Fig 1) also gives NH_4VOF_3 in the first step (also see Table 1) In the next stage the dissociation of NH_4VOF_3 continues as shown by the X-ray powder photograph of the intermediate phase with 30 30% mass loss, which has the same pattern as NH_4VOF_3 At higher temperatures vanadium becomes oxidized to V_2O_5 The observed mass loss depends on experimental conditions (65 80% for 2 °C min^{-1}, 69 72% for 6 °C min^{-1}, and 55 62% for isothermal decomposition at 295 °C) and exceeds considerably the calculated value of 49 20% for decomposition to V_2O_5 V_2O_5 was deposited on the cold part of the furnace, this was proven by X-ray photography V_2O_5 has low volatility at its decomposition temperature (calculations from heats of melting and

TABLE 3

Temperatures (°C) of DTG in DTA peaks of ammonium fluorooxovanadates(IV)

Compound	Atmosphere	DTG	DTA
$(NH_4)_2[VOF_4]$	Ar	260, 330	260, 330
$(NH_4)_2[VOF_4\ H_2O]$	Ar	80, 260, 328	69, 80, 262, 328
$(NH_4)_2[VOF_4]$	Air	268, 335, 383, 401	268, 335
$(NH_4)_3[VOF_5]$	Ar	155, 265, 322	108, 155, 266, 322
$(NH_4)_3[VOF_5]$	Air	165, 270, 330, 390	108, 169, 270, 330

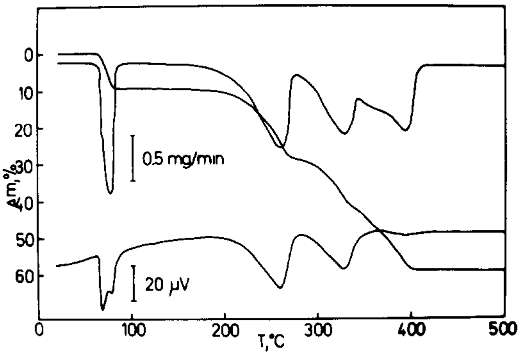


Fig. 3. TG, DTG in DTA curves (heating rate 2 °C $\min^{-1}$) of $(NH_4)_2[VOF_4\cdot H_2O]$ recorded in argon.

boiling of V_2O_5 [6] gave $P(V_2O_5) = 2.1 \times 10^{-7}$ Pa at 427 °C). VOF_3 has a boiling point of 110 °C and decomposes in air at 132 °C to V_2O_5 [7]. We propose VOF_3 as the intermediate phase of thermal decomposition of $(NH_4)_2[VOF_4]$ in air following the equations

$$(NH_4)_2[VOF_4] \rightarrow NH_4F + NH_4VOF_3$$

$$NH_4VOF_3 + O_2 \rightarrow 4VOF_3 + 2H_2O + 4NH_3$$

VOF_3 decomposes to V_2O_5 partially in the sample holder and partially in gas phase. This is in agreement with higher mass loss at higher heating rate, where the second reaction takes place at higher temperature.

$(NH_4)_2[VOF_4\cdot H_2O]$ dehydrates between 65 and 85 °C with 9.20% mass loss (calc. 9.14%). As shown by the thermoanalytical data (Fig. 3, Tables 1 and 3) the compound obtained decomposes further as already described.

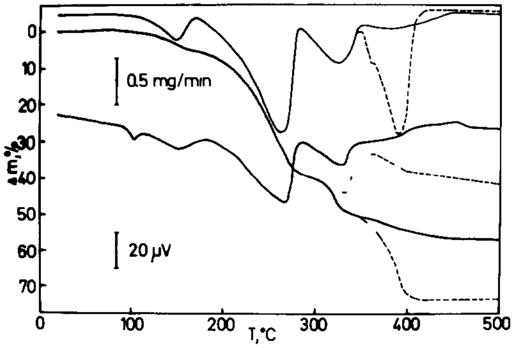


Fig. 4. TG, DTG in DTA curves (heating rate 2 °C $\min^{-1}$) of $(NH_4)_3[VOF_5]$ recorded in argon (———) and in air (— — —).

TABLE 4

X-Ray powder pattern of intermediate phase of thermal decomposition of $(NH_4)_3[VOF_5]$ (35 5% mass loss)

d (Å)	I_{rel}	Compound [a]	hkl [b]
6 90	9	IV	
6 40	3	III	110
6 00	1	III	020
5 80	10	IV	
5 18	7	I + III	031(I), 011(III)
4 80	3	IV	
4 68	2	III	120
4 52	1	I	002
4 41	1	I	130
4 27	8	III + IV	111(III)
3 81	9	IV	
3 51	3	IV	
3 43	9	IV	
3 35	2	IV	
3 28	1	III	031
3 18	6	I + III + IV	132(I), 220(III)
3 13	1	I + III	060(I), 201(III)
2 85	5	IV	
2 29	5	IV	
2 13	3	IV	

[a] I = $(NH_4)_3[VOF_5]$, III = $(NH_4)_2[VOF_4]$, IV = NH_4VOF_3 [b] Ref 4 ($(NH_4)_3[VOF_5]$), calculated from crystal structure data of $(NH_4)_2[VOF_4]$ [10]

TABLE 5

High temperature X-ray powder pattern of $(NH_4)_3[VOF_5]$

Phase below 40 ° C		Phase 40–90 ° C		Phase above 90 ° C			
d (Å)	I_{rel} [a]	d (Å)	I_{rel} [a]	d_{exp} (Å)	d_{calc} (Å)	I_{rel} [a]	hkl [b]
5 23	vs	5 35	vs	5 30	5 292	vs	111
4 56	m	4 65	s	4 60	4 583	s	200
4 47	m	3 22	s	3 28	3 241	s	220
3 21	s	2 39	vw	2 05	2 050	w	420
2 71	vw	2 04	w	1 83	1 833	w	500
2 61	w	1 964	vw	1 76	1 764	w	511
2 36	w	1 864	m				
2 30	m	1 757	m				
2 24	w						
2 00	w						
1 900	m						
1 864	vw						
1 838	vw						
1 772	m						
1 731	vw						
1 610	w						
1 548	w						

[a] s, strong, m, medium, w, weak, v, very [b] Indexed with cubic unit cell, $a = 9\ 17(2)$ Å

The thermal decomposition of $(NH_4)_3[VOF_5]$ is shown in Fig. 4 and Tables 1 and 3. There are three steps on the TG curve obtained in argon with mass losses of 5.70, 38.50 and 57.70% respectively. The calculated values for dissociation of 1/3, 1, 2 and 3 moles of NH_4F are 5.71, 17.14, 39.29 and 51.43%. The first intermediate phase with 5.7% mass loss agrees with the formula $(NH_4)_8V_3O_3F_{14}$ and has an X-ray powder pattern and IR spectrum the same as $(NH_4)_3[VOF_5]$ (Fig. 2). The stoichiometry of the anion $[V_3O_3F_{14}]^{5-}$ was found in compounds of vanadium(V) [8]. Dynamic thermal analysis of $(NH_4)_3[VOF_5]$ gives $(NH_4)_2VOF_4$ and NH_4VOF_3 as intermediates (Table 4) whereas in isothermal decomposition only NH_4VOF_3 was found (Table 2). The final decomposition product is again impure VF_3. Thermal decomposition in air gives firstly NH_4VOF_3 and finally results in V_2O_5. As already mentioned for $(NH_4)_2[VOF_4]$, the final mass loss depends on the heating rate (75.90% for 2 °C min^{-1}, 78.76% for 6 °C min^{-1}) and is much greater than the calculated value for decomposition to V_2O_5 (57.61%).

The endothermal DTA peak at 108 °C is not associated with mass loss and can be ascribed to a polymorphic transition of $(NH_4)_3[VOF_5]$. The changes in X-ray powder pattern were followed up to 140 °C. At 40 °C the number of lines decreased and at 90 °C the positions of these lines changed slightly. The temperature of the second transition is somewhat lower than that determined by DTA. The phase lines above 90 °C can be indexed on the basis of a cubic unit cell (Table 5). The transition to cubic form was followed by DSC (Fig. 5). The hysteresis of the reversible transition is 5 °C at a heating and cooling rate of 2.6 °C min^{-1} and the heat of transition is 0.96(24) kJ mol^{-1}. The value of 2.5(4) kJ mol^{-1} was determined for the heat of polymorphic transition of $(NH_4)_3VO_2F_4$ at 139 °C [9].

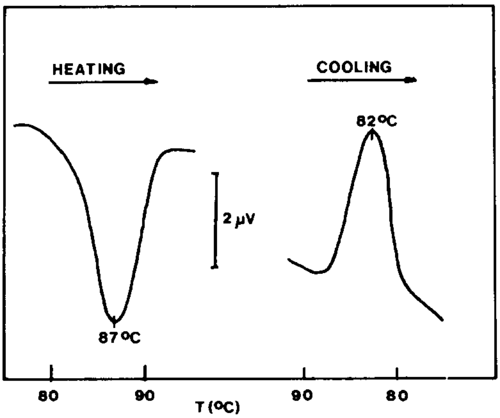
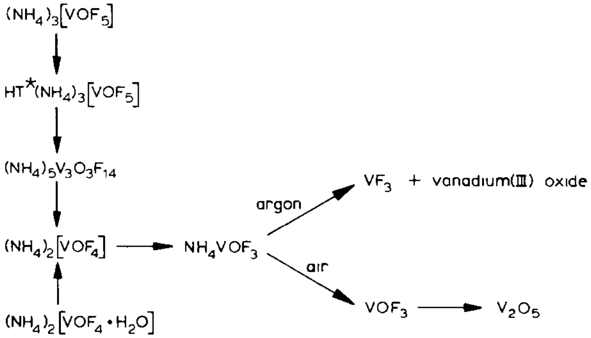


Fig. 5. DSC curve of the transition to the cubic form of $(NH_4)_3[VOF_5]$

The whole decomposition scheme can be represented as



* high temperature form

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