Thermochimica Acta, 215 (1993) 241–246
Elsevier Science Publishers B.V., Amsterdam

Thermal decomposition of guanidinium hexafluoroferrate(III)

T. Marčac Grahek and P. Bukovec

Department of Chemistry and Chemical Technology, University of Ljubljana, Murnikova 6, 61000 Ljubljana (Slovenia)

(Received 21 May 1992)

Abstract

The thermal decomposition of $[C(NH_2)_3]_3FeF_6$ has been studied by simultaneous TG and DTA in an argon atmosphere, FTIR spectroscopy, X-ray diffraction and mass spectrometry. The compound decomposes in at least two consecutive and partly overlapping processes. Decomposition of the organic part of the compound is mainly finished below 410°C. The evolved vapour contains melamine ($C_3H_6N_6$), NH_3, N_2, HF and several other compounds. In the last two stages $(CN)_2$ is evolved, the final decomposition products being Fe and FeF_2.

INTRODUCTION

Most of the simpler guanidinium salts decompose by a vigorous exothermic reaction, which accounts for their use in explosives. On the other hand, guanidinium tetraborate, sulfate, phosphate and polyphosphate are used as fireproofing agents [1]. A number of guanidinium salts have been examined by TG and DTA measurements [2], and some of them also by mass spectrometry [3]. Using thermophotometry, Wendlandt [4] found that some selected guanidinium salts exhibit light emission during their thermal decomposition. In an inert atmosphere [5], DSC curves of some guanidinium salts consist of two or more endothermic peaks, except for guanidinium chromate, for which one exothermic peak was observed, connected with light emission.

The thermal decomposition of guanidinium fluorometallates has not been reported up to now. The compound $[C(NH_2)_3]_3FeF_6$ [7] is cubic (space group Pa3) and consists of FeF_6 octahedra, which are placed at Na^+

Correspondence to: P. Bukovec, Department of Chemistry and Chemical Technology, University of Ljubljana, Murnikova 6, 61000 Ljubljana, Slovenia.

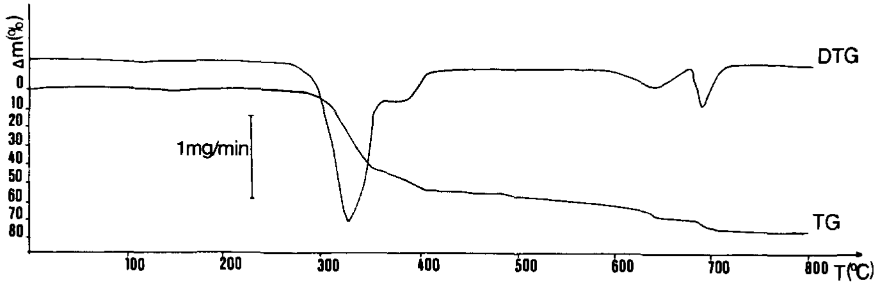


Fig. 1. TG and DTG curves of decomposition of $[C(NH_2)_3]_3FeF_6$.

and Cl^- sites in the NaCl lattice, and of guanidinium cations at the 24-fold general position.

EXPERIMENTAL

The compound $[C(NH_2)_3]_3FeF_6$ was prepared in an aqueous solution of the corresponding fluorides, as described elsewhere [6]. Thermogravimetric studies were carried out in a dynamic argon atmosphere on a Mettler TA1 thermoanalyzer at a heating rate of 4 K min^{-1} in the range 25–800°C. X-ray powder patterns of the solid residues were obtained with a Guinier de Wolff camera using Cu Kα radiation. Vibrational spectra of solid residues from the samples heated to various temperatures were recorded in KBr on a BIORAD FTIR 60 spectrometer in the range 4000–450 cm^{-1}. The C, H, N elemental analyses of the residues were effected on a Perkin–Elmer 204C analyzer. Mass spectral analyses were carried out using a Finnigan 3300 GC–MS System spectrometer with its ionization source operating at 70 eV.

RESULTS AND DISCUSSION

There are four stages in the decomposition of $[C(NH_2)_3]FeF_6$ (Fig. 1, Table 1), with the main part in the range 215–410°C (54.5% mass loss). The decomposition process in this range consists of two consecutive and partly overlapping steps. The organic part of the compound decomposes

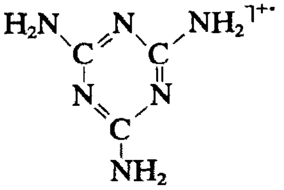
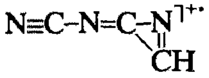
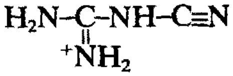
TABLE 1

Four stages in the decomposition of $[C(NH_2)_3]_3FeF_6$

Stage	Temperature range (°C)	DTG_{max}	Mass loss (%)
1	25–355	325	42.5
2	355–410	390	12.0
3	410–680	645	14.1
4	680–800	685	9.4

TABLE 2

Mass spectral data of $[C(NH_2)_3]_3FeF_6$

m/z	Ion	Relative abundance (%)
126		100
43	$H_2N^+{=}C{=}NH$	98
59	 $\left.H_2N{-}\underset{\underset{NH}{\Vert}}{C}{-}NH_2\right]^{+\cdot}$	76
44	$\left.H_2N{-}C{=}NH\right]^{+\cdot}$	49
42	$\left.H_2N{-}C{\equiv}N\right]^{+\cdot}$	46
79	 $\left.N{\equiv}C{-}N{=}C{-}\underset{\underset{CH}{\Vert}}{N}\right]^{+\cdot}$	45
81	$\left.N{\equiv}C{-}N{=}CH{-}N{=}CH_2\right]^{+\cdot}$	16
85	 $H_2N{-}\underset{\underset{{}^+NH_2}{\Vert}}{C}{-}NH{-}C{\equiv}N$	15

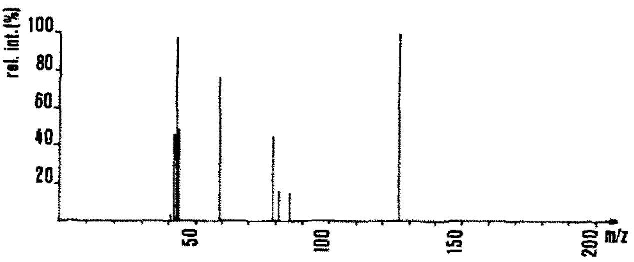


Fig. 2. Mass spectral data.

TABLE 3

X-ray powder diffraction data for the phase at 355°C

d (Å)	*I*	*d* (Å)	*I*
11.44	100	3.39	90
3.81	100	3.23	70
3.61	80	1.90	70

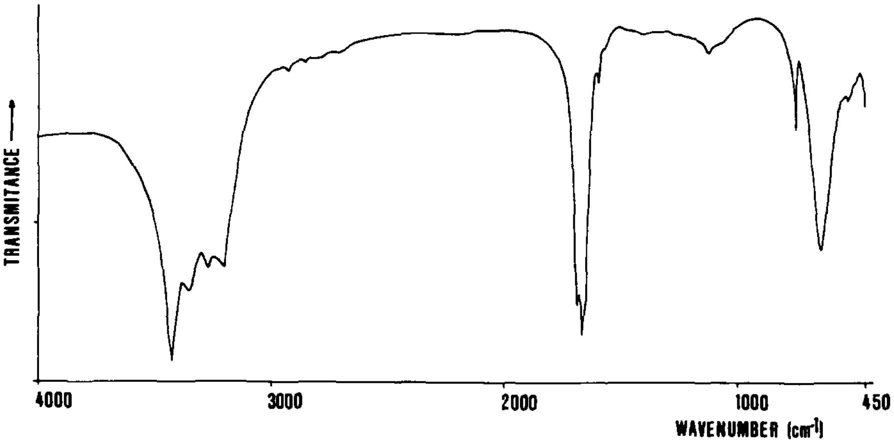


Fig. 3. IR spectrum of $[C(NH_2)_3]FeF_6$.

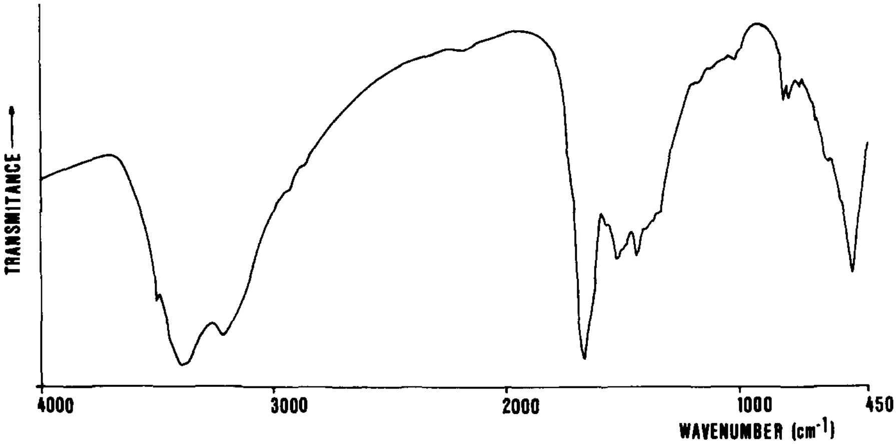


Fig. 4. IR spectrum of the phase at 355°C.

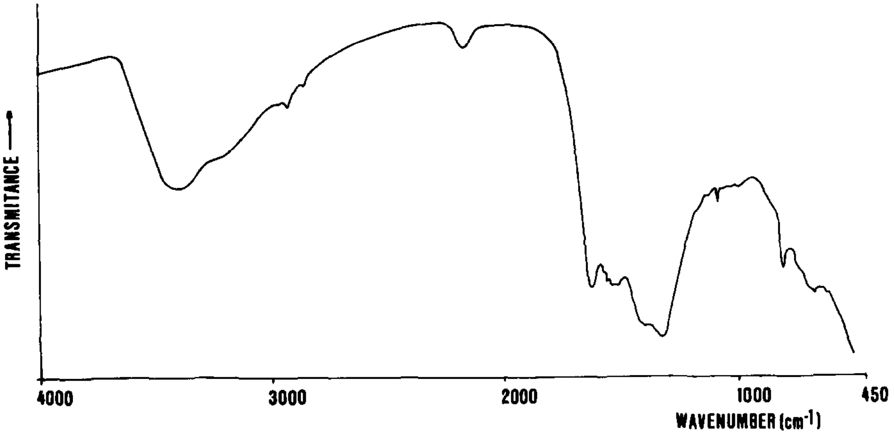


Fig. 5. IR spectrum of the phase at 410°C.

mainly below 410°C. In the vapors evolved, NH_3 and HF were detected by qualitative reactions. According to the mass spectral data (Table 2, Fig. 2), melamine is the main product of the decomposition. The formation of melamine was additionally proved by collecting the sublimate and comparing its IR spectrum with that of pure melamine. The guanidinium cation undergoes decomposition into neutral fragments which vaporize and polymerize. The decomposition product of guanidine is cyanamide ($m/z = 42$), which undergoes dimerization and trimerization to melamine ($m/z = 126$) [3]. Peaks in the mass spectra correspond to the fragmentation of melamine [11] and of smaller entities.

The solid phase isolated at 355°C (after the first DTG effect) has an entirely new X-ray powder pattern, which could not be identified by means of ASTM table (Table 3). The diffraction pattern of the next intermediate phase, isolated at 410°C (after the second DTG effect), shows the lines of FeF_2 [15]. Additional information on the intermediate phases has been obtained from the infrared spectra, which were compared with that of the initial compound as shown in Figs. 3–6. The spectrum of guanidinium hexafluoroferrate(III) (Fig. 3) is in good agreement with those for guanidinium chloride and iodide respectively [9] and for guanidine [10]. In the spectra of intermediate phases, new bands appear in the region 1600–1000 cm^{-1} indicating, in addition to FeF_2, the existence of phases containing N–H and C–N bonds. Elemental analysis of the residue at 410°C (C = 12.73%, H = 1.82%, N = 25.81%) suggests the same.

The X-ray powder pattern of the intermediate phase isolated at 680°C shows *d*-values characteristic of FeF_2 and $Fe(CN)_2$ [12–14]. The FTIR spectrum exhibits the bands ν(C–N) at 2083 and ν(Fe–C) at 648 cm^{-1}, together with a weak absorption in the N–H stretching region (Fig. 6), indicating that the decomposition products of the organic cation are still present at this stage.

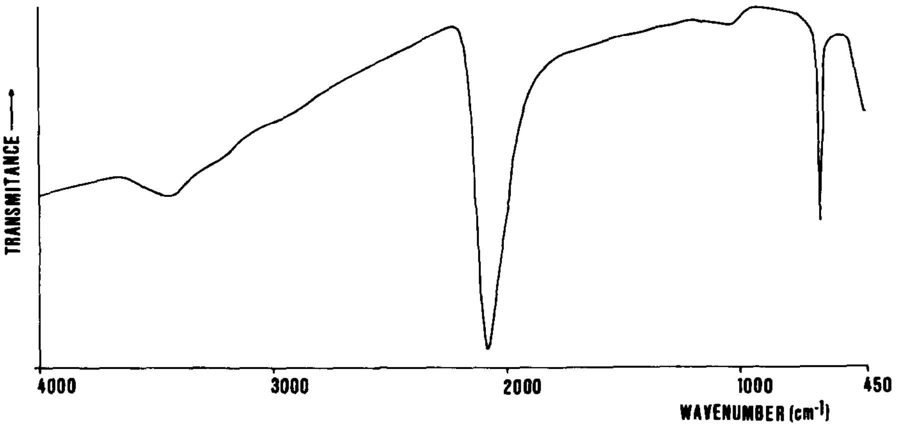


Fig. 6. IR spectrum of the phase at 680°C.

At 800°C the decomposition products are Fe and FeF_2, as proved by X-ray diffraction. A tentative overall decomposition reaction could be

$$2[C(NH_2)_3]_3FeF_6 \rightarrow FeF_2 + Fe + N_2 + (CN)_2 + NH_3 + HF + C_3H_6H_6 + \text{other gaseous products}$$

The experimental mass loss for this reaction is 78.1%, which is in good agreement with the theoretical value of 78.6%.

REFERENCES

1 K. Ohutchi, I. Hirotsu and M. Nishiuchi, Jpn. Patent 7,547,497.
2 M.I. Fauth, Anal. Chem., 32 (1960) 655.
3 M.R. Udupa, Thermochim. Acta, 53 (1982) 383.
4 W.W. Wendlandt, Thermochim. Acta, 70 (1983) 379.
5 W.W. Wendlandt, M. Kasper and S. Bellamy, Thermochim. Acta, 75 (1984) 239.
6 P. Bukovec, Monatsh. Chem., 114 (1983) 277.
7 J.L. Fourquet, F. Plet, Y. Calage and R. de Pape, J. Solid State Chem., 69(1) (1987) 76.
8 P. Bukovec and L. Golič, Abstr. Int. Symp. Fluorine Chem., Avignon, 3–7 September 1979.
9 C.L. Angell, N. Sheppard, A. Yamaguchi, T. Shimanouchi, T. Miyazawa and S. Mizushima, Trans. Faraday Soc., 53 (1957) 589.
10 J. Jones, Trans. Faraday Soc., 55 (1959) 524.
11 P.N. Preston, W. Steedman, M.H. Palmer, S.M. Mackenzie and M.F.G. Stevens, Org. Mass Spectrom., 3 (1970) 863.
12 G.B. Sejfer, Zh. Neorg. Khim., 8 (1963) 1172.
13 S.B. Etcheverry and E.J. Baran, Thermochim. Acta, 111 (1987) 375.
14 B. Mokai, A. Horvath and P.E. Honti, J. Therm. Anal., 31 (1986) 157.