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THERMAL DECOMPOSITION OF HYDRAZINIUM(2+) HEXAFLUOROZIRCONATE(IV) AND HEXAFLUOROHAFNATE(IV)

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SUMMARY

A study of the thermal decomposition of $N_2H_6ZrF_6$ and $N_2H_6HfF_6$ showed that in the first step $N_2H_5ZrF_5$ and $N_2H_5HfF_5$ are formed. In the second step the former gives NH_4ZrF_5 as an intermediate, but an analogous hafnium complex cannot be obtained in a pure state. The end products of the decompositions are the corresponding tetrafluorides. The intermediates were isolated and characterized by chemical analysis, X-ray diffraction patterns and vibrational spectroscopy.

INTRODUCTION

Zirconium and hafnium give a wide range of complex fluorides in which fluorometalate anions of the types $MF_8{}^{4-}$, $MF_7{}^{3-}$, $MF_6{}^{2-}$ and $MF_5{}^{-}$ (M = Zr, Hf) are formed. Many are polymeric (e.g. $Zr_2F_{12}{}^{4-}$, $Zr_2F_{13}{}^{5-}$, $Zr_2F_{14}{}^{6-}$) [1]. Research work carried out on the fluorozirconates and fluorohafnates have involved studies of phase equilibria, thermal stabilities, infrared and Raman spectra, n.m.r. spectra, mass spectra and X-ray structural analysis.

The hydrazinium(2+) ion complexes $N_2H_6MF_6$ and $(N_2H_6)_3M_2F_{14}$ (M = Zr, Hf) were described in the sixties [2,3]. Their thermal decompositions have also been studied, but only the final products were identified [3,4]. On the basis of the weight loss, the feasible first step intermediates of decomposition of the $N_2H_6MF_6$ complexes (M = Zr, Hf) have been suggested to be $(NH_4)_2ZrF_6.2NH_4ZrF_5$ and $(NH_4)_2HfF_6.2NH_4HfF_5$, respectively [5].

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The present study revealed that the thermal decomposition of $N_2H_6MF_6$ (M = Zr, Hf) occurred through new $N_2H_5^+$ complexes, $N_2H_5ZrF_5$ and $N_2H_5HfF_5$.

EXPERIMENTAL

$N_2H_6ZrF_6$ and $N_2H_6HfF_6$ were prepared by methods published in refs. 2 and 3. Their purities were checked by chemical analysis and their vibrational spectra were recorded.

Chemical analyses are summarized below:

$N_2H_6ZrF_6$

Found: N_2H_4, 13.4; Zr, 38.1; F, 47.6

Calcd.: N_2H_4, 13.4; Zr, 38.1; F, 47.6

$N_2H_6HfF_6$

Found: N_2H_4, 9.8; Hf, 54.6; F, 34.9

Calcd.: N_2H_4, 9.8; Hf, 54.7; F, 34.9

For thermal analysis a Mettler TA 1 Thermoanalyzer was used. In a typical run a 100 mg sample and in a macrothermogravimetric decomposition a 500 mg sample were used, and these were referenced against a 100 mg sample of α- Al_2O_3. The heating rate of the furnace was 1 $^{\circ}C\ min^{-1}$ and the decompositions were carried out in a dry argon atmosphere (flow rate 5 lh^{-1}). The DTG range was 10 mg min^{-1} and the DTA range was 100 μV for a 100 mg sample, the DTG range was 10 mg min^{-1} and the DTA range was 200 μV for a 500 mg sample.

The Raman spectra of the solids in Pyrex tubes were obtained using a Spex 1401 double monochromator. As exciting radiations the 514.5 nm line of an Ar^+ laser (Coherent Radiation) was used. The infrared spectra were recorded using a Perkin-Elmer spectrometer, with the solid pressed between CsBr windows. X-ray powder diffraction patterns were obtained by the Debye-Scherrer method on an ENRAF apparatus using graphite monochromated CuK_{α} radiation. Powdered samples were sealed in 0.5 mm thin walled Pyrex capillaries. In chemical analysis, hydrazine, total fluorine ion, ammonium ion and metals were determined. Hydrazine was determined potentiometrically [6], total fluorine by a modified distillation method [7], ammonium by a Kjeldahl method [8] and metals gravimetrically [9].

RESULTS AND DISCUSSION

Thermal decompositions of $N_2H_6^{2+}$ fluorometalates occur either in one step, e.g. $N_2H_6FeF_5$ [10] , $N_2H_6(AsF_6)_2$ [11] , or are more complex and occur in two or more steps through intermediates [12]. Thermal decomposition studies of $N_2H_6MF_6$ (M = Zr, Hf) showed that decomposition of $N_2H_6ZrF_6$ occurred in three steps [2] and $N_2H_6HfF_6$ in two [4] . Deductions about the composition of the intermediates solely on the basis of weight loss observed can lead to incorrect results, and therefore we repeated the thermal decomposition studies on $N_2H_6MF_6$ (M = Zr, Hf), and isolated and identified the intermediates obtained. Thermal decomposition of the $N_2H_6^{2+}$ compounds is probably related to the N-F ···· H hydrogen bonds in their structures, and decompositions through either the $N_2H_5^+$ or the NH_4^+ compounds might be dependent upon the strength of these bonds. Therefore, the formation of $N_2H_5MF_5$ in the first step of the decomposition of $N_2H_6MF_6$ could be explained by proton transfer between the $N_2H_6^{2+}$ ion and the fluoride ion, liberating gaseous HF and forming the $N_2H_5^+$ and MF_5^- ions (M = Zr, Hf).

$$N_2H_6MF_6 \longrightarrow N_2H_5MF_5 + HF$$

The decomposition of $N_2H_6ZrF_6$ begins at 50°C (Fig. 1).

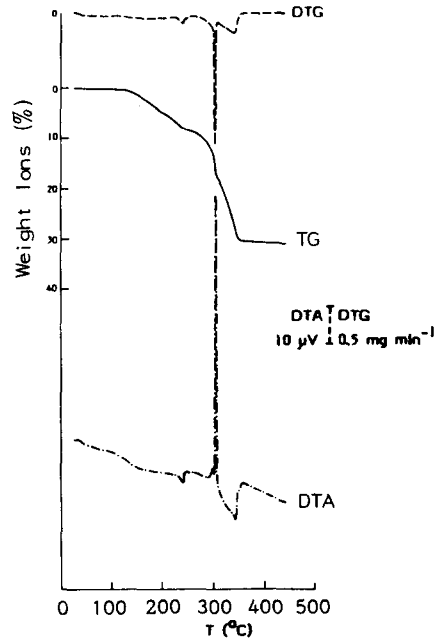

Fig. 1. TG, DTG and DTA curves of $N_2H_6ZrF_6$

The first step occurs endothermically with the DTA peak at 240°C and the DTG minimum at the same temperature. Up to 248°C the sample loses 8.4% of its weight and this corresponds to a loss of one mole of HF per mole of starting material (calcd. weight loss for formation of $N_2H_5ZrF_5$ is 8.36%). The next step between 248 and 305°C is strongly exothermic accompanied by a peak in the DTA curve and a minimum in the DTG curve at 302°C. Up to 305°C the sample loses a further 6.6% of its weight (calcd. weight loss for formation of NH_4ZrF_5 is 6.28%). In the last step, the decomposition is endothermic with a peak in the DTA curve and a minimum in the DTG curve at 342°C. Up to 440°C the cumulative weight loss is 29.7% which correlates well with the theoretical value (30.12%) for formation of ZrF_4.

The thermal decomposition of $N_2H_6ZrF_6$ follows the equations:

$$N_2H_6ZrF_6 \longrightarrow N_2H_5ZrF_5 + HF \qquad (1)$$

$$N_2H_5ZrF_5 \longrightarrow NH_4ZrF_5 + 0.5N_2 + 0.5H_2 \qquad (2)$$

$$NH_4ZrF_5 \longrightarrow ZrF_4 + NH_3 + HF \qquad (3)$$

The crystal structure of $N_2H_6ZrF_6$ is known [13] and the X-ray diffraction patterns of the hafnium analogue confirm that it is isomorphous with the

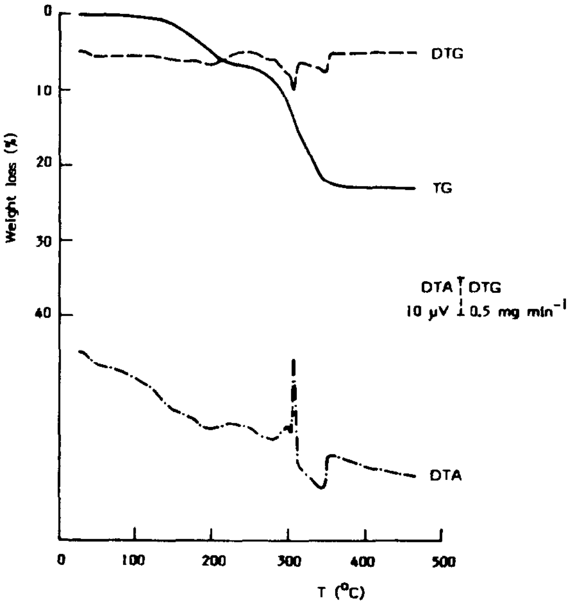

Fig. 2. TG, DTG and DTA curves of $N_2H_6HfF_6$

former. It was expected that the decomposition of $N_2H_6HfF_6$ would occur in a similar fashion to the zirconium compound. Indeed, in the first step the intermediate $N_2H_5HfF_5$ was isolated, but that was decomposed directly to HfF_4.

The decomposition of $N_2H_6HfF_6$ (Fig. 2) starts as low as at 30°C. In the first step up to 213°C the sample loses 6.1% of its weight and this is accompanied by an endothermic DTA peak and a minimum in the DTG curve at 195°C (calcd. weight loss for formation of $N_2H_5HfF_5$ is 6.13%). Further decomposition is exothermic, with two DTA peaks at 300 and 305°C, and a DTG minimum at 305°C. At 312°C we isolated the product but its chemical analysis showed that it contained both hydrazine and ammonium. Up to 465°C the sample loses 23.3% of its initial weight, and that corresponds to the formation of HfF_4 (calcd. weight loss is 22.07%). Between 312 and 465°C the decomposition is endothermic with a DTA peak at 340°C and a DTG minimum at 342°C. Although the DTA and DTG curves indicated that the decomposition of $N_2H_5HfF_5$ probably occurred through an ammonium compound, it was not possible to isolate it in a pure state.

The thermal decomposition follows the equations:

$$N_2H_6HfF_6 \longrightarrow N_2H_5HfF_5 + HF \tag{1}$$

$$N_2H_5HfF_5 \longrightarrow HfF_4 + NH_3 + 0.5H_2 + HF + 0.5N_2 \tag{2}$$

The intermediates, $N_2H_5ZrF_5$, NH_4ZrF_5 and $N_2H_5HfF_5$ were isolated in a macrogravimetric decomposition. Their chemical analysis is given in Table 1.

TABLE 1

Chemical analyses of intermediates

	Calcd. (%)				Found (%)			
	N_2H_4	NH_4	M	F	N_2H_4	NH_4	M	F
$N_2H_5ZrF_5$	14.62		41.60	43.32	14.4		41.6	43.4
NH_4ZrF_5		8.83	44.66	46.51		8.5		
$N_2H_5HfF_5$	10.45		58.23	31.99	10.2		57.9	32.0

X-ray diffraction patterns of $N_2H_5ZrF_5$ and $N_2H_5HfF_5$ are given in Table 2. D-spacings and intensities clearly show that the compounds are isomorphous.

TABLE 2

X-ray diffraction patterns of $N_2H_5ZrF_5$ and $N_2H_5HfF_5$

$N_2H_5ZrF_5$		$N_2H_5HfF_5$	
d	I	d	I
12.12	vs	12.33	vs
17.35	s	17.55	s
20.43	w	20.62	w
22.23	w	22.29	w
24.65	s	24.54	s
27.31	s	27.46	s
29.91	s	30.10	s
30.82	m	31.04	m
32.57	m	32.76	m
37.25	m	37.08	m
41.43	m	41.62	m
42.82	m	43.05	m
45.12	m	45.42	m
47.76	w	46.81	w
48.82	w	48.12	w
49.81	w	48.97	w
50.37	m	49.97	m

The vibrational spectra of $N_2H_6ZrF_6$ and $N_2H_5ZrF_5$, and the published infrared spectrum of NH_4ZrF_5 [14] are given in Table 3. The cationic part of the vibrational spectra is assigned to $N_2H_6^{2+}$ and $N_2H_5^+$, respectively. The criterion for distinguishing $N_2H_6^{2+}$ and $N_2H_5^+$ is the activity of the N-N stretching vibration which appears in $N_2H_6^{2+}$ compounds only in the Raman (in $N_2H_6ZrF_6$ at 1042 cm^{-1}) and in $N_2H_5^+$ compounds both in the Raman and the i.r. (in $N_2H_5ZrF_5$ at 970 cm^{-1} in the i.r., and at 978 cm^{-1} in the Raman), and the observed bands are in accordance with published data [15] .

The bands in the Raman and the absorptions in the i.r. between 1000 and 1700 cm^{-1} are attributed to deformation and rocking vibrations of the N-H bonds. In the anionic part of the vibrational spectra a large number of bands are observed. Those in the range 380-560 cm^{-1} are assigned to metal-fluorine stretching frequencies, and those in the range 200-350 cm^{-1} to bending vibrations of the metal-fluorine bond.

TABLE 3

Vibrational spectra (cm^{-1}) of $N_2H_6ZrF_6$, $N_2H_5ZrF_5$, NH_4ZrF_5

$N_2H_6ZrF_6$		$N_2H_5ZrF_5$		NH_4ZrF_5 [14]	Assignment
IR	R	IR	R	IR	
			188(35)		$(Zr\text{-}F)_b$
	250(16)		240(27)	256 br,s	
	300(10)	304 w	312(15)	295 br,s	
	328(16)				
347 m	364(16)	362 sh	368(33)		
	378(30)				$(Zr\text{-}F)_s$
		382 s	380(29)	385 m	
396 m	396(28)	404 sh			
		412 sh			
462 br,s	472(22)	451 s	470(25)	476 br,s	
				495 br,s	
559 m	540(13)	528 s	538(100)	521 sh	
	1042(100)	970 s	980(69)		$(N\text{-}N)_s$
1067 s					$(NH_3^+)_r$
	1100(10)	1114 vs			
1131 vs	1140(17)		1130(32)		
		1235 w			
1298 w		1295 w			
1324 w	1316(21)				
				1422	(NH_4^+)
1538 vs	1544(8.7)	1542 s			$(NH_3^+)_d$
1555 sh		1558 sh	1564(18)		
1588 vs		1607 s	1612(18)		
1622 s	1624(20)	1630 s			
	1672(8.7)		1656(18)		$(NH_2^+)_d$
				1709 br	(NH_4^+)
				1992 br	
				2857 sh	

The crystal structure of $N_2H_6ZrF_6$ showed that the zirconium atoms exhibited eightfold coordination, the zirconium polyhedron having C_s symmetry [13]. The coordination around zirconium in the ZrF_5^- anion is not clear, however, and for $NH_4ZrF_5.H_2O$ it was speculated that coordination entities probably occupied positions of low site-symmetry. For those compounds in which the zirconium-fluorine polyhedra have low site-symmetries many modes are expected to be i.r. and Raman active, and as the Zr-F bond lengths do not vary greatly the related absorption bands occur close together. This is observed to be so in the infrared spectra of various ammonium fluorozirconates [14] , as well as in the spectra of $N_2H_6ZrF_6$ and $N_2H_5ZrF_5$.

For the second step intermediate NH_4ZrF_5, only the infrared spectrum can be obtained, and is in agreement with the infrared spectrum published in ref. 14.

For $N_2H_6HfF_6$ and $N_2H_5HfF_5$, the vibrational spectra are similar to the corresponding zirconium complexes. The absorption frequencies and the assignment are given in Table 4.

TABLE 4

Vibrational spectra (cm^{-1}) of $N_2H_6HfF_6$ and $N_2H_5HfF_5$

$N_2H_6HfF_6$		$N_2H_5HfF_5$		Assignment
IR	R	IR	R	
			194(49)	$(Hf\text{-}F)_b$
			230(45)	
	268(19)			
353 sh	324(25)	343 sh	308(15)	
	370(20)	365 sh	362(29)	
390 m	394(28)	378 s	400(33)	$(Hf\text{-}F)_s$
460 br,s	482(18)	452 m	476(20)	
		492 s		
565 m	540(16)		544(100)	
	590(26)			
		970 s	982(76)	$(N\text{-}N)_s$
	1042(100)			
1065 s				
	1100(9)	1117 vs		$(NH_3^+)_r$
1131 vs	1140(15)		1130(31)	
		1238 w		
1294 w		1291 w		
1334 sh	1320(22)			
1536 s	1544(14)	1543 s	1528(24)	$(NH_3^+)_d$
1558 sh		1557 sh	1560(24)	
1586 s				
		1605 s		
1622 s	1624(27)	1632 s	1620(29)	
	1672(10)		1660(26)	$(NH_2^+)_d$

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