Journal of Thermal Analysis Vol. 33 (1988) 833–838

THERMAL BEHAVIOUR OF SOME NEW HYDRAZINIUM FLUOROMETALLATES

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Three new hydrazinium(1+) fluoro complexes, $N_2H_5AsF_6$, $(N_2H_5)_2ZrF_6$ and $(N_2H_5)_2HfF_6$, were prepared and characterized by means of chemical analysis, IR and Raman spectroscopy and X-ray powder diffraction. Study of their thermal behaviour via TG, DTG and DTA measurements showed that they decompose in stages; the decomposition of $N_2H_5AsF_6$ proceeded in two steps, through the intermediate NH_4AsF_6; $(N_2H_5)_2ZrF_6$. Decomposed in three steps, through $(NH_4)_2ZrF_6$ and NH_4ZrF_5. The thermal decomposition of $(N_2H_5)_2HfF_6$ is more complex; in the first step $(NH_4)_2HfF_6$ with some $N_2H_5HfF_5$ was obtained, and in the second NH_4HfF_5. The intermediates were identified by means of chemical analysis and vibrational spectroscopy.

In the 1960-s, the hydrazinium(2+) fluorometallates $N_2H_6MF_6$ and $(N_2H_6)_3M_2F_{14}$ (M = Zr or Hf) were isolated from aqueous solution [1, 2]. Later, we reported the preparation of hydrazinium(2+) hexafluoroarsenate in anhydrous hydrogen fluoride as solvent [3]. However, the corresponding hydrazinium(1+) compounds have not been prepared so far.

In the present study, we synthesized $N_2H_5AsF_6$ and $(N_2H_5)_2MF_6$ (M=Zr or Hf) and investigated their properties, particularly their thermal behaviour.

Experimental

Hydrazinium(1+) fluorometallates, $N_2H_5AsF_6$ and $(N_2H_5)_2MF_6$ (M = Zr or Hf), were prepared through the reactions of the corresponding hydrazinium(2+) fluorometallates with hydrazine hydrate:

$$N_2H_6MF_6 + N_2H_4 \cdot H_2O \rightarrow (N_2H_5)_2MF_6 + H_2O$$
(M = Zr or Hf)

$$N_2H_6(AsF_6)_2 + N_2H_4 \cdot H_2O \rightarrow 2\,N_2H_5AsF_6 + H_2O$$

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The chemical analyses are summarized below:
$N_2H_5AsF_6$:
found: N_2H_4, 14.4; calcd.: N_2H_4, 14.44;
$(N_2H_5)_2ZrF_6$:
found: N_2H_4, 23.3; Zr, 33.6; F, 41.5;
calcd.: N_2H_4, 23.62; Zr, 33.62; F, 42.01;
$(N_2H_5)_2HfF_6$:
found: N_2H_4, 17.9; Hf, 49.5; F, 31.2;
calcd.: N_2H_4, 17.87; Hf, 49.78; F, 31.79.

For thermal analysis, a Mettler TA 1 thermoanalyzer was used. In a typical run, a 100 mg sample was used; in a macrothermogravimetric decomposition, this was increased to 500 mg: both were referenced against a 100 mg sample of α-Al_2O_3. Platinum crucibles (1 ml) were used, the heating rate of the furnace was 1 deg min^{-1}, and the decompositions were carried out in a dry argon atmosphere with a flow rate of 5 l h^{-1}. The DTG range was 10 mg min^{-1} and the DTA range was 200 μV.

Infrared spectra of the solids pressed between CsBr discs were obtained by using a Perkin–Elmer 521 spectrometer. the Raman spectra of the samples in a Pyrex tube were recorded on a Spex 1401 double monochromator instrument, with exciting radiation from the 5145 Å line of a Coherent Radiation Laboratories (model Ar) ion laser.

X-ray powder diffraction data were obtained with a Debye–Scherrer camera and CuK_α radiation.

Hydrazine was determined potentiometrically [4], total fluorine by a modified distillation method [5], ammonium by a Kjeldahl method [6] and metals gravimetrically [7].

Results and discussion

The *d*-spacings and intensities in the X-ray powder diffraction photographs of $(N_2H_5)_2ZrF_6$ and $(N_2H_5)_2HfF_6$ clearly show that the compounds are isomorphous.

The thermal decomposition of $N_2H_5AsF_6$ (Fig. 1) begins at 185°. In the first step, up to 248°, the sample loses 22.0% of its weight; the gaseous components N_2, H_2, HF and AsF_5 are released (calculated weight loss 22.30%) and the intermediate is NH_4AsF_6 (found: NH_4, 14.4; calcd. for NH_4AsF_6: NH_4, 14.44). This step is accompanied by an endothermic DTA peak at 215°, exothermic DTA peaks at 222° and 230°, and DTG minima at 221° and 230°. With increasing temperature, complete decomposition occurs, yielding gaseous products. Up to 700°, the

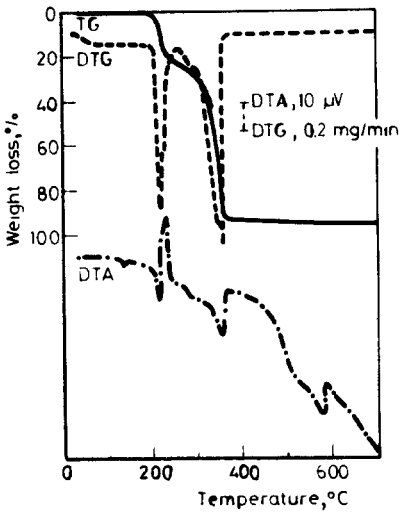

Fig. 1 TG, DTG and DTA curves of $N_2H_5AsF_6$

decomposition is endothermic, with the DTA peak at 357° and the minima in the DTG curve at 350° and 359°.

The thermal decomposition of $N_2H_5AsF_6$ can be described in terms of the equations:

$$6\,N_2H_5AsF_6 \rightarrow 5\,NH_4AsF_6 + AsF_5 + HF + 3.5N_2 + 4.5H_2 \quad (1)$$

$$NH_4AsF_6 \rightarrow AsF_5 + HF + 0.5N_2 + 1.5H_2 \quad (2)$$

The decomposition of $(N_2H_5)_2ZrF_6$ (Fig. 2) starts at 100°. The endothermic DTA peaks at 98°, 110°, 130° and 136°, which are not accompanied by weight loss, can be accounted for by phase changes in the sample. Between 146° and 220°, the decomposition is strongly exothermic, with DTA peaks at 194°, 199°, 210° and 294°, and a DTG minimum at 214°. Up to 220°, the sample loses 13.6% of its weight, corresponding to the loss of one mole of hydrogen and one mole of nitrogen per mole of starting material (theoretical weight loss 11.07%). The intermediate is $(NH_4)_2ZrF_6$ (found: NH_4, 14.4; calcd. for $(NH_4)_2ZrF_6$: NH_4, 14.95). In the temperature interval between 220° and 271°, a further 11.1% weight-loss occurs (the theoretical weight loss for the formation of NH_4ZrF_5 is 13.65%), and this is accompanied by an endothermic DTA peak and a DTG minimum at 262°. The intermediate NH_4ZrF_5 is isolated at 271° (found: NH_4, 8.1; calcd. for NH_4ZrF_5: NH_4, 8.23). In the last step the decomposition is endothermic, with a DTA peak and a DTG minimum at 340°. Up to 415°, the cumulative weight loss is 37.3%, which correlates well with the theoretical value (38.37%) for the formation of ZrF_4.

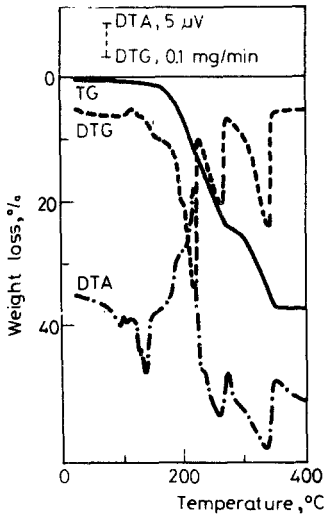

Fig. 2 TG, DTG and DTA curves of $(N_2H_5)_2ZrF_6$

The decomposition may be described in terms of the equations:

$$(N_2H_5)_2ZrF_6 \rightarrow (NH_4)_2ZrF_6 + H_2 + N_2 \quad (3)$$

$$(NH_4)_2ZrF_6 \rightarrow NH_4ZrF_5 + 1.5H_2 + 0.5N_2 + HF \quad (4)$$

$$NH_4ZrF_5 \rightarrow ZrF_4 + 1.5H_2 + 0.5N_2 + HF \quad (5)$$

The thermal decomposition of $(N_2H_5)_2HfF_6$ (Fig. 3) begins at 105°. Up to this temperature, DTA peaks are observed at 70°, 82° and 95°, as in the case of $(N_2H_5)_2ZrF_6$. In the first step, up to 219°, the sample loses 8.4% of its weight,

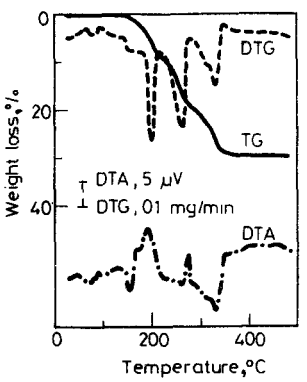

Fig. 3 TG, DTG and DTA curves of $(N_2H_5)_2HfF_6$

corresponding to the formation of $(NH_4)_2HfF_6$ (theoretical value 8.37%). However, $N_2H_5HfF_5$ is also present, as is proved by chemical analysis (found: NH_4, 6.5; N_2H_4, 5.5) and the vibrational spectrum of the first-step intermediate. This step is accompanied by an endothermic DTA peak at 153°, an exothermic DTA peak at 200°, and a DTG minimum at 200°. In the second step, between 219° and 271°, the decomposition is exothermic, with a DTA peak and a DTG minimum at 270°. Between 105° and 271°, the sample loses 19.1% of its weight and this corresponds to the formation of NH_4HfF_5 (theoretical weight loss 18.70%; found: NH_4, 6.3; calcd. for NH_4HfF_5: NH_4, 6.18). Further decomposition is endothermic, with a DTA peak and a DTG minimum at 332°. The cumulative weight loss of the sample up to 357° amounts to 29.0%, corresponding to the formation of HfF_4 (theoretical weight loss 29.03%).

The first step in the thermal decomposition of $(N_2H_5)_2HfF_6$ is more complex in comparison to that of $(N_2H_5)_2ZrF_6$. The decomposition is accompanied by exothermic and endothermic effects, and the intermediate besides $(NH_4)_2HfF_6$ still contains $N_2H_5HfF_5$. In the next two step, NH_4HfF_5 and HfF_4, analogous to the zirconium compound, are formed.

The vibrational spectra of the starting materials and of the intermediate compounds isolated in the thermal decomposition were recorded.

The bands observed in the Raman spectra and the absorptions in the infrared spectra between 940 and 1700 cm^{-1} are assigned to $N_2H_5^+$, and those between 3100 and 3330 cm^{-1} to NH_4^+. For the anionic part of the vibrational spectra, the bands in the 300–690 cm^{-1} interval are assigned to AsF_6^-, those in the 380–570 cm^{-1} interval to metal-fluorine stretching, and those in the 200–355 cm^{-1} interval to bending vibrations (metals Zr and Hf). The observed vibrational spectra are in accordance with the literature [8–11].

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We thank Miss B. Sedej for chemical analysis. The work was financed through the Research Community of Slovenia.

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Zusammenfassung — Die Hydrazinium(1+)-fluorokomplexe $N_2H_5AsF_6$, $(N_2H_5)_2ZrF_6$ und $(N_2H_5)_2HfF_6$ wurden dargestellt und durch chemische Analyse, IR- und Ramanspektren sowie Röntgenbeugungsdiagramme charakterisiert. Die Untersuchung ihres thermischen Verhaltens durch simultane TG–DTG–DTA-Messungen zeigte, dass sie sich schrittweise zersetzen: $N_2H_5AsF_6$ zersetzt sich in 2 Stufen mit NH_4AsF_6 als Zwischenprodukt; $(N_2H_5)_2ZrF_6$ zersetzt sich in 3 Stufen über $(NH_4)_2ZrF_6$ und NH_4ZrF_5. Die thermische Zersetzung von $(N_2H_5)_2HfF_6$ ist komplizierter, der erste Schritt liefert $(NH_4)_2HfF_6$ mit wenig $N_2H_5HfF_5$, der zweite NH_4HfF_5. Die Zwischenprodukte wurden durch chemische Analyse und Schwingungsspektroskopie identifiziert.

Резюме — Получены три новых фторокомплексы гидразиния $N_2H_5AsF_6$, $(N_2H_5)_2ZrF_6$ и $(N_2H_5)_2HfF_6$, строение которых подтверждено ИК- и Раман спектроскопией, а также рентгеноструктурным анализом. ТГ, ДТГ и ДТА измерения показали их разный многоступенчатый характер разложения. Так, соединение $N_2H_5AsF_6$ разлагается в две стадии с образоанием промежуточного продукта NH_4AsF_6, а соединение $(N_2H_5)_2ZrF_6$ — в три стадии с образованием промежуточных соединений $(NH_4)_2ZrF_6$ и NH_4ZrF_5. Термическое разложение $(N_2H_5)_2HfF_6$ протекает более сложным путем: на первой стадии образуется $(NH_4)_2HfF_6$ с некоторой примесью $N_2H_5HfF_5$, а на второй стадии происходит образование NH_4HfF_5. Промежуточные продукты идентифицированы химическим анализом и колебательной спектроскопией.