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# THERMAL DECOMPOSITION STUDIES OF HYDRAZINIUM(2 + ) HEXAFLUOROGERMANATE(IV) DIFLUORIDE AND HYDRAZINIUM(1 + ) HEXAFLUOROGERMANATE(IV)

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## ABSTRACT

The thermal decompositions of the complexes $(N_2H_6)_2(GeF_6)F_2$ and $(N_2H_5)_2GeF_6$ have been investigated by TG, DTG and DTA measurements. The decomposition of these compounds proceeded through intermediates which were isolated and characterized by chemical analysis and vibrational spectroscopy.

## INTRODUCTION

The synthesis, characterization and thermal decomposition studies of numerous new hydrazinium(1 + ) and (2 + ) fluorometalates have been published in recent years [1–6]. In 1981 an X-ray diffraction study of $N_2H_6$-$GeF_6 \cdot H_2O$ was carried out [7] and, recently, $(N_2H_5)_2GeF_6$ and $(N_2H_6)_2(GeF_6)F_2$ were prepared and characterized by their vibrational spectra; the crystal structure of the former was also determined [8]. In the present work the thermal properties of the last two compounds were also investigated by TG, DTG and DTA techniques, which showed that they decomposed by steps, for which the separate intermediates were isolated and identified.

## EXPERIMENTAL

The compounds investigated were prepared by methods published elsewhere [8], and their purities were monitored by chemical analysis and vibrational spectroscopy. Chemical analysis is summarized below.
$(N_2H_6)_2(GeF_6)F_2$
found: $N_2H_4$, 22.3; Ge, 25.1; F, 51.2
calcd.: $N_2H_4$, 21.89; Ge, 24.80; F, 51.93
$(N_2H_5)_2GeF_6$
found: $N_2H_4$, 25.7; Ge, 28.5, F, 45.0
calcd.: $N_2H_4$, 25.36; Ge, 28.73; F, 45.11

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For thermal analysis, a Mettler TA 1 thermoanalyser was used.

In a thermal decomposition study a 100-mg sample was used and it was referenced against a 100-mg sample of $\alpha$-$Al_2O_3$. The heating rate of the furnace was 2°C $min^{-1}$ 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 $\mu$V. In runs when the intermediates were isolated, 500 mg of starting material were used and the heating rate was 2°C $min^{-1}$.

Infrared spectra of the solids pressed between CsBr discs were obtained 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 the exciting radiation of the 5145 Å line of a Coherent Radiation Laboratories (Model Ar) ion laser.

In chemical analyses hydrazine, total fluoride ion and ammonium ion were determined. Hydrazine was determined potentiometrically [9], total fluoride ion was determined by the direct method using an ion-selective electrode [10] and ammonium was determined by a Kjeldahl method [11].

## RESULTS AND DISCUSSION

In the previous characterization of $(N_2H_6)_2(GeF_6)F_2$ by its Raman spectrum, slow decomposition of the solid in a laser beam was observed, and it was assumed that it occurred with the same mechanism as that suggested by Milićev and Maček [12] who studied the decomposition of $(N_2H_6)_2(TiF_6)F_2$. This decomposition was explained by proton transfer between $N_2H_6^{2+}$ and $F^-$ producing the $N_2H_5^+$ ion and liberating HF.

On a thermoanalyser the decomposition of $(N_2H_6)_2(GeF_6)F_2$ begins at 60°C. Figure 1 shows the TG, DTG and DTA curves, and the thermal behaviour is summarized in Table 1. In the first step up to 190°C the sample loses 13.1% of its weight, corresponding to a loss of two moles of HF per mole of starting material. The step is accompanied by endothermic peaks in the DTA curve at 127 and 180°C, and a minimum in the DTG curve at 132°C. The intermediate is identified as $(N_2H_5)_2GeF_6$. In the temperature interval between 190 and 262°C, decomposition is exothermic with the DTA peaks at 242 and 260°C, and a minimum in the DTG curve at 260°C. In this step the sample loses 25.6% of its initial weight and this corresponds to the formation of $(NH_4)_2GeF_6$. Up to 400°C the decomposition is endothermic, with the DTA peak at 360 and the minima in the DTG curve at 349 and 360°C. In this last step $(NH_4)_2GeF_6$ decomposes to gaseous products ($GeF_4$, $NH_3$, $N_2$, $H_2$, HF).

The thermal decomposition of $(N_2H_6)_2(GeF_6)F_2$ is described in terms of the equations

$$(N_2H_6)_2(GeF_6)F_2 \rightarrow (N_2H_5)_2GeF_6 + 2HF \qquad (1)$$

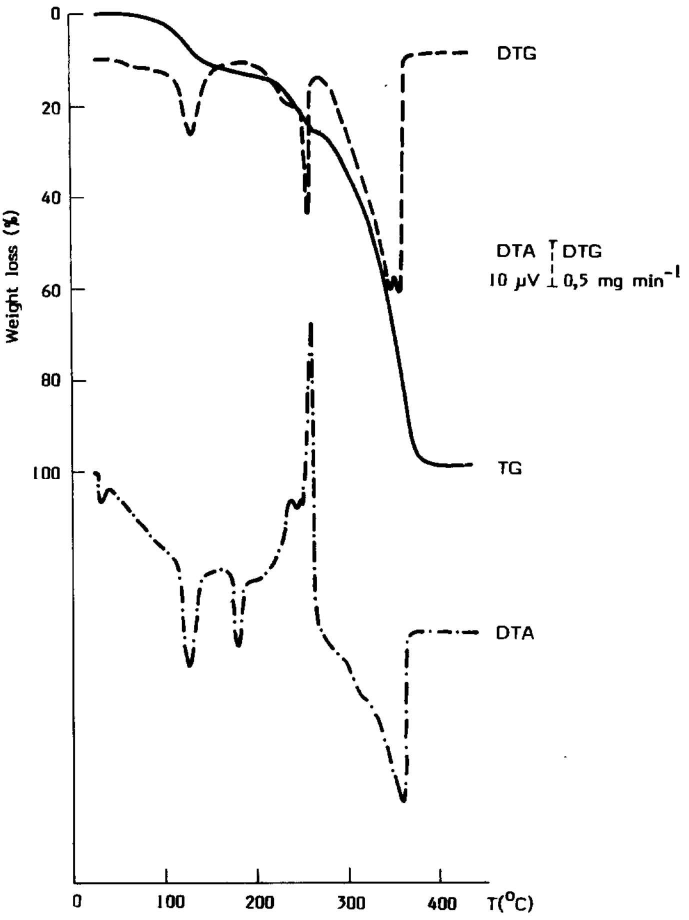

Fig. 1. TG, DTG and DTA curves of $(N_2H_6)_2(GeF_6)F_2$.

TABLE 1
Thermal behaviour of $(N_2H_6)_2(GeF_6)F_2$

| Temperature range (°C) | Transformation | Weight loss (%) | |
|---|---|---|---|
| | | Calcd. | Found |
| 60–190 | Removal of two HF molecules and formation of $(N_2H_5)_2GeF_6$ | 13.67 | 13.1 |
| 190–260 | Removal of one molecule of $N_2$ and one molecule of $H_2$ and formation of $(NH_4)_2GeF_6$ | 23.93 | 25.6 |
| 262–400 | Removal of gaseous components $GeF_4$, $NH_3$, $N_2$, $H_2$, HF; no residue | 100 | 98.2 |

TABLE 2
Chemical analysis of the intermediates

| | Calcd. (%) | | | Found (%) | | |
|---|---|---|---|---|---|---|
| | $N_2H_4$ | Ge | F | $N_2H_4$ | Ge | F |
| $(N_2H_5)_2GeF_6$ | 25.36 | 28.73 | 45.11 | 25.3 | – | 45.0 |
| $(NH_4)_2GeF_6$ | 16.20 | 32.60 | 51.19 | 16.2 | – | 50.8 |

$$(N_2H_5)_2GeF_6 \rightarrow (NH_4)_2GeF_6 + H_2 + N_2 \tag{2}$$

$$(NH_4)_2GeF_6 \rightarrow GeF_4 + NH_3 + 0.5N_2 + 1.5H_2 + 2HF \tag{3}$$

The intermediates, $(N_2H_5)_2GeF_6$ and $(NH_4)_2GeF_6$, were isolated in a macrogravimetric thermal decomposition. Their chemical analysis is given in Table 2. The vibrational spectrum of the first intermediate, $(N_2H_5)_2GeF_6$, confirms the presence of $N_2H_5^+$ and $GeF_6^{2-}$ ions. The strongest band at 621 $cm^{-1}$ in the Raman spectrum is assigned to the symmetric stretching vibration $\nu_1$ and the bands at 325 and 489 $cm^{-1}$ are attributed to the $\nu_5$ and $\nu_2$ modes of the $GeF_6^{2-}$ group. In the infrared spectrum the $\nu_3$ mode at 601 and 547 $cm^{-1}$ and the $\nu_4$ mode at 326 $cm^{-1}$ are observed. In the cationic part of the vibrational spectrum the strong bands at 979 and 968 in the infrared and at 993 and 980 $cm^{-1}$ in the Raman are assigned to the N–N stretching vibration in $N_2H_5^+$. The bands in the 1000–1700 $cm^{-1}$ interval in the infrared and in the Raman spectrum are in accordance with the literature for the $N_2H_5^+$ ion [13].

The infrared spectrum of $(NH_4)_2GeF_6$ is consistent with published data [14] (observed vibrational frequencies at 589, 402 and 335 $cm^{-1}$ for $GeF_6^{2-}$), and in the Raman spectrum the bands expected for the anionic species are observed at 627 ($\nu_1$), 331 ($\nu_2$) and at 472 $cm^{-1}$ ($\nu_5$), as well as the band at 3188 $cm^{-1}$ which is assigned to the $NH_4^+$ ion [15].

Thermal analysis of $(N_2H_5)_2GeF_6$ is given in Fig. 2 and Table 3. The decomposition starts at 35°C; up to 182°C the sample loses 2.2% of its initial weight. This step is accompanied by endothermic DTA peaks at 111 and 170°C, and a DTG minimum at 111°C. With increasing temperature the decomposition is exothermic due to the decomposition of hydrazine, with a DTA peak and a DTG minimum at 226°C. Up to 260°C the sample loses 11.7% of its initial weight, which agrees well with the formation of $(NH_4)_2GeF_6$. In the last step the product decomposes further to gaseous components with a DTA peak at 370°C and a DTG minimum at the same temperature. The decomposition is complete at 450°C and the cumulative weight loss is 98.7%.

Thermal decomposition of $(N_2H_5)_2GeF_6$ is described in terms of eqns. (2) and (3).

Chemical analysis of the intermediate, $(NH_4)_2GeF_6$, is given in Table 4. The vibrational spectrum of $(NH_4)_2GeF_6$ is in agreement with the spectrum

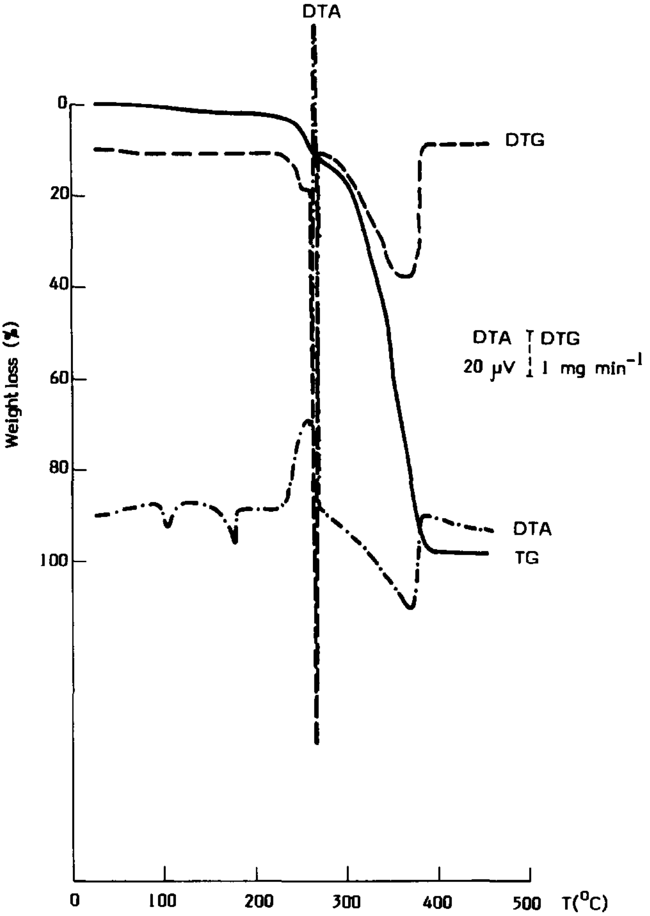

Fig. 2. TG, DTG and DTA curves of $(N_2H_5)_2GeF_6$.

of the same compound isolated in the second step of the decomposition of $(N_2H_6)_2(GeF_6)F_2$, and the bands are unambiguously assigned to the $GeF_6^{2-}$ and $NH_4^+$ ions.

TABLE 3
Thermal behaviour of $(N_2H_5)_2GeF_6$

| Temperature range (°C) | Transformation | Weight loss (%) | |
|---|---|---|---|
| | | Calcd. | Found |
| 35–260 | Removal of one molecule of $N_2$ and $H_2$ and formation of $(NH_4)_2GeF_6$ | 11.80 | 11.7 |
| 260–450 | Removal of gaseous products $GeF_4$, $NH_3$, $N_2$, $H_2$, HF; no residue | 100 | 98.7 |

TABLE 4
Chemical analysis of $(NH_4)_2GeF_6$

| Calcd. (%) | | | Found (%) | | |
|---|---|---|---|---|---|
| $NH_4$ | Ge | F | $NH_4$ | Ge | F |
| 16.20 | 32.60 | 51.19 | 16.1 | – | 50.5 |

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