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DIFFERENTIAL SCANNING CALORIMETRY STUDY OF FLUORIDE COMPLEXES OF GERMANIUM, TUNGSTEN, URANIUM, LITHIUM AND GALLIUM

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ABSTRACT

The enthalpy and temperature of the sublimation, transition and dissociation of nitrosyl fluoride-germanium, tungsten, uranium, lithium and gallium fluoride adducts were determined from DSC measurements. A closed-cell DSC technique was employed for this purpose and to postulate possible reaction mechanisms of the dissociation.

INTRODUCTION

A series of the DSC measurements for the adducts of acceptor fluorides with nitrosyl or nitryl fluorides[1–3] was extended to those of the other five elements. It is known that the fluorides of germanium[4], tungsten[4] and uranium[4] produce adducts with nitrosyl fluoride. The chemical formation of these reactions is as follows

$$\mathrm{Ge} + 5\,\mathrm{NOF} \rightarrow \mathrm{NOGeF_5} + 4\,\mathrm{NO} \tag{1}$$
$$\mathrm{W} + 7\,\mathrm{NOF} \rightarrow \mathrm{NOWF_7} + 6\,\mathrm{NO} \tag{2}$$
$$\mathrm{U} + 6\,\mathrm{NOF} \rightarrow \mathrm{NOUF_6} + 5\,\mathrm{NO} \tag{3}$$

It is probable that the fluorides of lithium and gallium also produce the fluoride complexes according to the following reactions

$$5\,\mathrm{Li} + 7\,\mathrm{NOF} \rightarrow \mathrm{(NO)_2Li_5F_7} + 5\,\mathrm{NO} \tag{4}$$
$$2\,\mathrm{Ga} + 9\,\mathrm{NOF} \rightarrow \mathrm{(NO)_3Ga_2F_9} + 6\,\mathrm{NO} \tag{5}$$

MATERIALS AND EXPERIMENTAL

The fluoride complexes, $NOGeF_5$, $NOWF_7$, $NOUF_6$, $(NO)_2Li_5F_7$ and $(NO)_3Ga_2F_9$ were prepared and analyzed as follows. The guaranteed metallic germanium was added little by little to the 80 mole % HF–20 mole % NO_2 solvent until the solution was almost saturated. After a violent reaction, colourless, transparent, needle-shaped crystals precipitated from the solution on cooling to −20°C. These crystals were separated centrifugally from the solution. The same method was applied to prepare $NOWF_7$, though a slight evacuation at room temperature was necessary to eliminate the solvent adsorbed on the crystal surface. In the case of $NOUF_6$, the 80 mole % HF–20 mole % NO_2 solvent was added to metallic uranium in a reaction tube made of Kel-F plastic. The reaction tube was kept at room temperature until all the metal had reacted satisfactorily. A whitish blue compound was obtained on separating the solution centrifugally. In this case, the atmosphere for all these treatments must be free from moisture as completely as possible, because the moisture, even a very small amount, reacts with $NOUF_6$ to produce UF_4 which causes inevitable errors in the DSC measurements for $NOUF_6$. Since the 80 mole % HF–20 mole % NO_2 solvent itself is hygroscopic, its addition to the metal was done in a distillating manner in a closed system. The X-ray diffraction pattern of this whitish blue compound coincided with that of $NOUF_6$ which is listed on the ASTM cards[5]. In the case of $(NO)_2Li_5F_7$, the 80 mole % HF–20 mole % NO_2 solvent was added to lithium carbonate until the reaction was complete. A white precipitate was deposited by cooling the supernatant solution to −20°C. This precipitate was separated centrifugally from the solution, and was evacuated at −20°C to eliminate the solvent adsorbed on the particle surface. In the case of $(NO)_3Ga_2F_9$, a slight excess of 80 mole % HF–20 mole % NO_2 solvent was added little by little to the guaranteed reagent metallic gallium. The sticky solution obtained was evacuated at 0°C to constant weight. After this procedure, a colourless crystal of gallium fluoride complex was obtained.

All these compounds were analyzed for metal ion, fluorine and nitrogen. The quantitative analyses of fluorine and nitrogen were performed as previously described[6]. The content of germanium in the germanium fluoride complex was determined from the constant weight which was attained by evacuating the solution of a definite amount of germanium in the 80 mole % HF–20 mole % NO_2 solvent at −10°C. It was confirmed beforehand that the DSC curve for this sample coincided satisfactorily with that for $NOGeF_5$ previously prepared. The quantitative analysis of tungsten was performed by weighing the tungstic acid anhydride which was precipitated from the aqueous solution of $NOWF_7$ with hydrochloric acid. The amount of uranium in $NOUF_6$ was determined by weighing the triuranium octoxide produced by igniting the ammonium uranate which was precipitated from the uranyl solution. The amount of lithium was determined by atomic-absorption spectrophotometry using a Hitachi Model 208 atomic-absorption spectrophotometer. The content of gallium was calculated from the amount of gallium used and the weight of gallium compound obtained. These results are shown in Table 1.

The reaction enthalpies and temperatures were determined using a Rigaku-Denki Model DSC-8055 differential scanning calorimeter. The same methods were used as those which have previously been described[1−3]. The DSC chamber was first evacuated and then filled with nitrogen. The evacuation was performed at −20°C for germanium and lithium, and at −10°C for gallium because their compounds were to be subjected to dissociation or sublimation at a higher temperature. During each measurement nitrogen was allowed to flow through the sample chamber at a rate of

TABLE 1

COMPOSITION OF SAMPLE

		Found (%)	Calculated (%)
$NOGeF_5$	Ge	37.04	36.74
	F	47.53	48.08
	N	7.13	7.09
$NOWF_7$	W	52.90	53.01
	F	37.44	38.34
	N	3.98	4.04
$NOUF_6$	U	62.38	62.31
	F	29.56	29.84
	N	3.45	3.67
$(NO)_2Li_5F_7$	Li	15.26	15.24
	F	58.57	58.41
	N	12.16	12.30
$(NO)_3Ga_2F_9$	Ga	34.92	34.82
	F	42.10	42.70
	N	10.03	10.49

30 ml min^{-1}. 2 to 40 mg of the sample was employed at a heating rate of 5 or 10°C min^{-1}. A flat cylindrical closed cell with a pin-hole on its surface was used. Cells made of aluminum were used in the cases of tungsten and lithium. In the other cases, platinum cells were needed because the reaction between the aluminum cell and the sample was not negligibly small. The reaction temperature and the peak area of each DSC curve were measured by the same method as described previously[3].

RESULTS AND DISCUSSION

The DSC curve for the germanium fluoride complex is given in Fig. 1 (curve A). As shown in the figure, $NOGeF_5$ sublimates simply without transition, melting or preceeding dissociation, which were observed for many fluoride complexes. The behaviour of $NOGeF_5$ was similar to that of $(NO)_2SiF_6$[2], $NOPF_6$[3] and $NOVF_6$[2], as described previously. The enthalpy and temperature of sublimation estimated from the DSC curve are listed in Table 2.

The DSC curve for the tungsten fluoride complex is given in Fig. 1 (curve B). As shown in this figure, two small peaks were observed before a decisive large peak, similar to the case of $NOSbF_6$[2]. The former two peaks were entirely reversible, and neither weight changes nor melting reactions were observed with the peaks. Therefore, it is clear that these peaks originate from the transition of the crystal lattice. At the higher temperature sublimation of this material was observed. The enthalpies and

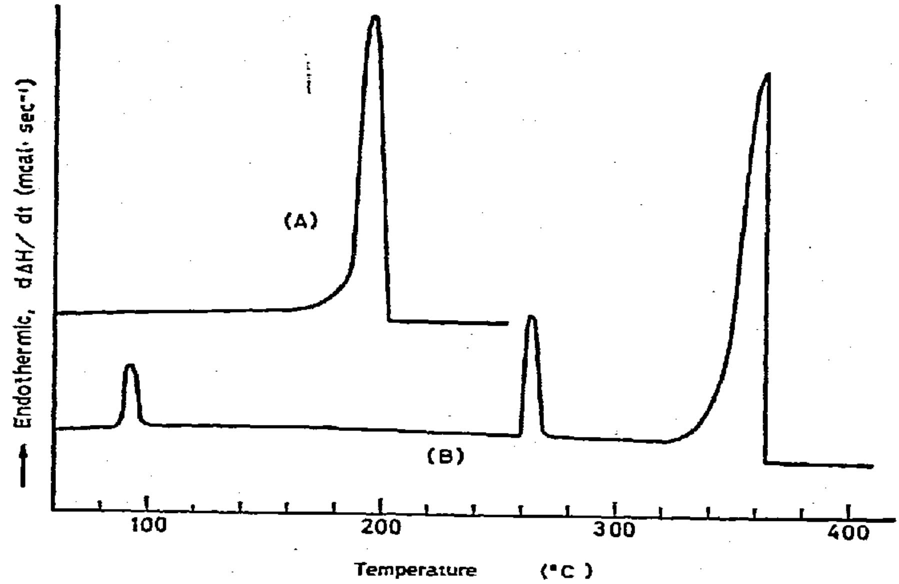

Fig. 1. DSC curve for $NOGeF_5$ (A) and $NOWF_7$ (B).

TABLE 2

REACTION ENTHALPIES FOR $NOGeF_5$ AND $NOWF_7$

Reaction	*Temp. (°C)*	*ΔH(kcal mole^{-1})*
$NOGeF_5$, sublimation	185	36.47
$NOWF_7$, transition	88	1.20
transition	260	2.92
sublimation	346	21.84

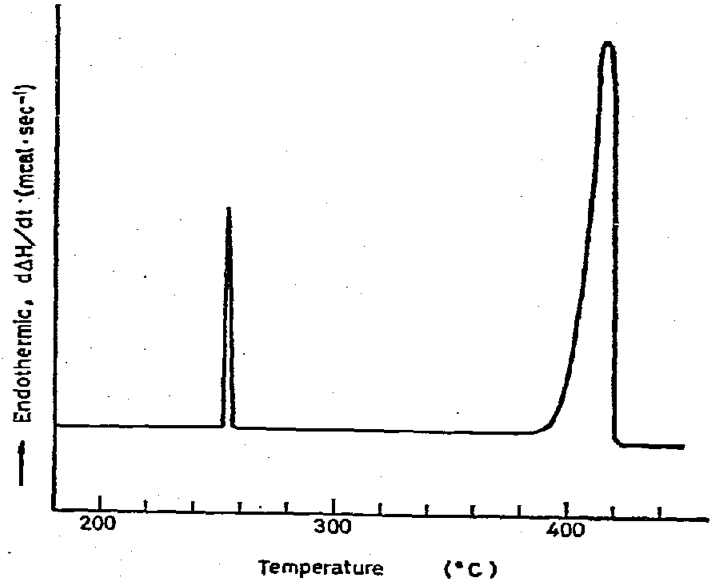

Fig. 2. DSC curve for $NOUF_6$.

TABLE 3

REACTION ENTHALPIES FOR $NOUF_6$ AND $(NO)_2Li_5F_7$

Reaction	*Temp. (°C)*	*ΔH(kcal mole^{-1})*
$NOUF_6$, transition	252	1.886
sublimation	397	25.80
$(NO)_2Li_5F_7 \rightarrow 5\ LiF + 2\ NOF$	143	29.80 (per mole of NOF)

temperatures of transitions and sublimation estimated from the DSC curve are listed in Table 2.

The DSC curve for the uranium fluoride complex is given in Fig. 2. As shown in the figure, there was a sharp peak before a decisive large one. With the former peak, neither a weight change nor any other reactions were observed except for the reversible change in colour of whitish blue to dark blue. Therefore, it is clear that this peak originates from the transition of the crystal lattice. At the higher temperature, which corresponded to the last peak of the DSC curve, sublimation of this material was observed. The enthalpies and temperatures of transition and sublimation estimated from the DSC curve are listed in Table 3.

As previously described, every sublimation phenomenon for the adduct of NOF-acceptor fluoride was simple; that is, in these cases a deposit which was formed by the sublimation and following condensation was confirmed to be the same material as the original[1]. However, in the present case the decomposition of $NOUF_6$ subsequent to the sublimation must be taken into account. A dark green deposit was found around the platinum cell after every DSC measurement. In most cases the same deposit was also found in the cell though the amount was very small. In general, a small amount of light green fine powder coexisted with these deposits. This light green product was concluded to be UF_4 which was formed by decomposition of the dendritic $NOUF_6$, as described later. The mean values of chemical analysis of these materials were in good agreement with the composition of UF_4 as follows: U: found, 75.26%, calculated, 75.80%; F: found, 24.51%, calculated, 24.20%. It is suggested from this fact that $NOUF_6$ decomposed in the vapour phase as the following reaction, when the vapour was diluted by the nitrogen atmosphere.

$$2\ NOUF_6 \rightarrow UF_4 + UF_6 + 2\ NOF \qquad (6)$$

This suggestion could be justified from the fact that the weight of the deposit raked up after each DSC measurement was close to that of UF_4 calculated from eqn. (6), as shown in Table 4. In mid-course of the sublimation of $NOUF_6$, whitish blue dendrites were observed mixed in with the dark green deposit. The mean chemical composition of these materials was as follows: U, 73.31%; F, 25.24%; N, 0.68%. These values correspond to 81.43 and 18.57% of UF_4 and $NOUF_6$, respectively, and the existence of whitish blue dendrite in the deposit endorses the latter. The dendrite seems to be

TABLE 4

COMPARISON OF AMOUNT OF UF_4 FOUND AND CALCULATED

$NOUF_6$ *(mg)*	*Found (mg)*	*Calculated (mg)*
4.69	1.99	1.93
28.85	12.19	11.86
30.40	12.01	12.49
31.41	13.65	12.91
33.03	13.90	13.58
33.25	12.17	13.66
34.01	14.90	13.98
37.11	15.16	15.25

formed by the condensation of some parts of the $NOUF_6$ vapour or the recombination of UF_4, UF_6 and NOF. The existence of the dendrite in mid-course of the sublimation could account for that of the light green compound which was found mixed with the dark green deposit at the end of the DSC measurement.

The DSC curve for the fluoride complex of lithium is given in Fig. 3. As shown in the figure, there was only one decisive peak different from the cases of tungsten and uranium. With the reaction which causes this peak, a weight decrease of 43.07% was observed. This value is in good agreement with the decrease in weight, 43.04%, where 2 moles of NOF per 1 mole of $(NO)_2Li_5F_7$ are evolved, leaving 5 moles of LiF. The results of the chemical analysis of the solid product were found to be also in close

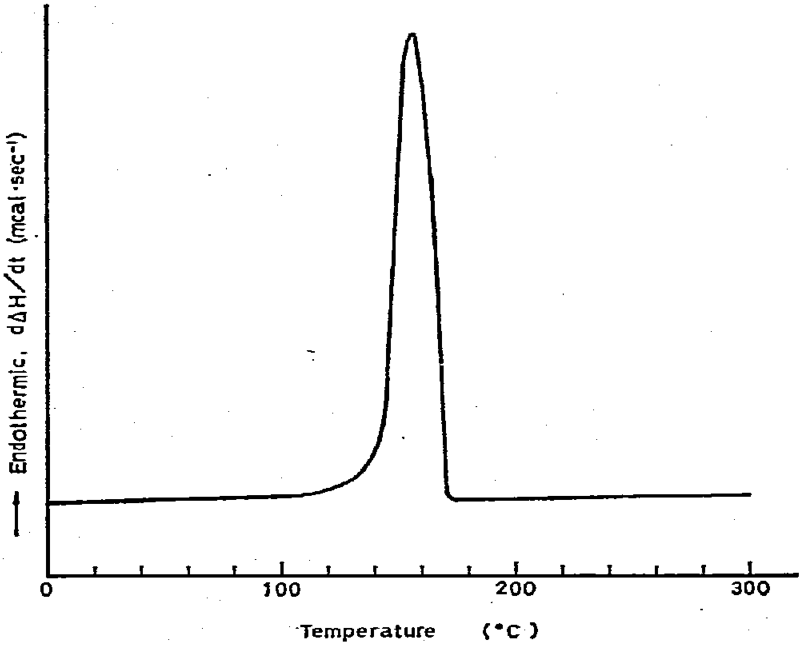

Fig. 3. DSC curve for $(NO)_2Li_5F_7$.

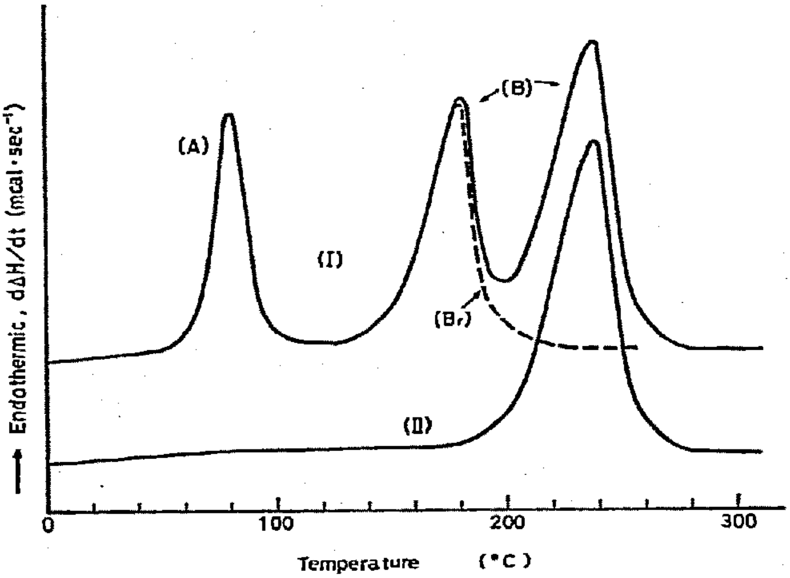

Fig. 4. DSC curve for $(NO)_3Ga_2F_9$ (I) and $(NO)_2Ga_3F_{11}$ (II).

agreement with the composition of LiF. These facts indicate that the peak originated from the following reaction

$$(NO)_2Li_5F_7 \rightarrow 5\ LiF + 2\ NOF \tag{7}$$

The enthalpies and temperatures estimated from the DSC curve are listed in Table 3.

A typical DSC curve for the gallium fluoride complex is given in Fig. 4 (curve I). The existence of three dissociation reactions must be considered for $(NO)_3Ga_2F_9$. With the reaction which causes the first peak (A), a weight decrease of 12.35% was observed. This value is close to the decrease in weight, 12.24%, for the reaction where 1 mole of NOF dissociates per 1 mole of $(NO)_3Ga_2F_9$, leaving 2 moles of $NOGaF_4$. This indicates that the peak (A) was derived from eqn. (8).

$$(NO)_3GaF_9 \rightarrow 2\ NOGaF_4 + NOF \tag{8}$$

The decrease in weight of 27.59% was observed by the reaction which causes the second peak (B). This value is close to that of the decrease in weight, 27.89%, where 1 mole of NOF per 1 mole of $NOGaF_4$ is evolved, leaving 1 mole of GaF_3. However, it is suggested from the shape that the peak (B) is derived from two overlapping reactions.

The material of a definite composition was obtained with a weight decrease of 9.14% by heating the $NOGaF_4$ at 150 °C in the platinum cell for almost 1 h. This value is close to that of the decrease in weight, 9.30%, where 1 mole of NOF per 3 moles of $NOGaF_4$ is evolved, leaving 1 mole of $(NO)_2Ga_3F_{11}$. The DSC curve for the material which was produced by this heating is also shown in Fig. 4 (curve II). The decrease in weight of 20.31% was observed by the reaction which causes the peak. This value is close to that of the decrease in weight, 20.47%, where 2 moles of NOF per 1 mole of

TABLE 5

REACTION ENTHALPIES FOR $(NO)_3Ga_2F_9$

Reaction	*Temp. (°C)*	*ΔH (kcal per mole of NOF)*
$(NO)_3Ga_2F_9 \rightarrow 2\ NOGaF_4 + NOF$	67	14.95
$3\ NOGaF_4 \rightarrow (NO)_2Ga_3F_{11} + NOF$	150	27.23
$(NO)_2Ga_3F_{11} \rightarrow 3\ GaF_3 + 2\ NOF$	202	23.40

$(NO)_2Ga_3F_{11}$ is evolved, leaving 3 moles of GaF_3. The gallium content in the final product calculated from the decrease in weight was 55.03%. This value and the result of chemical analysis on fluorine were close to the composition of GaF_3 as follows: Ga: calculated, 55.02%; F: found, 44.67%, calculated, 44.98%.

Then, the peak (B_1), which is derived from the following dissociation reaction alone, was obtained by subtracting the peak in curve II from the peak (B) in curve I

$$3\ NOGaF_4 \rightarrow (NO)_2Ga_3F_{11} + NOF \tag{9}$$

Needless to say, the following reaction causes the peak in curve II

$$(NO)_2Ga_3F_{11} \rightarrow 3\ GaF_3 + 2\ NOF \tag{10}$$

The enthalpies and temperatures for reactions (8), (9) and (10) estimated from the DSC curves are listed in Table 5.

CONCLUSION

Adducts of nitrosyl fluoride with fluorides of germanium, tungsten, uranium, lithium and gallium were produced using 80 mole % HF–20 mole % NO_2 solvent.

The following facts were found from the DSC measurements of these adducts. $(NO)_2Li_5F_7$ is converted into LiF through one thermal dissociation step. Three thermal dissociation steps are observed for the reaction of $(NO)_3Ga_2F_9$ to the final form of GaF_3. $NOGeF_5$ sublimates without preceding reaction, but in the cases of $NOWF_7$ and $NOUF_6$ one and two transitions are observed, respectively, prior to their sublimation. The enthalpies and temperatures of all these reactions were estimated from the DSC curves.

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