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DIFFERENTIAL SCANNING CALORIMETRY STUDY OF COMPLEX FLUORIDES OF ZIRCONIUM, TIN, VANADIUM, SILICON, ANTIMONY, MOLYBDENUM AND TELLURIUM

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ABSTRACT

The enthalpy and temperature of the sublimation, evaporation and dissociation of nitrosyl or nitryl fluoride-zirconium, tin, vanadium, silicon, antimony, molybdenum and tellurium 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

It is known that a number of acceptor fluorides produce adducts with nitrosyl fluoride or nitryl fluoride. The application of some of their characteristic phenomena has been investigated as a means of separating and refining the elements from their ores[1,2]. However, the kinetic constants of these adducts are not fully known.

In a previous paper[3], it was found that the enthalpy and temperature of the thermal dissociation reactions of $NOTiF_5$, NO_2NbF_6 and $(NO)_2TaF_7$, and the sublimation reactions of $NOTi_2F_9$, $NONbF_6$ and $NOTaF_6$ could be determined by DSC measurements.

In this investigation, the DSC measurements are extended to the complex fluorides of the other seven elements. It is evident that the fluorides of zirconium[1], molybdenum[4], silicon[2], antimony[4] and tellurium[4] produce adducts with nitrosyl fluoride. The chemical formation of these reactions is as follows:

$$Zi + 6NOF \rightarrow (NO)_2ZrF_6 + 4NO \quad (1)$$

$$Mo + 4NOF \rightarrow NOMoF_4 + 3NO \quad (2)$$

$$Si + 6NOF \rightarrow (NO)_2SiF_6 + 4NO \quad (3)$$

$$Sb + 6NOF \rightarrow NOSbF_6 + 5NO \quad (4)$$

$$2Te + 11NOF \rightarrow (NO)_3Te_2F_{11} + 8NO \quad (5)$$

It is also probable that the fluorides of tin and vanadium produce the complex

fluorides according to the following reactions:

$$Sn + 6NOF \rightarrow (NO)_2SnF_6 + 4NO \quad (6)$$

$$V + 6NOF \rightarrow NOVF_6 + 5NO \quad (7)$$

MATERIALS AND EXPERIMENTAL

The compounds, $(NO)_2ZrF_6$, NO_2MoF_4, $(NO)_2SiF_6$, $NOSbF_6$, $(NO)_2SnF_6$, $(NO)_3Te_2F_{11}$ and $NOVF_6$ were prepared and analyzed as follows. In the case of $(NO)_2ZrF_6$, an 80 mol% HF–20 mol% NO_2 solvent, prepared as described before[5], was added gradually to the metallic zirconium granule until all of the metal had reacted satisfactorily and had been converted to a white precipitate. This compound was separated centrifugally from the solution. The remaining solution was separated from the particles by filter-paper. $NOSbF_6$ was prepared, using metallic antimony, by the same procedure as that used in preparing the zirconium compound. $(NO)_2SiF_6$ was prepared by adding a slight excess of the 80 mol% HF–20 mol% NO_2 solution to the guaranteed reagent silicon dioxide and it was kept at 30°C, and then, after a violent reaction, a transparent solution was obtained. Colorless, transparent and needle-shaped crystals precipitated on cooling the solution to −20°C. These crystals were separated centrifugally. The same method was applied to prepare $NOVF_6$, NO_2MoF_4, $(NO)_2SnF_6$ and $(NO)_3Te_2F_{11}$ using vanadium pentaoxide, molybdenum trioxide, metallic tin and tellurium as reagents, respectively.

All these compounds, except for vanadium, antimony, molybdenum and tellurium, which are similar to the complex fluoride of silicon, were analyzed on metal ion, fluorine and nitrogen as previously described[6]. The quantitative analyses of vanadium and antimony were performed by the potassium permanganate titration of the oxidation reactions to pentavalent ions from tri- and tetravalent ones, respectively. The amount of molybdenum was determined by weighing the lead molybdate which was formed by adding lead acetate solution to the solution to be examined in the presence of acetic acid. In this case, it stands to reason that the solution should be free from fluorine ion. The amount of tellurium was determined by weighing the elementary tellurium which was produced by the reduction reaction with hydrazine dihydrochloride and sulfurous acid. The results are shown in Table 1.

The reaction enthalpies and the reaction 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[3]. The normal operating procedure for the calorimeter requires that the DSC chamber is first evacuated and then filled with nitrogen. However, this evacuation was omitted in the cases where the samples, such as the compounds of zirconium, molybdenum and silicon, were to be subjected to dissociation or sublimation. During each measurement nitrogen was allowed to flow through the sample chamber at a rate of 30 ml min^{-1}, as described previously. From 1–10 mg of the sample was employed at a heating rate of 2.5–10°C min^{-1}. A flat cylindrical closed cell with a pin hole on its surface was used. Cells

made of aluminum were used except when platinum cells were needed. The heat of evaporation of mercury and the heat of transition of KNO_3 were used as the standards.

TABLE 1

COMPOSITION OF SAMPLE

		Found (%)	*Calculated* (%)
$(NO)_2ZrF_6$	Zr	34.22	34.39
	F	43.19	42.98
	N	10.60	10.56
$(NO)_2SnF_6$	Sn	40.47	40.55
	F	39.17	38.95
	N	9.62	9.57
$NOVF_6$	V	25.82	26.13
	F	58.66	58.48
	N	7.20	7.19
$(NO)_2SiF_6$	Si	13.82	13.90
	F	57.07	56.41
	N	13.91	13.86
$NOSbF_6$	Sb	45.11	45.81
	F	42.99	42.89
	N	4.76	5.27
NO_2MoF_4	Mo	44.31	44.02
	F	36.76	34.87
	N	6.47	6.43
$(NO)_3Te_2F_{11}$	Te	45.65	46.05
	F	37.72	37.71
	N	7.60	7.58

RESULTS AND DISCUSSION

The DSC curve for zirconium complex fluorides is given in Fig. 1 (curve A). The dissociation of $(NO)_2ZrF_6$ appears to begin at 85 °C. A weight decrease of 19.0% was observed when this material was heated to 110 °C. The dissociation of a single mole of NOF, per one mole of $(NO)_2ZrF_6$, leaving $NOZrF_5$, could account for the observed weight decrease because the weight decrease is 18.48% in the following reaction:

$$(NO)_2ZrF_6 \rightarrow NOZrF_5 + NOF \quad (8)$$

The results of chemical analysis of the solid product were also very close to the composition of $NOZrF_5$ as follows: Zr, found, 42.85%, calc., 42.19%; F, found, 43.50%, calc., 43.93%; N, found, 6.38%, calc., 6.48%. At 151 °C another dissociation reaction seems to begin. A weight decrease of 22.1% was observed by the reaction which causes this peak. This value is close to the decrease in weight, 22.66%,

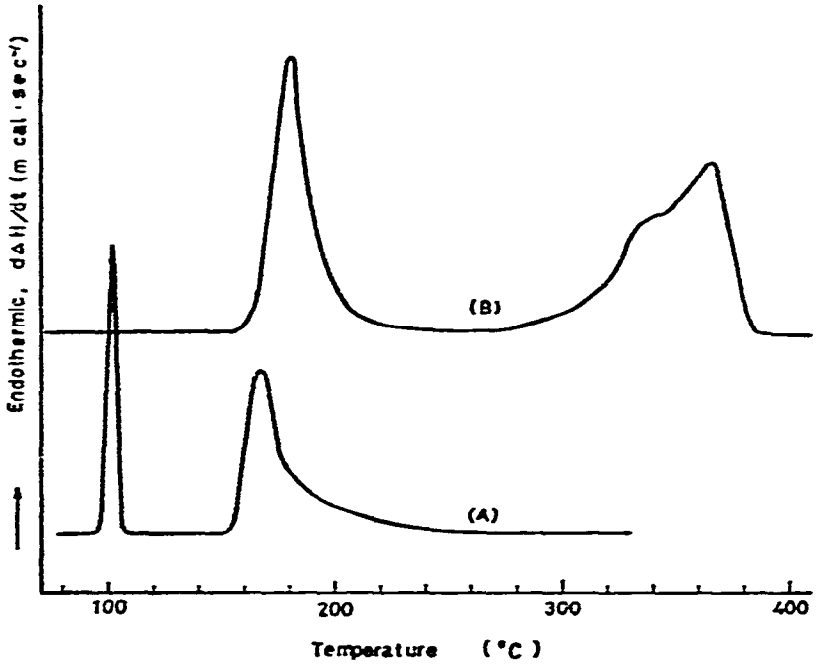

Fig. 1. DSC curve for complex fluoride of zirconium (A) and tin (B).

where one mole of NOF per one mole $NOZrF_5$ is evolved, leaving ZrF_4. The result of chemical analysis of the solid product was also found to be in close agreement with the composition of ZrF_4. Therefore, the second peak in curve A was found to derive from the following reaction:

$$NOZrF_5 \rightarrow NOF + ZrF_4 \tag{9}$$

The DSC curve for tin complex fluorides was similar to that for zirconium, as shown in Fig. 1 (curve B). A weight decrease of 17.1% was observed when $(NO)_2SnF_6$ was heated to 170°C. This value is close to the decrease in weight, 16.74%, for the following dissociation reaction:

$$(NO)_2SnF_6 \rightarrow NOSnF_5 + NOF \tag{10}$$

The result of chemical analysis of the solid product is also very close to the composition of $NOSnF_5$ as follows: Sn, found, 38.79%, calc., 38.95%; N, found, 5.70%, calc., 5.75%. This indicates that the first peak in the DSC curve of $(NO)_2SnF_6$ was derived from eqn (10). At higher temperature, another peak which causes a weight decrease of 19.8% was observed. This value is close to the decrease in weight, 20.11%, predicted by the following reaction:

$$NOSnF_5 \rightarrow SnF_4 + NOF \tag{11}$$

The result of chemical analysis of the solid product was also found to be in close agreement with the composition of SnF_4.

Enthalpies and temperatures of dissociation estimated from the DSC curves of complex fluorides of zirconium and tin are listed in Table 2.

TABLE 2

REACTION ENTHALPIES FOR $(NO)_2ZrF_6$ AND $(NO)_2SnF_6$

Reaction	*Peak temp.* (°C)	*H* (*kcal mol*$^{-1}$)
$(NO)_2ZrF_6 \rightarrow NOZrF_5 + NOF$	85~105	11.0 (per mole of NOF)
$NOZrF_5 \rightarrow ZrF_4 + NOF$	151~260	17.5 (per mole of NOF)
$(NO)_2SnF_6 \rightarrow NOSnF_5 + NOF$	155~242	18.8 (per mole of NOF)
$NOSnF_5 \rightarrow SnF_4 + NOF$	260~386	24.6 (per mole of NOF)

The DSC curves for $NOVF_6$ and $(NO)_2SiF_6$ are given in Fig. 2, curve A and B, respectively. In both cases, cells made of platinum were used because the reaction between aluminum cells and the samples was not negligibly small. As shown in both

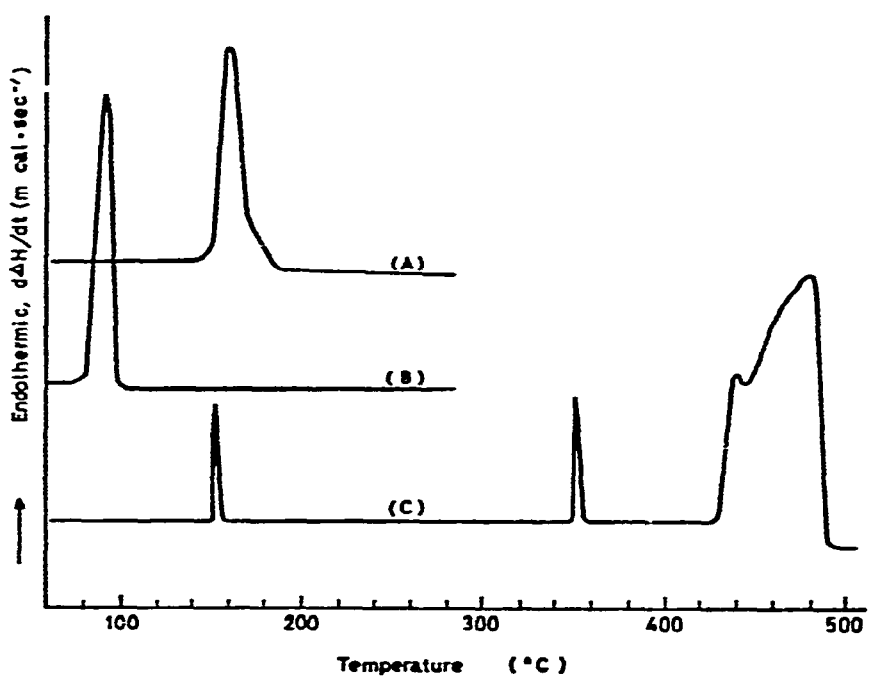

Fig. 2. DSC curve for complex fluoride of vanadium (A), silicon (B) and antimony (C).

curves, $NOVF_6$ and $(NO)_2SiF_6$ sublimated without transition or preceding dissociation which were observed for $NOTiF_5$[3] or $(NO)_2ZrF_6$. The enthalpies and temperatures of sublimation are shown in Table 3.

The DSC curves for $NOSbF_6$ are also given in Fig. 2 (curve C). The platinum cell was used in a similar way. As shown in the figure, there were two sharp peaks

TABLE 3

REACTION ENTHALPIES FOR $NOVF_6$, $(NO)_2SiF_6$ AND $NOSbF_6$

Reaction	*Peak temp. (°C)*	*H (kcal mol^{-1})*
$NOVF_6$, sublimation	150	44.0
$(NO)_2SiF_6$, sublimation	80	39.2
$NOSbF_6$, transition(I)	156	1.54
transition(II)	346	1.69
sublimation	426	42.3

before a decisive broad peak different from the cases of complex fluorides of vanadium and silicon. With these two peaks, neither a weight change nor a melting reaction were observed. 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 temperatures of transition and sublimation estimated from the DSC curve and are listed in Table 3.

The DSC curves for molybdenum complex fluoride are given in Fig. 3. The dissociation of NO_2MoF_4 appears to occur at the temperature range of 184 to 300°C,

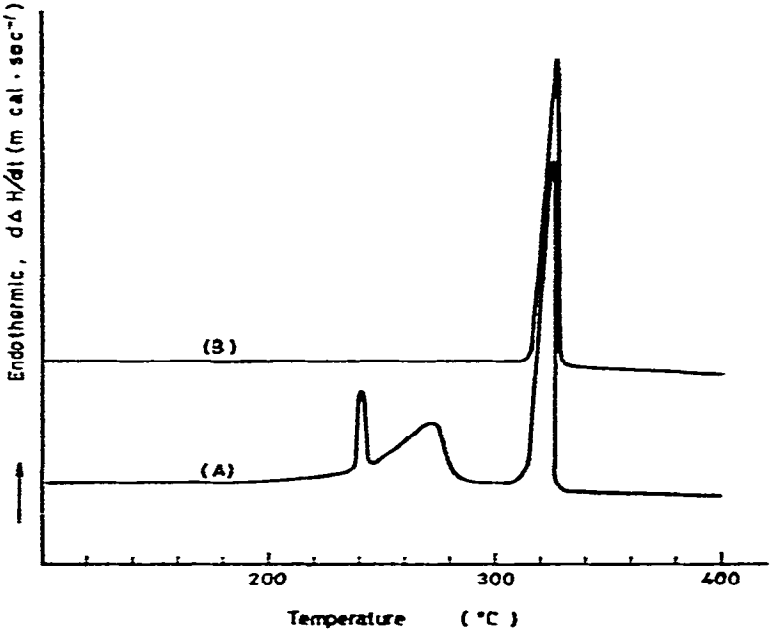

Fig. 3. DSC curve for complex fluoride of molybdenum. (A) NO_2MoF_4; (B) $NOMoF_4$.

overlapping with another reaction at 238°C (curve A). Through these reactions, a weight decrease of about 10%, which is poor in reproducibility, was observed. On the other hand, the transparent liquid was obtained as a result of heating NO_2MoF_4 to 250°C in a semi-closed vessel. The viscosity of this liquid increased gradually on

cooling, and subsequently, this material became a glassy solid at room temperature. The results of the analysis of this material were as follows: Mo, 47.09%; F, 38.26%; N, 6.71%. These values are very close to those of the components of $NOMoF_4$: Mo, 47.51%; F, 37.63%; N, 6.94%. This indicates that half a mole of oxygen per one mole of NO_2MoF_4 is apparently evolved, leaving $NOMoF_4$ as in the following equation:

$$NO_2MoF_4 \rightarrow NOMoF_4 + \tfrac{1}{2}O_2 \quad (12)$$

On these grounds it is suggested that the sharp peak at 238 °C was derived from the phase change with the dissociation reaction of NO_2MoF_4. In the DSC curve of $NOMoF_4$, these peaks no longer appear (curve B). This indicates that $NOMoF_4$ is an amorphous glassy material. At 314 °C the $NOMoF_4$ evaporated without prior decomposition or dissociation. The disagreement in weight decrease between the result found and that calculated from eqn (12), 7.34%, is attributed to the fact that the temperature of evaporation of $NOMoF_4$ is near to that of reaction (12).

Enthalpies estimated from the DSC curves of dissociation and evaporation are listed in Table 4.

TABLE 4

REACTION ENTHALPIES FOR NO_2MoF_4 AND $(NO)_3Te_2F_{11}$

Reaction	*Peak temp. (°C)*	*H (kcal mol^{-1})*
$NO_2MoF_4 \rightarrow NOMoF_4 + \frac{1}{2}O_2$	184~290	24.3 (per mole of O_2)
$NOMoF_4$, vaporization	314	23.5
$(NO)_3Te_2F_{11} \rightarrow 2NOTeF_5 + NOF$	66~128	15.1 (per mole of NOF)
$NOTeF_5$, vaporization	302	14.7

In the case of tellurium complex fluoride, a phenomenon similar to that observed in the case of molybdenum was noted. The DSC curves for tellurium complex fluoride are given in Fig. 4. The decrease in weight of 9.24% was observed by the reaction which causes the first broad peak (curve A). This value is very close to that of the decrease in weight, 9.20%, where one mole of NOF per one mole of $(NO)_3Te_2F_{11}$ is evolved leaving two moles of $NOTeF_5$. On the other hand, the colorless liquid was obtained by heating $(NO)_3Te_2F_{11}$ up to 120 °C in the loosely-plugged vessel. This material was a viscid liquid at room temperature and a transparent glassy solid at −20 °C. The results of the analysis of this material were as follows: Te, 48.36%; F, 38.11%; N, 5.62%. These values are close to those of the components of $NOTeF_5$: Te, 50.72%; F, 37.76%; N, 5.57%. Therefore, this broad peak was found to originate from the following dissociation reaction:

$$(NO)_3Te_2F_{11} \rightarrow 2NOTeF_5 + NOF \quad (13)$$

In the DSC curves of $NOTeF_5$, similar to the case of $NOMoF_4$, the sharp peaks which

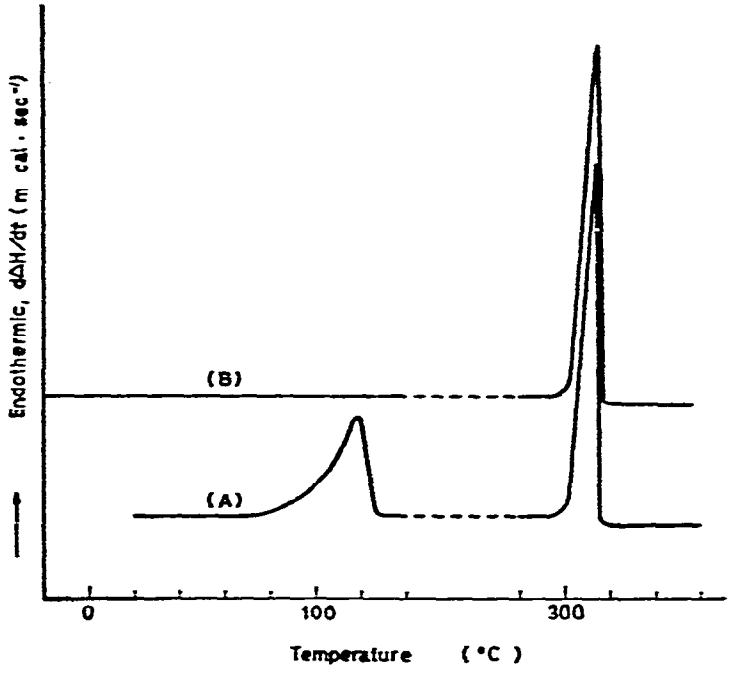

Fig. 4. DSC curve for complex fluoride of tellurium. (A) $(NO)_3Te_2F_{11}$; (B) $NOTeF_5$.

represented melting were not observed (curve B). This also indicates that $NOTeF_5$ is amorphous. At the higher temperature, which was detected to be 318 °C, this material was evaporated as $NOMoF_4$. Enthalpies estimated from the DSC curves of dissociation and evaporation are listed in Table 4.

CONCLUSION

Adducts of nitrosyl or nitryl fluoride with fluorides of zirconium, tin, vanadium, silicon, antimony, molybdenum and tellurium were produced using 80 mol% HF–20 mol% NO_2 as solvent.

The following facts were found from the DSC measurements of these adducts. $(NO)_2ZrF_6$ and $(NO)_2SnF_6$ are converted into ZrF_4 and SnF_4, respectively, through two thermal dissociation steps. $NOVF_6$, $(NO)_2SiF_6$ and $NOSbF_6$ sublimate without prior thermal dissociation, but in the case of $NOSbF_6$ two transitions are observed. NO_2MoF_4 and $(NO)_3Te_2F_{11}$ are converted into glassy melts with thermal dissociation prior to final evaporation. The enthalpies and temperatures of all these reactions are estimated from the DSC measurements.

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