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DIFFERENTIAL SCANNING CALORIMETRY STUDY OF FLUORIDE COMPLEXES OF CHROMIUM, IRON, BORON, ALUMINUM, INDIUM AND PHOSPHORUS

AKIICHI KIGOSHI

Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Sendai 980 (Japan)

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ABSTRACT

The enthalpy and temperature of the sublimation, dissociation and transition of nitrosyl fluoride or nitryl fluoride-chromium, iron, boron, aluminum, indium and phosphorus 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

In previous papers[1,2], it was shown that the enthalpy and the temperature of the thermal dissociation reactions of $NOTiF_5$, NO_2NbF_6, $(NO)_2TaF_7$, $(NO)_2ZrF_6$, $NOZrF_5$, $(NO)_2SnF_6$, $NOSnF_5$, NO_2MoF_4 and $(NO)_3TeF_{11}$, the sublimation reactions of $NOTi_2F_9$, $NONbF_6$, $NOTaF_6$, $NOVF_6$, $(NO)_2SiF_6$ and $NOSbF_6$, and the vaporization reactions of $NOMoF_4$ and $NOTeF_5$ could be determined by DSC measurements. The transition reactions of some of these compounds were also discussed.

In the present paper, the DSC measurements are extended to the complex fluorides of the other six elements. It is known that the fluorides of iron[3], boron[4] and phosphorus[3] produce adducts with nitrosyl or nitryl fluoride. The chemical formation of these reactions is as follows:

$$Fe+4NOF \rightarrow NOFeF_4+3NO \quad (1)$$

$$B+4NO_2F \rightarrow NO_2BF_4+3NO_2 \quad (2)$$

$$P+6NOF \rightarrow NOPF_6+5NO \quad (3)$$

It is also probable that the fluorides of chromium[3], aluminum[5] and indium produce the fluoride complexes according to the following reactions:

$$Cr+4NOF \rightarrow NOCrF_4+3NO \quad (4)$$

$$3Al+11NOF \rightarrow (NO)_2Al_3F_{11}+9NO \quad (5)$$

$$3In+11NOF \rightarrow (NO)_2In_3F_{11}+9NO \quad (6)$$

MATERIALS AND EXPERIMENTAL

The compounds, $NOCrF_4$, $NOFeF_4$, NO_2BF_4, $(NO)_2Al_3F_{11}$, $(NO)_2In_3F_{11}$ and $NOPF_6$ were prepared and analyzed as follows. In the case of $NOCrF_4$, the guaranteed reagent chromic acid anhydride was added little by little to an 80 mol% HF–20 mol% NO_2 solvent, prepared as described before[6], until the solution was almost saturated with a chromium compound. A water-soluble dark green compound precipitated on evaporating the excess solvent at 40°C. The same method was applied to prepare $NOFeF_4$, $(NO)_2Al_3F_{11}$ and $(NO)_2In_3F_{11}$ using metallic iron, aluminum oxide and metallic indium as reagents, respectively. The compounds formed are a water-soluble white powder. Aluminum oxide was made by thermal decomposition of the guaranteed reagent aluminum nitrate. NO_2BF_4 was prepared by adding the guaranteed reagent boric acid little by little to the 80 mol%HF–20 mol% NO_2 solvent until the solution was almost saturated. After a violent reaction, colorless, transparent and needle-shaped crystals precipitated from the solution on cooling it to −20°C. These crystals were separated centrifugally from the solution. Almost the same procedure was employed to obtain $NOPF_6$. In this case the guaranteed reagent phosphorus pentoxide was used. A little more time than in the case of boron was required to complete the crystallization of colorless needle-shaped $NOPF_6$ at −20°C. Furthermore, a slight evacuation of the crystal was necessary to eliminate the solvent adsorbed on the crystal surface.

All these compounds were analyzed on metal ion, fluorine and nitrogen. The qualitative analyses of fluorine and nitrogen were performed as previously described[5]. The amount of chromium, boron, aluminum and indium were determined by atomic-absorption spectrophotometry using a Hitachi Model 208 atomic-absorption spectrophotometer. The amount of iron was determined by the potassium permanganate titration of the oxidation reaction from the divalent to trivalent ion. The amount of phosphorus was determined by weighing the magnesium pyrophosphate produced by igniting the six-hydrated magnesium ammonium phosphate which was precipitated by the reaction with the phosphate ion and magnesia mixture. 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 previously described[1,2]. 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 case of the fluoride complex of aluminum where the sample was to be subjected to dissociation. During each measurement nitrogen was allowed to flow through the sample chamber at a rate of 30 ml min^{-1} so as to lead the gas produced out of the system. 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 dissociation or sublimation temperature was determined by measuring the point where the extension of the baseline intersects the

TABLE 1

COMPOSITION OF SAMPLE

Sample	*Components*	*Found* (%)	*Calc.* (%)
$NOCrF_4$	Cr	32.86	32.91
	F	48.03	48.10
	N	8.58	8.87
$NOFeF_4$	Fe	34.58	34.50
	F	45.98	46.95
	N	8.33	8.65
NO_2BF_4	B	8.43	8.14
	F	57.24	57.22
	N	10.63	10.55
$(NO)_2Al_3F_{11}$	Al	23.32	23.13
	F	60.20	59.72
	N	8.05	8.01
$(NO)_2In_3F_{11}$	In	56.12	56.15
	F	34.14	34.07
	N	4.55	4.57
$NOPF_6$	P	17.62	17.70
	F	65.29	65.15
	N	7.86	8.01

tangent of the peak curve on the DSC curve. The peak area was determined by measuring the area surrounded by the peak and the straight line from the point of contact between the DSC curve and its baseline to the point where the final baseline begins. The validity of these methods was confirmed by DSC curves of mercury, potassium nitrate and water as previously described[1,2].

RESULTS AND DISCUSSION

The DSC curve for chromium fluoride complex is given in Fig. 1. A partial dissociation of $NOCrF_4$ appears to occur at 201°C (peak A) with the final one at 287°C (peak B). A weight decrease of 24.69% was observed by the reaction of the peak (A). The result of the chemical analysis of the greenish grey material subsequent to the peak (A) corresponds to the composition of $(NOF)\cdot 5CrF_3$ as follows: Cr, found, 43.78%, calc., 43.77%; N, found, 2.21%, calc., 2.36%; F, found, 50.19%, calc., 51.18%. While the weight decrease of the reaction where four moles of NOF per five moles of $NOCrF_4$ are evolved leaving $(NOF)\cdot 5CrF_3$ is 24.81%. These facts indicate that peak (A) in the DSC curve of $NOCrF_4$ was derived from the following reaction:

$$5NOCrF_4 \rightarrow (NOF)\cdot 5CrF_3 + 4NOF \quad (7)$$

A weight decrease of 8.65% was observed by the reaction of peak (B). The result of

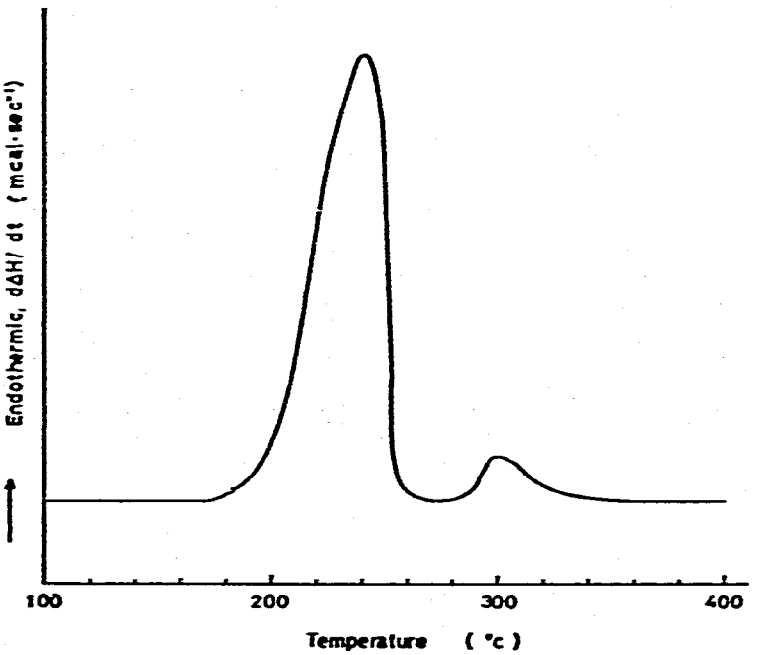

Fig. 1. DSC curve for fluoride complex of chromium.

the chemical analysis of the final product is close to the composition of CrF_3 as follows: Cr, found, 47.69%, calc., 47.71%; F, found, 51.59%, calc., 52.29%. These results indicate that one mole of NOF per one mole of $(NOF)\cdot 5CrF_3$ is apparently evolved leaving five moles of CrF_3 because the weight decrease is 8.25% in the following reaction:

$$(NOF)\cdot 5CrF_3 \rightarrow 5CrF_3 + NOF \quad (8)$$

The enthalpies for reactions (7) and (8) estimated from the DSC curve are listed in Table 2.

TABLE 2

REACTION ENTHALPIES FOR $NOCrF_4$

Reaction	*Temp. (°C)*	*ΔH (kcal mol⁻¹)*
$5NOCrF_4 \rightarrow (NOF)\cdot 5CrF_3 + 4NOF$	201	40.98 (per mole of NOF)
$(NOF)\cdot 5CrF_3 \rightarrow 5CrF_3 + NOF$	287	11.18 (per mole of NOF)

The DSC curve for iron fluoride complex is given in Fig. 2.
The platinum cell was used because the reaction between the aluminum cell and the sample could not be neglected. The dissociation appears to occur at 122°C (peak A). A weight decrease of 20.12% was observed by the reaction of the peak (A). The

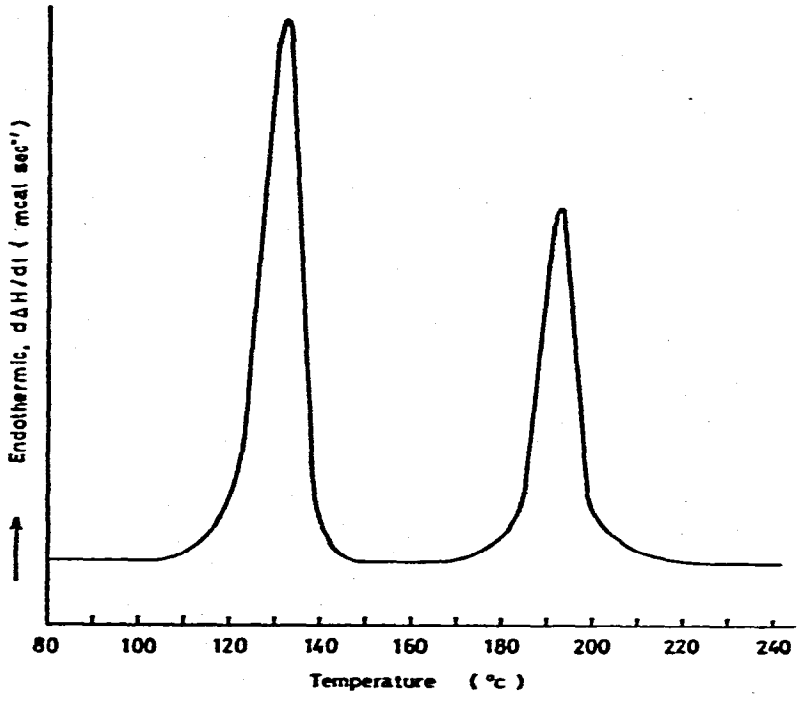

Fig. 2. DSC curve for fluoride complex of iron.

dissociation of two moles of NOF per three moles of $NOFeF_4$, leaving $NOF \cdot 3FeF_3$, could account for the observed weight decrease because the weight decrease is 20.19% in the following reaction:

$$3NOFeF_4 \rightarrow NOF \cdot 3FeF_3 + 2NOF \quad (9)$$

The results of the chemical analysis of the blueish white solid product were also close to the composition of $NOF \cdot 3FeF_3$ as follows: Fe, found, 43.25%, calc., 43.23%; F, found, 48.87%, calc., 49.02%; N, found, 3.45%, calc., 3.61%. At 183°C another dissociation reaction seems to occur (peak B). A weight decrease of 12.64% was observed by the reaction which causes this peak. This value is very close to the decrease in weight, 12.65% where one mole of NOF per one mole of $NOF \cdot 3FeF_3$ is evolved, leaving three moles of FeF_3. The result of the chemical analysis of the solid product was also found to be in close agreement with the composition of FeF_3 as

TABLE 3

REACTION ENTHALPIES FOR $NOFeF_4$

Reaction	*Temp. (°C)*	*ΔH (kcal mol⁻¹)*
$3NOFeF_4 \rightarrow NOF \cdot 3FeF_3 + 2NOF$	122	20.79 (per mole of NOF)
$NOF \cdot 3FeF_3 \rightarrow 3FeF_3 + NOF$	183	25.32 (per mole of NOF)

follows: Fe, found, 49.04%, calc., 49.49%; F, found, 50.68%, calc., 50.51%. Therefore, peak (B) was found to derive from the following reaction:

$$NOF \cdot 3FeF_3 \rightarrow 3FeF_3 + NOF \quad (10)$$

The enthalpies for reactions (9) and (10) estimated from the DSC curve are listed in Table 3.

The DSC curve for boron fluoride complex is given in Fig. 3 (curve I). The dissociation of NO_2BF_4 appears to occur at 163 °C overlapping with another reaction at the same temperature. A weight decrease of 12.00% was observed as a result of heating this material up to 200 °C in a semi-closed vessel. The results of the analysis

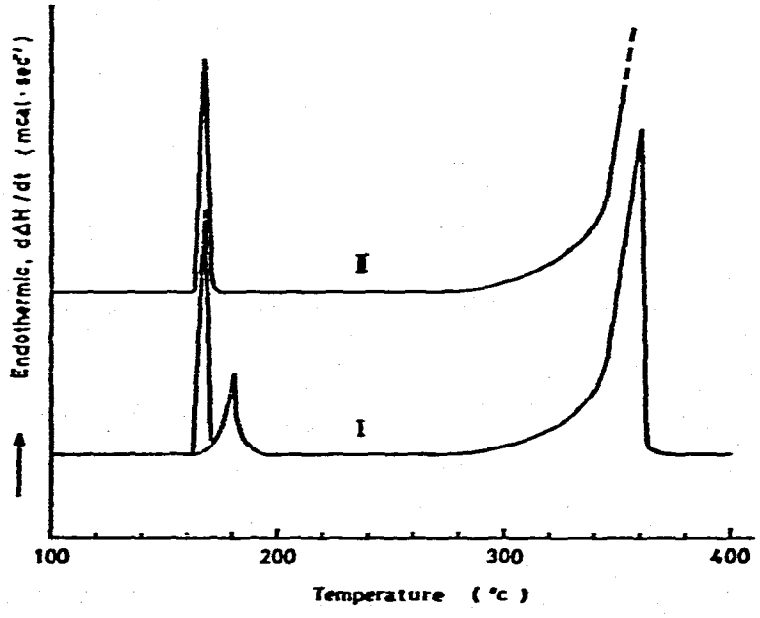

Fig. 3. DSC curve for fluoride complex of boron. (I) NO_2BF_4; (II) $NOBF_4$.

of the material, needle-shaped colorless crystal, subsequent to this heating were as follows: B, 9.32%; F, 65.02%; N, 11.96%. These values are very close to those of the components of $NOBF_4$: B, 9.26%; F, 65.06%; N, 11.99%. This indicates that one mole of oxygen per two moles of NO_2BF_4 is apparently evolved, leaving two moles of $NOBF_4$, because the weight decrease is 12.05% in the following reaction:

$$2NO_2BF_4 \rightarrow 2NOBF_4 + O_2 \quad (11)$$

In the DSC curve of $NOBF_4$, the broad peak no longer appears leaving the sharp peak at 163 °C (curve II). Neither a melting reaction nor a weight change was observed with this sharp peak and it was completely reversible. On these grounds, it is suggested that the broad peak was derived from the dissociation reaction represented by reaction (11), and the sharp peak overlapping with the broad one derived from the transition of the crystal lattice of $NOBF_4$. A dotted curve in curve I was obtained by

subtracting curve II from curve I. The broad peak completed by this dotted line should be the peak which is derived from the dissociation reaction (11) alone. The enthalpies for the dissociation and the transition estimated from the DSC curves are listed in Table 4.

TABLE 4

REACTION ENTHALPIES FOR NO_2BF_4

Reaction	*Temp.* (°C)	ΔH (*kcal mol*$^{-1}$)
$2NO_2BF_4 \rightarrow 2NOBF_4 + O_2$	173	2.66 (per mole of O_2)
Transition	163	2.34
Sublimation	339	33.27

At the higher temperature $NOBF_4$ sublimated without prior dissociation or decomposition (curve I). The enthalpy for the sublimation estimated from this curve is also listed in Table 4.

A typical DSC curve for aluminum fluoride complex is given in Fig. 4 (curve I). The platinum cell was used in a similar way to the case of $NOFeF_4$. The existence of three dissociation reactions must be considered for $(NO)_2Al_3F_{11}$. The decrease in weight of 19.37% was observed by the reaction which causes the first broad peak (A). The same weight decrease was observed by keeping $(NO)_2Al_3F_{11}$ at 165°C in a semi-closed vessel. The results of the analysis of the solid product were as follows:

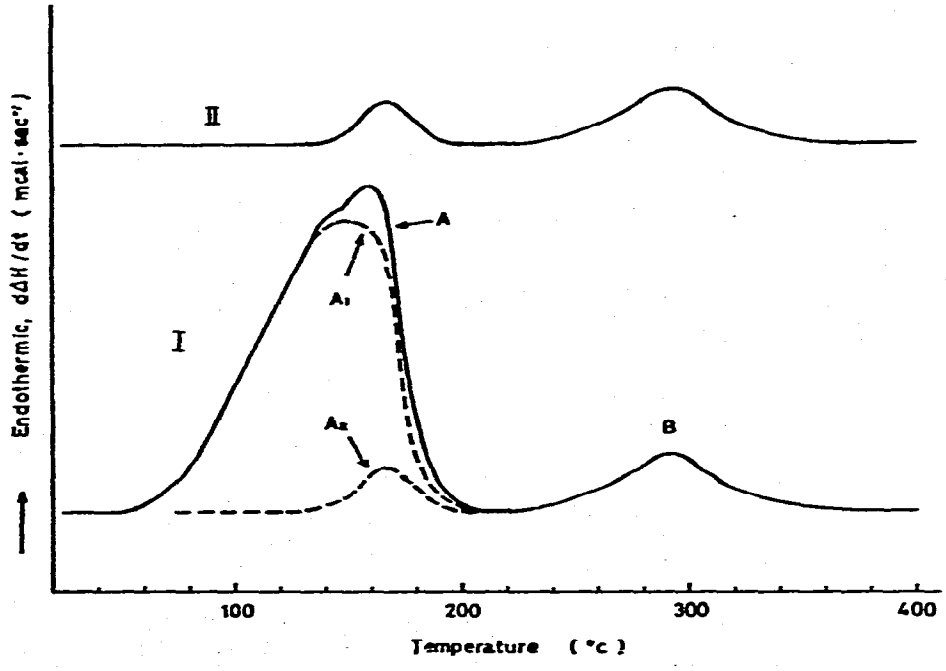

Fig. 4. DSC curve for fluoride complex of aluminum. (I) $(NO)_2Al_3F_{11}$; (II) $NOF{\cdot}3AlF_3$.

Al, 28.69%; F, 64.62%; N, 2.95%. These values are close to those of the components of $NOF \cdot 5AlF_3$: Al, 28.77%; F, 64.83%; N, 2.99%. The weight decrease of the reaction where seven moles of NOF dissociate per five moles of $(NO)_2Al_3F_{11}$ leaving three moles of $NOF \cdot 5AlF_3$ is 19.60%. This value is also close to the observed value. On these grounds, this dissociation could account for the reaction which causes the first broad peak (A). However, it is suggested from the shape that the peak is derived from two overlapping reactions.

The material of a definite composition was obtained with a weight decrease of 14.02% by heating $(NO)_2Al_3F_{11}$ up to 72–105°C in a semi-closed vessel. This value is very close to that of the decrease in weight, 14.00%, where 1 mole of NOF per 1 mole of $(NO)_2Al_3F_{11}$ is evolved leaving one mole of $NOF \cdot 3AlF_3$. While the results of the analysis of this material were as follows: Al, 27.10%; F, 63.73%; N, 4.70%. These values are also close to those of the components of $NOF \cdot 3AlF_3$: Al, 26.90%; F, 63.13%; N, 4.65%. The DSC curve for the product which was made by heating $(NO)_2Al_3F_{11}$ to 72–105°C in a semi-closed vessel is shown in Fig. 4 (curve II). The second peak of this DSC curve was found to coincide with that of curve I. Therefore, it is clear that the first peak in curve II is one of the components of the peak (A) in curve I. Then, the peak (A_1), which is derived from the following dissociation reaction alone, was obtained by subtracting the first peak in curve II from the peak (A) in curve I:

$$(NO)_2Al_3F_{11} \rightarrow NOF \cdot 3AlF_3 + NOF \qquad (12)$$

It is needless to say that the following reaction causes the first peak in curve II or the peak (A_2) in curve I:

$$5NOF \cdot 3AlF_3 \rightarrow 3NOF \cdot 5AlF_3 + 2NOF \qquad (13)$$

The decrease in weight of 10.14% was observed by the reaction which causes the second peak (curve I, II). This value is close to that of the decrease in weight, 10.45%, where one mole of NOF per mole of $NOF \cdot 5AlF_3$ is evolved, leaving five moles of AlF_3. The results of the chemical analysis of the solid product were also close to the composition of AlF_3 as follows: Al, found, 32.11%, calc., 32.13%; F, found, 67.82%, calc., 67.87%. Therefore, the last peak was found to originate from the following dissociation reaction:

$$NOF \cdot 5AlF_3 \rightarrow 5AlF_3 + NOF \qquad (14)$$

The enthalpies for reactions (12), (13) and (14) estimated from the respective DSC curves are listed in Table 5.

The DSC curve for the indium fluoride complex is given in Fig. 5, curve I. As shown in the figure, there was only one decisive peak different from the cases of fluoride complexes of boron and aluminum. With the reaction which causes this peak, a weight decrease of 15.62% was observed. This value is close to the decrease in weight, 15.97%, where two moles of NOF per one mole of $(NO)_2In_3F_{11}$ are evolved, leaving three moles of InF_3. The results of the chemical analysis of the solid product

TABLE 5

REACTION ENTHALPIES FOR $(NO)_2Al_3F_{11}$

Reaction	*Temp. (°C)*	ΔH *(kcal mol^{-1})*
$(NO)_2Al_3F_{11} \rightarrow NOF{\cdot}3AlF_3 + NOF$	72	34.92 (per mole of NOF)
$5NOF{\cdot}3AlF_3 \rightarrow 3NOF{\cdot}5AlF_3 + 2NOF$	145	5.28 (per mole of NOF)
$NOF{\cdot}5AlF_3 \rightarrow 5AlF_3 + NOF$	242	7.69 (per mole of NOF)

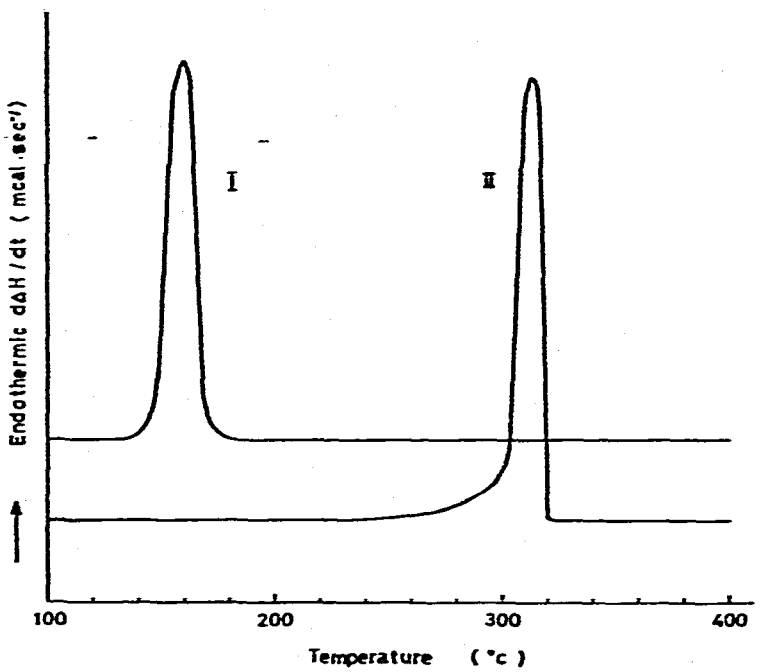

Fig. 5. DSC curve for fluoride complex of indium (I) and phosphorus (II).

were also found to be in close agreement with the composition of InF_3 as follows: In, found, 66.51%, calc., 66.83%; F, found, 33.45%, calc., 33.17%. These facts indicate that the peak originated from the following dissociation reaction:

$$(NO)_2In_3F_{11} \rightarrow 3InF_3 + 2NOF \quad (15)$$

The enthalpy estimated from the DSC curve of dissociation is listed in Table 6.

TABLE 6

REACTION ENTHALPIES FOR $(NO)_2In_3F_{11}$ AND $NOPF_6$

Reaction	*Temp. (°C)*	ΔH *(kcal mol^{-1})*
$(NO)_2In_3F_{11} \rightarrow 3InF_3 + 2NOF$	147	28.17 (per mole of NOF)
$NOPF_6$, sublimation	303	35.70

The DSC curve for phosphorus complex fluoride is given in Fig. 5, curve II. As shown in the figure, $NOPF_6$ sublimates simply without transition or preceding dissociation which were observed for NO_2BF_4. The behavior of $NOPF_6$ is similar to that of $(NO)_2SiF_6$ and $NOVF_6$ as previously described[2]. The enthalpy of sublimation estimated from the DSC curve is listed in Table 6.

CONCLUSION

Adducts of nitrosyl fluoride with fluorides of chromium, iron, aluminum, indium and phosphorus, and that of nitryl fluoride with boron fluoride were produced using the 80 mol% HF–20 mol% NO_2 solvent.

The following facts were found from the DSC measurements of these adducts. $NOCrF_4$ and $NOFeF_4$ are converted into CrF_3 and FeF_3, respectively, through two thermal dissociation steps. Three and one thermal dissociation steps are observed for the reaction of $(NO)_2Al_3F_{11}$ and $(NO)_2In_3F_{11}$, respectively, to the final forms of AlF_3 and InF_3. $NOPF_6$ sublimates without preceding reaction, but in the case of NO_2BF_4, thermal dissociation into $NOBF_4$ and transition are observed prior to its sublimation. The enthalpies and temperatures of all these reactions were estimated from the DSC curves.

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