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DIFFERENTIAL SCANNING CALORIMETRY STUDY OF COMPLEX FLUORIDES OF TITANIUM, NIOBIUM AND TANTALUM

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ABSTRACT

The enthalpy and temperature of the sublimation of nitrosyl fluoride or nitryl fluoride–titanium, niobium and tantalum fluoride adducts were determined from DSC measurements. A closed-cell DSC technique was employed to determine the enthalpies and temperatures and to study the dissociation reactions of some of these adducts.

INTRODUCTION

During the past decade it has become known that a great variety of acceptor fluorides interact in a characteristic manner with nitrosyl fluoride or nitryl fluoride[1]. The majority of the NOF or NO_2F-acceptor fluoride adducts are stable salts which contain the nitrosyl or nitryl cation at room temperature. Some of them are known to sublime without decomposition on heating. However, the possibility of the existence of the molecular complex, $NO_nF \cdot XF_m$, must be taken into account and some of these adducts lose NO_nF easily on heating or even pumping.

It is also known that the fluorides of titanium, niobium and tantalum produce adducts with nitrosyl fluoride or nitryl fluoride according to the following equations[2,3]:

$$Ti+5NOF \rightarrow NOTiF_5+4NO \quad (1)$$

$$Nb+6NOF \rightarrow NONbF_6+5NO \quad (2)$$

$$Nb+6NO_2F \rightarrow NO_2NbF_6+5NO_2 \quad (3)$$

$$Ta+6NOF \rightarrow NOTaF_6+5NO \quad (4)$$

These adducts can be represented as $NOF \cdot TiF_4$ or $NO_2F \cdot NbF_5$, but generally they are named nitrosylium pentafluorotitanate, nitrosylium hexafluoroniobate or nitrosylium hexafluorotantalate. Because these adducts sublimate at characteristic conditions, the application of this phenomenon has been investigated as a means of separating and refining the elements from their ores[2,3]. However, the kinetic constants of these adducts are not known.

In this paper, an attempt is made to determine the enthalpies and temperatures of sublimation, transition and dissociation under atmospheric pressure by DSC measurements.

MATERIALS AND EXPERIMENTAL

The compounds, $NOTiF_5$, $NONbF_6$, NO_2NbF_6, $NOTaF_6$ and $(NO)_2TaF_7$ were prepared and analyzed as follows. In the case of $NOTiF_5$, 80 mol % HF–20 mol % NO_2 solvents prepared as described before[2] were added to the guaranteed reagent, titanium dioxide. After a first violent reaction, the solvent was added little by little until all of the solids were dissolved in the solution. Colorless, transparent and needle-sharp crystals precipitated from the solution on cooling by ice. These crystals were separated centrifugally from the solution. In the case of $NONbF_6$ and $NOTaF_6$, 80 mol % HF–20 mol % NO_2 solvents or 52° material were added carefully little by little to the metallic niobium or tantalum until all of the metal had reacted satisfactorily and had been converted to a white precipitate. NO_2NbF_6 was produced by the reaction of metallic niobium and 68° material[4]. Incidentally, the reaction product of metallic tantalum and 68° material was not NO_2TaF_6, but $NOTaF_6$. When metallic tantalum was added carefully to an excess amount of solvent such as 68° material or 80 mol % HF–20 mol % NO_2, $(NO)_2TaF_7$ was obtained instead of $NOTaF_6$ as a solid product:

$$Ta+7NOF \rightarrow (NO)_2TaF_7+5NO \qquad (5)$$

All these compounds were analyzed on metal ion, fluorine and nitrogen as previously described[4], and the results are shown in Table 1. The compound $NOTi_2F_9$, in this

TABLE 1

COMPOSITION OF SAMPLE

		Found (%)	*Calculated* (%)
$NOTiF_5$	Ti	27.49	27.70
	N	8.16	8.10
	F	55.33	54.94
$NOTi_2F_9$	Ti	31.84	32.28
	N	4.83	4.72
	F	57.01	57.61
$NONbF_6$	Nb	39.42	39.22
	N	5.92	5.91
	F	48.20	48.12
NO_2NbF_6	Nb	36.04	36.74
	F	5.60	5.54
	N	45.57	45.07
$NOTaF_6$	Ta	55.75	55.69
	N	4.31	4.31
	F	35.07	35.08
$(NO)_2TaF_7$	Ta	48.63	48.39
	N	7.39	7.49
	F	35.86	35.56

table, was produced by heating $NOTiF_5$ up to 225°C in a nitrogen atmosphere according to the following equation:

$$2NOTiF_5 \rightarrow NOTi_2F_9 + NOF \qquad (6)$$

The reaction enthalpies and the reaction temperatures were determined using a Rigaku-Denki Model DSC-8055 differential scanning calorimeter. In order to prevent corrosion of the DSC sample chamber by the gas from the sample, the metallic copper cover of the sample chamber was replaced by a Monel cap with a Monel tube which was connected to the evacuation system as shown in Fig. 1. Under normal operating conditions, the chamber was first evacuated and then filled with nitrogen. During the measurement nitrogen was allowed to flow as shown in Fig. 1 at a rate of 30 ml min⁻¹. By this device, the gas produced during the reaction was easily led out of the system with nitrogen without any disturbance of the temperature in the chamber.

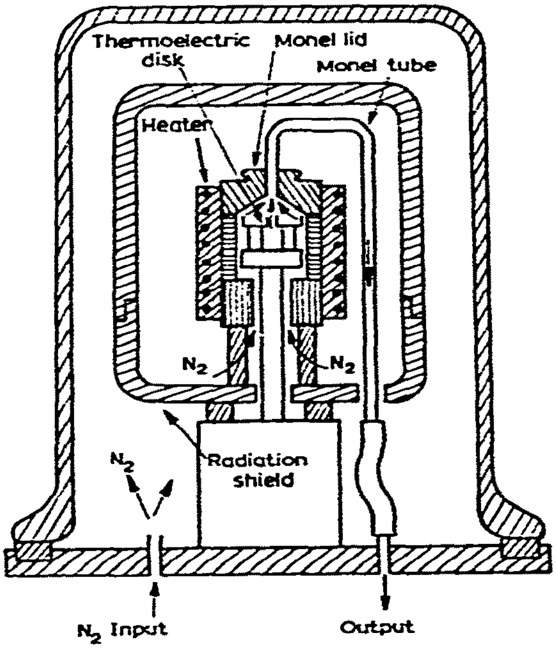

Fig. 1. Modified DSC mount.

From 1–10 mg of the sample was employed at a heating rate of 10°C min^{-1}. A flat cylindrical closed cell with a pin hole on its surface was used. For most of the experiments, cells made of aluminum were used, since no significant differences were recognized between the results with aluminum cells and those of platinum which were obtained in preliminary tests.

The conversion factor relating the peak area on the chart to calories was obtained by a calibration using the heat of vaporation of pure mercury because of its resemblance to the present samples in the shape and temperature range of the DSC curves. The method for measuring the peak area of mercury was standardized by comparing it with that for the transition of KNO_3. The determination of the sublimation point was also based on the DSC curve of pure mercury. The validity of these methods was also confirmed by the boiling point of pure water.

RESULTS AND DISCUSSION

A typical DSC curve for mercury is given in Fig. 2. The DSC curve is almost straight up to the region of 300°C. On account that the escape of mercury vapor through the pin hole becomes significant at the higher temperature, the curve deviates from the baseline, until a sharp peak is observed near the boiling point. As shown in this figure, the extension of the baseline intersects the tangent of the peak curve at the point which corresponds to 357°C. From the results of experiments with up to 12.7 mg of mercury, it was found that the temperatures obtained by this method agreed well with the boiling point of mercury. Therefore the determination of the sublimation point was based on this method. In Fig. 2, 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 (generally it is a little lower than the initial line)

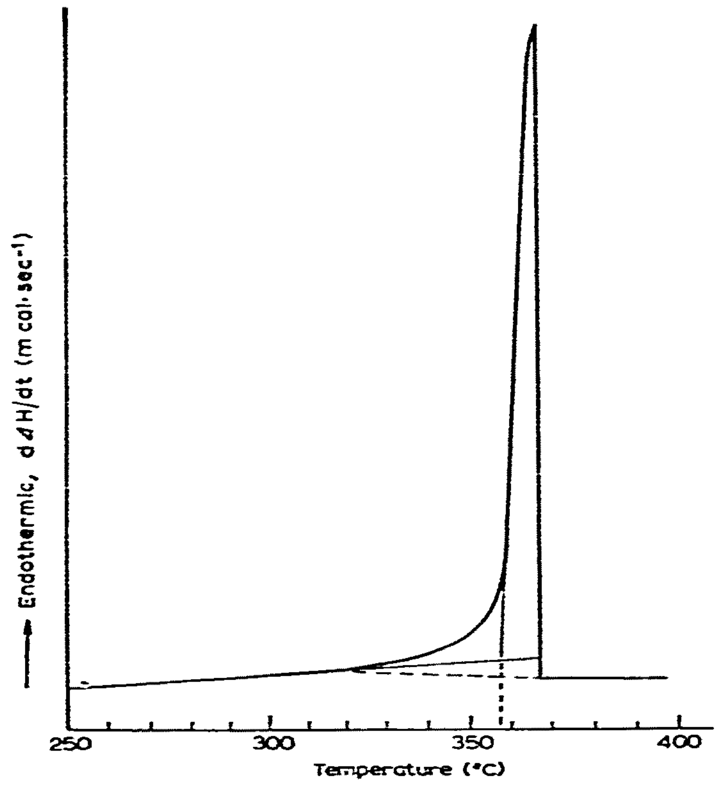

Fig. 2. Typical DSC curve for Hg.

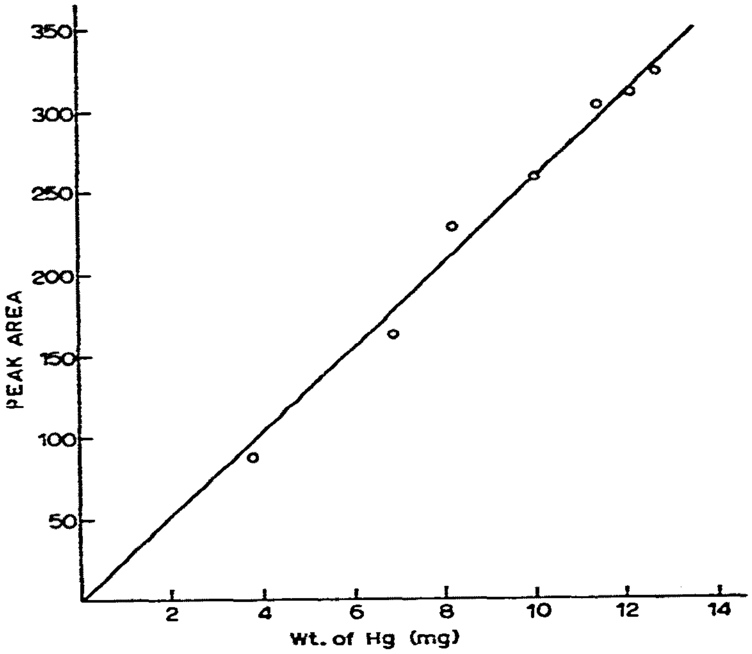

Fig. 3. Relation between weight of mercury and peak area.

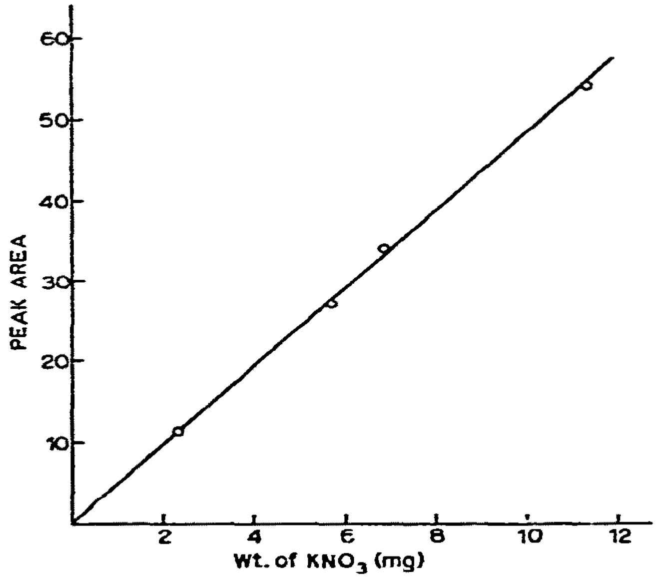

Fig. 4. Relation between weight of KNO_3 and peak area.

is almost proportional to the amount of mercury as shown in Fig. 3. From this relation and the heat of evaporation for mercury (68 cal g^{-1}), a conversion factor of 2.649 was obtained. The possibility of other methods to measure a peak area, for example, surrounded by a baseline and a peak, may be considered. With this method a conversion factor of 3.109 was obtained. However, the former method was applied in this investigation for the reason described next. The heat of transition of potassium nitrate at 128°C (12.8 cal g^{-1}) is often used as the standard for thermal analysis. The relation of the peak area and the weight of KNO_3 obtained by recrystallization is shown in Fig. 4. From this result, the conversion factor is calculated to be 2.645. This value is in good agreement with that in the former case. When this method is checked by the boiling point and the heat of vaporization of water, values of 100.5°C and 542 cal g^{-1} are obtained, respectively. For reference, the latter method described above offered a value of 478 cal per gram of water.

The DSC curves for titanium complex fluorides are given in Fig. 5. The dissociation of $NOTiF_5$ appears to occur at the temperature range of 100 to 180°C overlapping with another reaction at 164°C (curve A). A weight decrease of 14.4% was observed on heating this material up to 225°C. This indicates that a single mole of NOF per two moles of $NOTiF_5$ is apparently evolved leaving $NOTi_2F_9$ or $NOF(TiF_4)_2$ because the weight decrease is 14.2% in the following reaction:

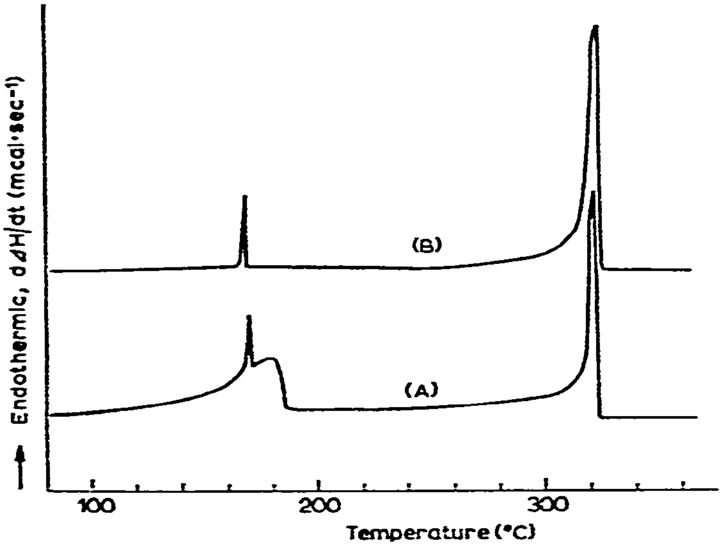

Fig. 5. DSC curve for titanium complex fluoride. (A) $NOTiF_5$; (B) $NOTi_2F_9$.

$$2NOTiF_5 \rightarrow NOTi_2F_9 + NOF \qquad (7)$$

The result of chemical analysis of this material is also very close to the composition of $NOTi_2F_9$ as listed in Table 1. In the DSC curves of this material, the broad peaks which were found in curve A overlapping with the keen peak at 164°C disappeared (curve B). It is considered that the peak at 164 °C was derived from the transition of crystal lattice. These facts indicate that perhaps the one mole of NOF per two moles of $NOTiF_5$ is situated in its crystal lattice in a different manner than another. At the higher temperature, this material sublimated without decomposition or dissociation. The temperature of the sublimation was detected to be 319 °C.

Enthalpies and temperatures estimated from the DSC curves of dissociation, transition and sublimation are listed in Table 2.

TABLE 2

REACTION ENTHALPIES FOR $NOTi_2F_9$

Reaction	*Peak temp. (°C)*	*ΔH (kcal mol^{-1})*
$2NOTiF_5 \rightarrow NOTi_2F_9 + NOF$	100~180	11.9 (per mole of NOF)
Transition	164	0.47
Sublimation	319	20.2

Typical DSC curves for niobium and tantalum complex fluorides are given in Fig. 6. The existence of transition and sublimation must be considered for $NONbF_6$ (curve A) similar to the case of $NOTi_2F_9$. In the case of NO_2NbF_6, the peak by transition was observed at the same temperature as in the case of $NONbF_6$. But before this peak there was a broad peak which was not observed on $NONbF_6$ (curve B). The decrease in weight of 17.2% was observed by the reaction which causes the broad

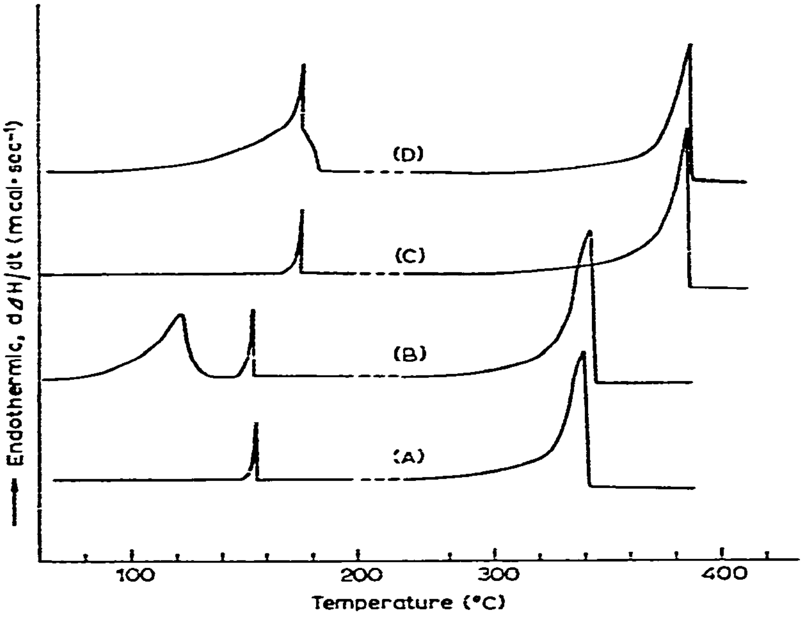

Fig. 6. DSC curve for niobium and tantalum complex fluoride. (A) $NONbF_6$; (B) NO_2NbF_6; (C) $NOTaF_6$; and (D) $(NO)_2TaF_7$.

peak. This value is very close to the value of the decrease in weight, 17.1%, where one mole of oxygen per two moles of NO_2NbF_6 is evolved leaving $NONbF_6$. The result of chemical analysis of the solid product was also found to be in good agreement with the composition of $NONbF_6$. Therefore, this broad peak was found to derive from the reaction where a loosely bound oxygen in the crystal lattice evolves as in the following equation:

$$2NO_2NbF_6 \rightarrow 2NONbF_6+O_2 \qquad (8)$$

The DSC curve for $NOTaF_6$ is close to that for $NONbF_6$ except for the temperatures of transition and sublimation (curve C). Dissociation of $(NO)_2TaF_7$ occurs apparently overlapping the transition of $NOTaF_6$ similar to the case of $NOTiF_5$ (curve D). The decrease in weight for this reaction is found to be 13.1%, which is very close to the value calculated from the following equation:

$$(NO)_2TaF_7 \rightarrow NOTaF_6+NOF \qquad (9)$$

The DSC curve for the product which was made by heating $(NO)_2TaF_7$ at 240°C in a nitrogen atmosphere was found to coincide with that of $NOTaF_6$ (curve C). The formation of $NOTaF_6$ was also estimated by chemical analysis of the product formed by heating $(NO)_2TaF_7$. These facts prove that one mole of NOF per one mole of $(NO)_2TaF_7$ is situated in its crystal lattice in a different manner than the other one similar to the case of $NOTiF_5$.

The DSC curves for $NONbF_6$ and $NOTaF_6$ indicate that no further dissociation of these compounds occurs by heating them in the nitrogen atmosphere up to their respective sublimation points. This was also ascertained by the following experiments. The platinum vessel filled with the niobium or tantalum complex fluorides was inserted into the reaction tube, through which nitrogen had been passed previously, and maintained at 370 and 400°C, respectively. The vapor produced by the sublimation of the niobium or tantalum compound was carried by the nitrogen flow into the condenser which was connected to the reaction tube, and condensed there. After several minutes the vessel was taken out of the reaction tube, and the residue in the vessel and the deposit in the condenser were both analyzed. It was found that the chemical composition of the residue as well as of the deposit were in good agreement with that of $NONbN_6$ or $NOTaF_6$. The DSC curves for these materials were also found to coincide with that of $NONbF_6$ or $NOTaF_6$ shown in Fig. 6.

According to the same experiment performed on $NOTiF_5$ at 350°C, it was found that the chemical composition of both the residue and the deposit were equal to that of $NOTi_2F_9$. Their DSC curves also coincided with that of $NOTi_2F_9$. However, if nitrogen was added by, at least, 50 vol.% of the vapor of the 52° material, both the residue and the deposit were not $NOTi_2F_9$ but $NOTiF_5$ as described in the previous paper[2].

The enthalpies and temperatures of dissociation, transition and sublimation estimated from the DSC curves for niobium and tantalum complex fluorides are listed in Tables 3 and 4, respectively.

TABLE 3

REACTION ENTHALPIES FOR $NONbF_6$

Reaction	*Peak temp.* (°*C*)	ΔH (*kcal mol*$^{-1}$)
$2NO_2NbF_6 \rightarrow 2NONbF_6 + O_2$	70~130	14.1 (per mole of O_2)
Transition	150	1.65
Sublimation	328	27.4

TABLE 4

REACTION ENTHALPIES FOR $NOTaF_6$

Reaction	*Peak temp.* (°*C*)	ΔH (*kcal mol*$^{-1}$)
$(NO)_2TaF_7 \rightarrow NOTaF_6 + NOF$	90~180	12.2 (per mole of NOF)
Transition	169	1.06
Sublimation	374	17.6

CONCLUSION

The reaction of titanium dioxide, metallic niobium and tantalum with the 80 mol% HF–20 mol % NO_2 solvent, the 52° or 68° material produce adducts of their fluorides with NOF or NO_2F.

It was found from DSC measurements that the adducts, $NOTiF_5$, NO_2NbF_6 and $(NO)_2TaF_7$, are converted into $NOTi_2F_9$, $NONbF_6$ and $NOTaF_6$, respectively, by thermal dissociation. And the heat of dissociation, transition and sublimation, and their temperatures were determined.

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