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REACTION BETWEEN RARE EARTH ELEMENTS AND $HF–NO_2$ SOLUTION *

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ABSTRACT

Rare earth elements react with $HF–NO_2$ solution to produce nitrosylium fluorometallates $(NO)_x LnF_{x+3}$. The value of x is 1.0 or 1.5 for light rare earth elements and 0.5 or 1.0 for heavy rare earths. Nitrosylium fluorometallates of rare earth elements can be decomposed into the simple fluoride and nitrosyl fluoride at low temperatures (46–68°C).

INTRODUCTION

Rare earth elements are in great demand as optical glass, lighting equipment, magnetic alloys, neutron absorbers, etc., and their consumption has been dramatically increased in recent years. There is insufficient information regarding many of their properties. We have been studying the possibility of rare metal metallurgy on an industrial scale by using the reaction between $HF–NO_2$ solution and each metal. In treating thorium ore, the separation of rare earth elements coexisting in the ore is economically very important because of the valuable by-products. However, there is no report about the reaction between rare earth elements and $HF–NO_2$ solution.

Geichman et al. and Kigoshi reported that some metals react with $HF–NO_2$ solution to produce nitrosylium fluorometallates as shown in eqns. (1)–(3) [1–3]

$$U + 6\,NOF = NOUF_6 + 5\,NO \quad (1)$$

$$Ti + 5\,NOF = NOTiF_5 + 4\,NO \quad (2)$$

$$Fe + 4\,NOF = NOFeF_4 + 3\,NO \quad (3)$$

These salts are classified into three types according to their thermal proper-

* This paper is taken in part from the Dr. Eng dissertation of N. Sato

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ties: sublimation type, vaporization type, and thermal decomposition type [4]. In this paper, we study the reaction between rare earth elements and $HF-NO_2$ solution based on the above information.

EXPERIMENTS

Thirteen samples of 12 rare earth elements were used and are listed in Table 1. A solution of 80 mole% HF–20 mole% NO_2 was prepared as described previously [2]. Samples were placed in polyethylene vessels and reacted with 80 mole% HF–20 mole% NO_2 solutions for 1 day at room temperature and atmospheric pressure. Reaction products were obtained by centrifuging the solutions. The molecular formulae of the products were determined and their thermal properties were investigated using differential scanning calorimetry, thermal gravitational–differential thermal analyses and chemical analyses of the products.

RESULTS AND DISCUSSION

Molecular formula and thermal properties of the lanthanum product

The TG–DTA curve and chemical analysis of the lanthanum product are given in Fig. 1 and Table 2, respectively. From the results, it is clear that the product is a nitrosylium fluorometallate, $NOLaF_4$, which decomposes at about 60°C with 20% weight loss and becomes stable in the temperature range 60–720°C. The significance of these facts is considered as follows. Lanthanum reacts with $HF-NO_2$ solution to produce nitrosyliun fluorometallate as shown in eqn. (4)

$$La + 4\ NOF \rightarrow NOLaF_4 + 3\ NO \qquad (4)$$

TABLE 1

Samples of rare earth elements

$LaCl_3\ 7\ H_2O$	Gd_2O_3
CeO_2	Tb_2O_3
$Ce_2(CH_3COO)_3 \cdot H_2O$	Dy_2O_3
Pr_2O_3	Ho_2O_3
Nd_2O_3	Er_2O_3
Sm_2O_3	Y_2O_3
Eu_2O_3	

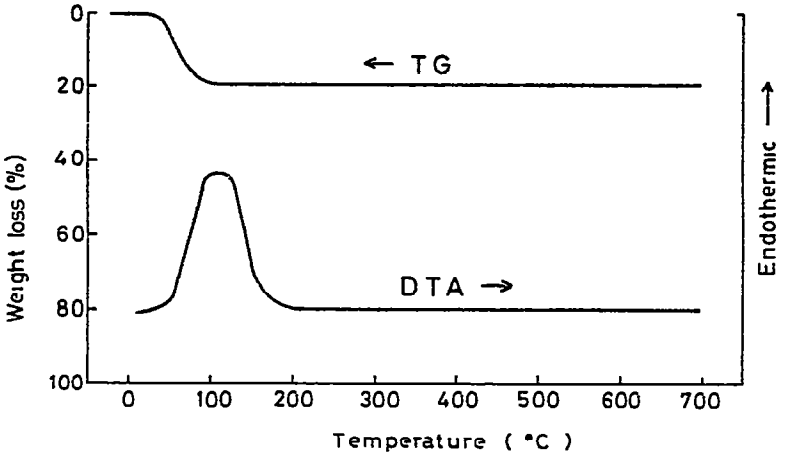

Fig. 1. TG and DTA curves for the lanthanum product.

This salt is a nitrosyl fluoride-acceptor fluoride adduct and decomposes into the nitrosyl fluoride and simple fluoride of lanthanum at 58°C according to eqn. (5)

$$NOLaF_4 \rightarrow LaF_3 + NOF \quad (5)$$

In fact, the 20.01% weight loss calculated from eqn. (4) is in close agreement with the experimental value of 19.90%.

Similarity of rare earth elements in the reaction with HF–NO_2 solution

In the reaction with HF–NO_2 solution, the case of lanthanum is applied to other rare earth elements whose chemical properties are similar to that of lanthanum. TG–DTA curves of the products of other rare earth elements indicate that the products decompose at 50–60°C with 10–30% weight loss and become stable like a lanthanum product. The molecular formulae. colour, decomposition temperature and the enthalpy of decomposition of the products, obtained from the experiments, are given in Table 3. From the

TABLE 2

Chemical analysis (wt.%) of the lanthanum product ($NOLaF_4$)

	La	F	N
Calcd.	56.72	31.03	5.72
Found	56.57	31.05	5.69

TABLE 3

The products of rare earth elements

Molecular formula	Colour	Decomposition (°C)	Enthalpy of decomposition (kcal g^{-1})
$(NOF)_{1.0}LaF_3$	White	52	75.0
$(NOF)_{1.5}CeF_3$	Beige	52	75.1
$(NOF)_{1.0}PrF_3$	Yellow green	55	52 3
$(NOF)_{1.5}NdF_3$	Whitish purple	64	98.4
$(NOF)_{1.0}SmF_3$	White	64	85.6
$(NOF)_{1.5}EuF_3$	White	61	105 0
$(NOF)_{1.5}GdF_3$	White	58	56.2
$(NOF)_{0.5}TbF_3$	Coffee	57	33.4
$(NOF)_{1.0}DyF_3$	White	55	54 1
$(NOF)_{0.5}HoF_3$	Light beige	48	37 8
$(NOF)_{0.5}ErF_3$	Pink	59	41.3
$(NOF)_{1.0}YF_3$	White	55	69.6

results, it is concluded that each rare earth element reacts with $HF-NO_2$ solution to produce nitrosylium fluorometallate, $(NO)_xLnF_{x+3}$, according to eqn. (6)

$$Ln + (x+3)NOF = (NO)_xLnF_{x+3} + 3\ NO \quad (6)$$

The value of x is 1.0 or 1.5 for light rare earth elements and 0.5 or 1.0 for heavy rare earths. The colour of each nitrosylium fluorometallate resembles that of each simple fluoride. It is considered that each nitrosylium fluorometallate decomposes into its simple fluoride and nitrosyl fluoride at the

TABLE 4

Weight loss of the products on thermal decomposition

Product	Wt. loss (%)		Product	Wt loss (%)	
	Calcd.	Found		Calcd.	Found
$(NOF)_{1.0}LaF_3$	20.01	19 90	$(NOF)_{0.5}GdF_3$	10.26	10.97
$(NOF)_{1.5}CeF_3$	27.16	27.08	$(NOF)_{0.5}TbF_3$	10.19	9.51
$(NOF)_{1.0}PrF_3$	14.17	14.20	$(NOF)_{1.0}DyF_3$	18.25	17.03
$(NOF)_{1.5}NdF_3$	26.75	27.07	$(NOF)_{0.5}HoF_3$	9 94	10.33
$(NOF)_{1.0}SmF_3$	19.12	19 25	$(NOF)_{0.5}ErF_3$	9 85	10.81
$(NOF)_{1.5}EuF_3$	26.02	25.89	$(NOF)_{1.0}YF_3$	25.14	26 70

respective temperatures as shown in eqn. (7)

$$(NO)_x LnF_{x+3} \rightarrow LnF_3 + x\ NOF \qquad (7)$$

The values of weight loss on thermal decomposition from both calculation and experiment are given in Table 4. The fact that both the values are in good agreement indicates the validity of eqn. (7). It also becomes clear that the same salts are obtained regardless of the starting compound. In conclusion, nitrosylium fluorometallates of rare earth elements belong to the thermal decomposition type, like iron.

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