Thermochimica Acta, 10 (1974) 285–298
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A THERMAL STUDY OF THE TRIFLUOROACETATES AND PENTAFLUOROPROPIONATES OF PRASEODYMIUM, SAMARIUM AND ERBIUM*

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(Received 28 June 1974)

ABSTRACT

Several lanthanide salts of trifluoroacetic and pentafluoropropionic acid have been prepared and characterized.

Powder X-ray diffraction and thermal studies have shown the compounds to be isomorphous within their respective series and to dehydrate in definite steps. Decomposition was found to be exothermic resulting in the formation of LnF_3, LnOF and Ln_2O_3 at various stages. The volatile decomposition products were identified by IR analysis and found to consist of CO, CO_2, CF_3COF, $(CF_3CO)_2O$, CF_3CF_2COF and $(CF_3CF_2CO)_2O$.

Quantitative studies revealed the general reaction scheme for the trifluoroacetates to proceed as follows:

$$Ln(CF_3CO_2)_3 \rightarrow LnF_3 + (CF_3CO)_2O + CO_2 + CO$$

secondary decomposition produces

$$(CF_3CO)_2O \rightarrow CF_3COF + CO + COF_2$$

Similar studies on the pentafluoropropionates were complicated by what appeared to be a carbon-to-carbon cleavage resulting in mixed products of CF_3COF and CF_3CF_2COF.

INTRODUCTION

Salts of trifluoroacetic acid were first reported by Swarts[1] in 1939. Recent investigations have included studies on the transition metal[2], group IVA and IVB[3], Pt, Pd, Ru[4,5], Mo[6], Bi[7], and lanthanide salts[8,9] of trifluoroacetic acid. Little attention has been given to the thermal behavior of the above compounds. In the present study several lanthanide salts of trifluoroacetic acid and pentafluoropropionic acid have

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*This paper is based on a portion of the Ph.D. Dissertation of K. W. Rillings, University of Massachusetts, Amherst, Mass., U.S.A., 1973.

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been prepared for the first time. A comparison has been made regarding hydration states, thermal behavior and volatile and non-volatile decomposition products. Information thus obtained has been utilized in postulating a decomposition mechanism. Similar studies of lanthanide salts of heptafluorobutyric acid have been made and will be reported in a future paper.

EXPERIMENTAL

Reagents

Trifluoroacetic acid and pentafluoropropionic acid (Matheson, Coleman and Bell) were fractionally distilled twice over a column packed with glass helices. Titration of each acid with sodium hydroxide revealed a minimum purity of 99.9%. Lanthanide oxides, A. D. McKay or from private stock, were of 99.9% purity or better. Prior to use the oxides were freshly ignited at 800°C in platinum crucibles.

Preparation of salts

Excess lanthanide oxide was added to a 50% aqueous solution of the respective acids. The lighter oxides (Sm, Pr) reacted immediately while the heavy oxides (Er) required refluxing for approximately 30 min. The solutions were allowed to stand for several hours after which the excess oxides were filtered off. After slow evaporation on a steam-bath the solutions, upon standing, gave crystals of the respective salts. The crystals were separated by filtration and air-dried.

Compounds for study were prepared by drying the compounds over magnesium perchlorate under vacuum for several days. Rehydration in a hygrostat over deliquescent sodium bromide (58% relative humidity) yielded pure trihydrate.

Analytical methods

The lanthanide content of the respective salts was determined by precipitation as the oxalate and ignition to the oxide.

Carbon and fluorine analyses were provided by the office of Research Services, University of Massachusetts, Amherst, Mass. under the direction of the late Mr. Charles F. Meade.

X-Ray diffraction

Powder X-ray diffraction data were obtained using both nickel filtered copper $K\alpha$X-rays and vanadium oxide filtered chromium $K\alpha$X-rays with a General Electric unit. The powder camera was a Phillips type 52056 with a diameter of 114.6 mm. Samples were packed in glass capillaries having diameters of 0.2 and 0.5 mm. Most exposures were taken for a 12-h period under operating conditions of 40 kV and 20 mA for the chromium tube and 50 kV and 20 mA for the copper tube.

Thermal analysis

Thermogravimetric analyses were performed on a Dupont Model 950 instrument. The ordinate of the recorder was in all cases calibrated to read directly in weight %. The abscissa read temperature directly in degrees Celsius. Heating rates of 5°C min^{-1} and 2°C min^{-1} were employed. Except where indicated otherwise a flowing (40 ml min^{-1}) dried air atmosphere was used. The chromel–alumel thermocouple was located directly beneath the sample pan. The sample pan was an open platinum type. Sample sizes were approximately 10 mg.

Differential thermal analysis work was performed on the Dupont Model 900 high temperature DTA cell (1200°C max.). The ordinate sensitivity varied and is indicated on all thermal curves. The abscissa is displayed as degrees Celsius. A heating rate of 10°C min^{-1} was used in all cases. Sample sizes were approximately 10 mg. The reference material was Al_2O_3. The sample container consisted of the micro platinum holder (without liner) supplied with the instrument. The thermocouples were Pt–Pt 13% Rh and were located in the center of the sample cups. Except where indicated otherwise the atmosphere consisted of dried flowing air at 60 ml min^{-1}.

Infrared spectra were obtained with a Perkin-Elmer Model 137 NaCl spectrometer and a Beckman IR 10. Qualitative identifications were made on the 137 while IR assignments were accomplished on the IR 10. In most cases samples were run in KBr discs.

Vapor phase samples were run in a micro gas cell having a volume of 7.5 cc and a path length of 5 cm equipped with both Irtran and NaCl windows.

RESULTS

Results of the hydration studies revealed the rare earth trifluoroacetates and pentafluoropropionates to exist as the trihydrates. Powder X-ray diffraction studies indicate the compounds to be isomorphous within a group by virtue of similar d spacings and line intensities (Table 1). IR curves suggested similar structural arrangements for each of the compounds in their respective series. The water molecules present in the compounds, were found by IR methods to be bonded in several different ways. Infrared bands, attributed to the OH stretching frequency, which appeared at 3690 cm^{-1} and 3650 cm^{-1} may be due to very weakly held water while the broad OH band at 3450 cm^{-1} may be due to more strongly hydrogen-bonded water in the compounds.

Thermogravimetric studies revealed the decomposition to proceed in several stages (Fig. 1). The first stage involved a stepwise dehydration to the anhydrous state, followed by decomposition of the salt to a stable product. Subsequent decomposition of this product comprised the final stage.

$Pr(C_2F_3O_2)_3 \cdot 3H_2O$ (*Fig. 2*)

This compound began to lose water of hydration at 60°C giving two poorly defined breaks in the curve prior to reaching the anhydrous state. The first break at 86°C corresponded to the unstable dihydrate while the second break at 112°C appeared to be the monohydrate. In an effort to confirm these breaks as real inter-

TABLE I

POWDER X-RAY DIFFRACTION DATA OF HYDRATED SALTS

Rel. Intensity	*d* (Å)			*Rel. Intensity*	*d* (Å)		
	$Pr(C_2F_3O_2)_3 \cdot 3H_2O$	$Sm(C_2F_3O_2)_3 \cdot H_2O$	$Er(C_2F_3O_2)_3 \cdot 3H_2O$		$Pr(C_3F_5O_2)_3 \cdot 3H_2O$	$Sm(C_3F_5O_2)_3 \cdot 3H_2O$	$Er(C_3F_5O_2)_3 \cdot 3H_2O$
s	9.47	9.52	9.40	s	10.65	10.87	10.78
vs	8.13	8.12	8.03	m	9.99	9.95	9.84
m	7.40	7.34	7.26	m	7.77	7.76	7.65
m	6.12	6.11	6.03	m	7.11	7.05	7.00
s	4.58	4.55	4.50	s	5.06	5.00	4.99
m	4.26	4.23	4.32	m	4.98	4.99	4.93
m	4.17	4.15	4.17	s	4.67	4.64	4.59
s	4.09	4.07	4.03	m	4.51	4.54	4.52
m	4.02	4.00	3.95	s	4.21	4.21	4.16
m	2.65	2.63	2.67	m	4.10	4.07	3.98
s	2.59	2.59	2.56				
m	2.45	2.43	2.41				

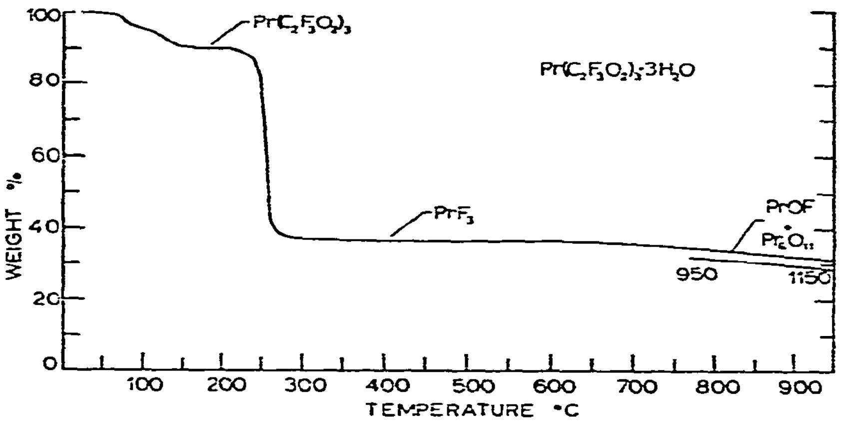

Fig. 1. Thermogravimetric curve for praseodymium trifluoroacetate in air at atmospheric pressure.

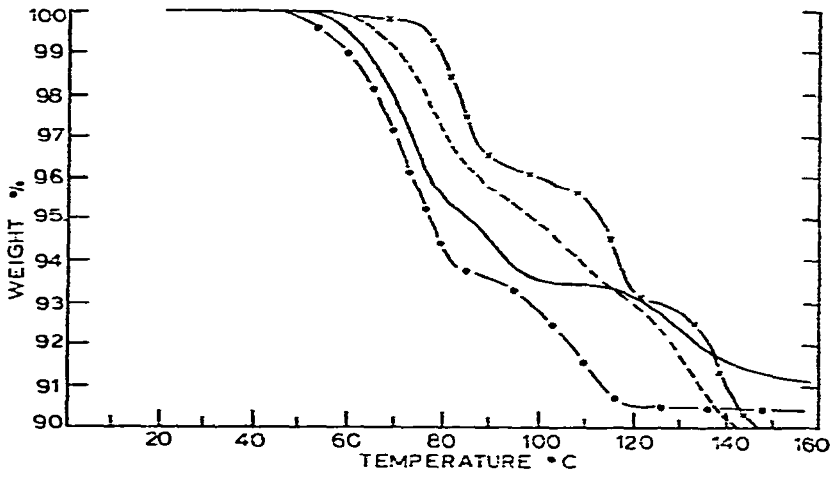

Fig. 2. Dehydration thermogravimetric curves. — — —, $Pr(C_2F_3O_2)_3 \cdot 3H_2O$; ———, $Sm(C_2F_3O_2)_3 \cdot 3H_2O$; —·—·—, $Er(C_2F_3O_2)_3 \cdot 3H_2O$; –×–×, $Pr(C_2F_3O_2)_3 \cdot 3H_2O$ wet atmosphere.

mediate hydrates the compound was rerun in an air atmosphere saturated with water vapor. Figure 2 shows the enhanced breaks obtained on the TG curve run in the wet atmosphere, therefore indicating that the poorly defined breaks were indeed unstable intermediates. The anhydrous plateau was not quite horizontal suggesting a slow decomposition to take place. More rapid decomposition at 220 °C resulted in a sharp weight loss to a horizontal plateau. The final weight (Table 2) corresponds to PrF_3. The plateau remained horizontal until a temperature of 680 °C was reached. Slow decomposition was observed from 680 to 890 °C after which an unstable intermediate corresponding to PrOF was obtained. Further heating to 1200 °C revealed a slow weight loss without indications of a stable plateau.

TABLE 2

TG DATA FOR LANTHANIDE SALTS

Compound	*Procedural decomposition temperature (°C)*	*Wt. % as anhydrous*		*Wt. % as LnF_3*		*Wt. % as LnOF*		*Temperature of LnOF formation (°C)*
		Theory	*Found*	*Theory*	*Found*	*Theory*	*Found*	
$Pr(C_2F_3O_2)_3 \cdot 3H_2O$	248	89.9	90.0	37.1	36.5	32.9	32.0	680
$Sm(C_2F_3O_2)_3 \cdot 3H_2O$	284	90.1	90.0	38.2	38.5	34.1	34.0	660
$Er(C_2F_3O_2)_3 \cdot 3H_2O$	288	90.4	90.5	40.0	40.1	35.9	36.0	600
$Pr(C_3F_5O_2)_3 \cdot 3H_2O$	292	92.1	92.0	28.9	29.2	25.7	25.0	670
$Sm(C_3F_5O_2)_3 \cdot 3H_2O$	297	92.2	92.0	29.9	30.0	26.7	26.5	650
$Er(C_3F_5O_2)_3 \cdot 3H_2O$	312	92.4	92.2	31.6	31.5	28.5	28.0	600

In an effort to confirm the products remaining after decomposition, samples of the salt were subjected to thermal decomposition and residues removed at 450 and 925 °C for X-ray diffraction studies. X-ray analysis of a green residue removed at 450 °C confirmed the product to be PrF_3. The brown-black sample removed at 925 °C was found to contain a mixture of PrOF and Pr_6O_{11}. Since it was believed that the decomposition of PrF_3 to PrOF is a hydrolysis reaction, hydrolysis was hastened by rerunning the sample in a wet atmosphere. As suspected PrF_3 was stable over a considerably shorter temperature range in that decomposition began at approximately 580 °C in the wet atmosphere. Under these conditions a stable brown compound was obtained at 710 °C. X-ray analysis revealed this compound to be PrOF. Further heating in the wet atmosphere produced additional hydrolysis until a stable plateau was reached at 1100 °C. The black compound formed was found to be Pr_6O_{11}. In general all of the compounds in this study decomposed initially to the LnF_3 product. The LnOF and Ln_2O_3 products were formed upon further decomposition under the conditions described above.

DTA studies revealed a rather complex curve (Fig. 3) in the temperature region at which dehydration takes place in that three strong endotherms are present. The first endotherm with a peak temperature of 105 °C corresponds to the loss of the first hydrate water molecule. The second endotherm at 120 °C, and of the same intensity as that of the first, probably results from the loss of the second water molecule.

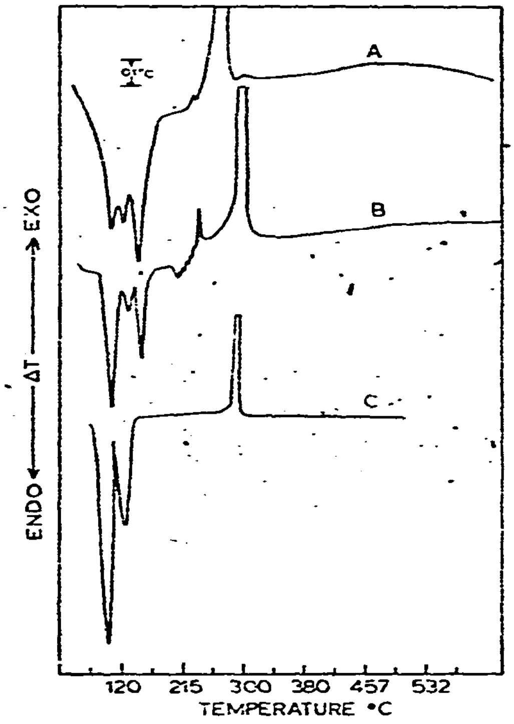

Fig. 3. Differential thermal analysis curves. A, $Pr(C_2F_3O_2)_3 \cdot 3H_2O$; B, $Sm(C_2F_3O_2)_3 \cdot 3H_2O$; C, $Er(C_2F_3O_2)_3 \cdot 3H_2O$.

A study of this compound by means of hot stage microscopy at similar heating rates to DTA studies, revealed the compound to "melt" at approximately 150 °C. Further heating on the hot stage produced what appeared to be gradual boiling of the solution. Finally at a temperature approaching 200 °C recrystallization took place with the formation of a compound prior to decomposition. It seems likely that the third and most intense endotherm at 150 °C results from both the loss of the third water molecule and the solution effect. It is anticipated that the solution, observed during the microscopy studies, is not a result of melting but a result of the anhydrous compound dissolving in its own evolved water of hydration. This conclusion is supported by the lack of reversibility of the endotherm upon cooling. The broad and shallow endotherm may result from gradual boiling observed above. The small exotherm at 235 °C is most likely the recrystallization of the compound. The large exotherm at approximately 250 °C is due to the decomposition of the compound. Accurate temperature measurement is difficult since the heat evolved during decomposition was great enough to override the temperature programmer resulting in a skewed peak. Procedural decomposition temperatures, obtained by reporting the intersection of tangents drawn to the anhydrous plateau and the sloping decomposition curve, are listed in Table 2.

$Sm(C_2F_3O_2)_3 \cdot 3H_2O$ (Fig. 2)

Hydrate water began to evolve at 52 °C resulting in the first break at 80 °C which corresponded to the 1.5 hydrate. Additional dehydration of 0.5 water molecules produced another break at 98 °C to a plateau which was not quite horizontal. Further heating resulted in what appeared to be the loss of an additional 0.5 waters and then a gradual loss of the remaining 0.5 water molecules finally reaching an unstable anhydrous state at 230 °C.

DTA studies (Fig. 3) revealed four endothermic peaks. The first strong endotherm at 105 °C corresponds to the loss of 1.5 water molecules while the weak shoulder at a temperature of 135 °C probably results from the additional loss of 0.5 water molecules. The third endotherm at 152 °C is associated with the loss of the last water molecule. Microscopy studies also revealed this compound to "melt" at a higher temperature (approx. 180 °C) than the Pr compound and also exhibit recrystallization prior to decomposition. The weak broad endotherm appearing at 210 °C most likely results from the solution effect and a slight amount of boiling. The sharp exotherm at 240 °C corresponds to the recrystallization.

$Er(C_2F_3O_2)_3 \cdot 3H_2O$ (Fig. 2)

Hydrate water began to evolve at 45 °C giving two breaks in the TG curve. The first break at 84 °C corresponds to the loss of two water molecules with the resultant formation of the monohydrate, while the second break at 120 °C is due to the anhydrous state. In this case the anhydrous compound is stable to a temperature of 220 °C.

DTA studies revealed two endothermic peaks (Fig. 3). The first endotherm which has approximately twice the area of the second shows a peak temperature of

100 °C. The second endotherm begins at approximately 105 °C and peaks at 128 °C. Both the magnitude and temperature range indicate these endotherms result from the loss of two and one water of hydration, respectively. Examination of this compound on the hot stage revealed the compound to remain a solid up to decomposition. The resulting thermal curve reflects this difference in that no endotherm or exotherm previously attributed to boiling and recrystallization are present.

$Pr(C_3F_5O_2)_3 \cdot 3H_2O$ (Fig. 4)

Hydrate water began to evolve at 35 °C giving two breaks prior to reaching the anhydrous state. The first break appeared at 54 °C and corresponded to the 1.5 hydrate. This intermediate was not quite stable as evidenced by a gradual weight loss to 80 °C and then a more rapid weight loss to a second break at 120 °C corresponding to an unstable monohydrate. Further dehydration took place immediately to 135 °C and then more gradual decomposition to the anhydrous state at 200 °C. The anhydrous compound was unstable and gradually decomposed.

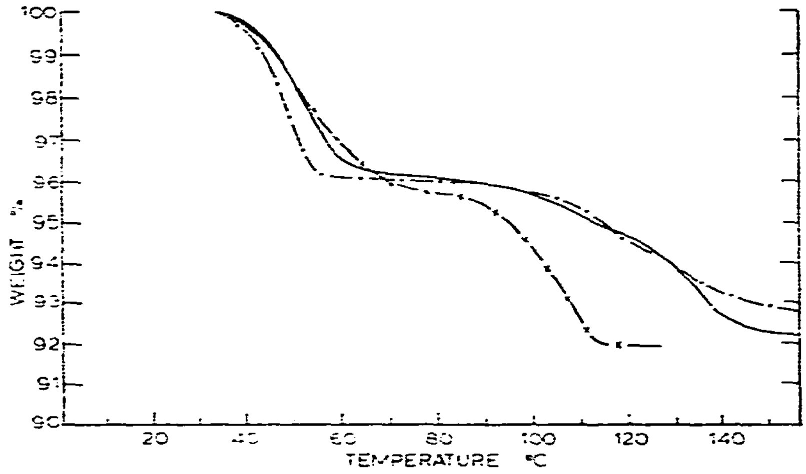

Fig. 4. Dehydration thermogravimetric curves. ———, $Pr(C_3F_5O_2)_3 \cdot 3H_2O$; —·—·—, $Sm(C_3F_5O_2)_3 \cdot 3H_2O$; –×–×, $Er(C_3F_5O_2)_3 \cdot 3H_2O$.

DTA studies (Fig. 5) revealed a strong endotherm at 70 °C corresponding to the loss of 1.5 water molecules. Further heating resulted in a broad complex endotherm which contained two endothermic peaks. The peak at 140 °C probably results from the loss of 0.5 water molecules while the more intense endotherm at 153 °C corresponds to the loss of the last water molecule.

Microscopic examination revealed the compound to undergo an incongruent "melt" at approximately 160 °C. Further heating resulted in recrystallization similar to the trifluoroacetates. The weak endotherm at 190 °C may result from the formation of the solution observed microscopically. The small exotherm at 260 °C results from

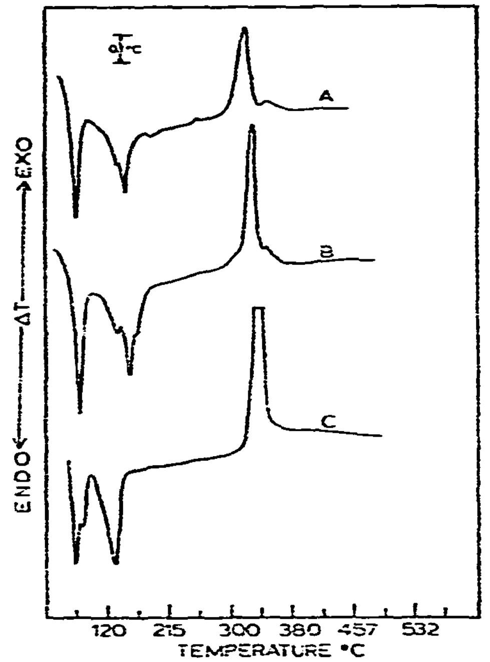

Fig. 5. Differential thermal analysis curves. A, $Pr(C_3F_5O_2)_3 \cdot 3H_2O$; B, $Sm(C_3F_5O_2)_3 \cdot 3H_2O$; C, $Er(C_3F_5O_2)_3 \cdot 3H_2O$.

recrystallization. Decomposition proceeded exothermically in several stages at a temperature of approximately 325 °C.

$Sm(C_3F_5O_2)_3 \cdot 3H_2O$ (Fig. 4)

Dehydration was very similar to the Pr salt in that the hydrate water began to evolve at 35 °C giving two breaks before reaching the anhydrous state. The first break, corresponding to the 1.5 hydrate, occurred at 62 °C and showed a similar stability to that observed in the Pr compound. Further dehydration resulted in a break for the unstable monohydrate at 114 °C then more rapid dehydration to the stable anhydrous state at 142 °C. The anhydrous compound was stable to a temperature of 310 °C.

The DTA curve (Fig. 5) revealed three endotherms. The most intense endotherm at 72 °C corresponds to the loss of 1.5 water molecules. The weak endotherm at 135 °C agrees with the loss of 0.5 water molecule found to occur by TG analysis. The more intense endotherm at 155 °C corresponds to the loss of the last water molecule. The Sm compound differs from the Pr compound in that microscopic studies have shown that no solution effect takes place. This accounts for the difference observed between the two DTA curves. Decomposition proceeds exothermically in what appears to be a several step process.

$Er(C_3F_5O_2)_3 \cdot 3H_2O$ (Fig. 4)

Hydrate water began to evolve at 35 °C giving one break prior to reaching the anhydrous state. The break in the TG curve appeared at 75 °C and corresponded to the 1.5 hydrate. This intermediate existed over a shorter temperature range (84–102 °C) than the Pr and Sm compounds. The anhydrous compound was stable to a temperature of 260 °C.

The DTA curve revealed essentially two endotherms of equal intensity. The first endotherm at 66 °C results from the dehydration of 1.5 water molecules. A small shoulder of unknown origin also appeared at approximately 70 °C. The second endotherm at 135 °C results from the loss of the remaining 1.5 water molecules.

Volatile decomposition products

Anhydrous trifluoroacetates were heated in air and vacuum (5–10 μ Hg). The evolved gases (Table 3) were identified by infrared analysis and found to be a mixture of fluorinated compounds, carbon monoxide and carbon dioxide. The fluorinated mixture consisted of carbonyl difluoride, trifluoroacetyl fluoride, and trifluoroacetic anhydride. Silicon tetrafluoride was also present and believed to be a reaction product between the carbonyl difluoride and the quartz pyrolysis tube. Pyrolysis of the pentafluoropropionates produced pentafluoropropionyl fluoride, trifluoroacetyl fluoride, pentafluoropropionic anhydride, carbon monoxide and carbon dioxide. Repeated analyses did not reveal any carbonyl difluoride to be present. A temperature dependence existed in regards to the quantities of each product produced in that the anhydride was converted to the acid fluoride as the temperature increased.

TABLE 3

PYROLYSIS PRODUCTS OF ANHYDROUS LANTHANIDE SALTS

Compound	*Pyrolysis temp. (°C)*	*Atmosphere*	*Volatile products*	*Solid residue*
$Pr(C_2F_3O_2)_3$	275	Air Vacuum	CO_2, CO, COF_2, $(CF_3CO)_2O$ (major) CF_3COF (major) SiF_4	PrF_3
$Pr(C_2F_3O_2)_3$	350	Vacuum	CO_2, CO, COF_2, $(CF_3CO)_2O$ (minor) CF_3COF (major) SiF_4	PrF_3
$Er(C_2F_3O_2)_3$	285	Air Vacuum	CO_2, CO, COF_2, $(CF_3CO)_2O$ (major) CF_3COF (major) SiF_4	ErF_3
$Er(C_3F_5O_2)_3$	300	Air Vacuum	CO_2, CO, $(CF_3CF_2CO)_2O$ (major) CF_3CF_2COF(trace), CF_3COF(trace) SiF_4	ErF_3
$Er(C_3F_5O_2)_3$	350	Vacuum	CO_2, CO, $(CF_3CF_2CO)_2O$ (minor) CF_3COF (major) CF_3CF_2 COF (trace) SiF_4	ErF_3

Although the presence of various decomposition products suggested a complex reaction path, it seemed important to obtain some estimate of the relative amounts of the products. Anhydrous salts were heated in a quartz tube (air and N_2 atmosphere) at 275°C. The evolved gases were passed through water to remove the acid fluoride and anhydride. The carbon dioxide was absorbed on ascarite, passing the residual gas over hot copper oxide and again absorbing it on ascarite. The water solution of the acid fluoride and anhydride was titrated with standard base. In an air atmosphere 1.33 mmoles of $Er(C_2F_3O_2)_3$ produced 1.29 mmoles of ErF_3, 1.96 mmoles of fluorinated volatiles, 2.35 mmoles of CO_2, and 1.85 mmoles of CO. Pyrolysis of 1.66 mmoles of $Er(C_2F_3O_2)_3$ in a nitrogen atmosphere produced 1.60 mmoles of ErF_3, 2.24 mmoles of fluorinated volatiles, 2.76 mmoles of CO_2, and 2.34 mmoles of CO. Indications are that some of the CO is air oxidized to CO_2 in the air atmosphere. Semi-quantitatively it appears that the starting product and ErF_3 are in equal molar quantities. CO, CO_2 and the fluorinated volatiles are also equal molar having a ratio of 1.5:1 with respect to the starting product.

Pyrolysis of the pentafluoropropionates in both air and nitrogen revealed equal molar quantities of starting product and the resultant trifluorides. The volatile fluorinated products were found to have a 2:1 molar ratio with respect to the starting product. Repeated analyses of CO_2 and CO placed their molar ratios at 1.5:1 and 1:1 with respect to the starting product.

DISCUSSION

The low temperature of dehydration indicates that the water molecules are not strongly bonded to the salts. These findings are in agreement with the IR data in that the spectra revealed weakly bonded water molecules. Both types of salts showed dehydration to proceed in a series of steps with the number of water molecules released per step increasing with an increase in atomic number. This observation is clearly shown in Figs. 2 and 4 in that a variety of intermediates are formed. The trifluoroacetates show mono-, sesqui-, and dihydrate intermediates for the first step of dehydration while the pentafluoropropionates show sesqui- and dihydrate intermediates. The trifluoroacetate compounds showed no preference for any one particular intermediate while the pentafluoropropionates all formed the 1.5 hydrate intermediate before becoming anhydrous. X-ray studies of the 1.5 hydrate revealed a crystalline change in that a different powder pattern was obtained upon dehydration to the 1.5 intermediate. Although it would be expected that further dehydration to the anhydrous compound would show another change in crystalline structure no further structural changes could be detected upon reaching the anhydrous state. A crystalline change was also observed for the trifluoroacetate compounds upon dehydration; however, since the intermediates were very unstable no specific intermediate could be singled out as the one showing the change. These data suggest that certain water molecules play special roles in the coordination of the ligands with the lanthanide metal. Similar findings to these were reported by Wendlandt[10,11] during his work with hydrated lanthanide oxalate salts. Three groups of compounds based on the intermediates formed during dehydration were reported by this investigator.

TG studies revealed the anhydrous Pr and Sm trifluoroacetates and Pr pentafluoropropionate compounds to exhibit slow decomposition. These compounds were found to "melt" and gradually boil which may account for their instability.

The procedural decomposition temperatures increased as the atomic number of the lanthanide increased thus reflecting the lanthanide contraction and decreasing base strength of the elements. Both TG and DTA analyses revealed the decomposition of the salts to be highly exothermic; however, qualitative measurements indicate the decomposition of the trifluoroacetates was more exothermic than that of the pentafluoropropionates.

Table 2 summarizes the temperature of initial formation of the LnOF from hydrolysis of LnF_3. From these data it can be seen that the temperature at which the oxyfluoride is formed is substantially lowered with an increase in atomic number of the rare earth element. The same effect was observed by Wendlandt[12] during studies of the lanthanide metal chlorides to metal oxychlorides. Wendlandt attributed this effect to the lowering of the basicity of the higher atomic number elements. Thermodynamic data from studies by Koch and Cunningham[13] on the hydrolysis of La, Pr and Nd chlorides also suggest a similar trend in that the heats of hydrolysis show a gradual decrease as the atomic number increases. Although similar thermodynamic data for the hydrolysis of the lanthanide fluorides are not available the heats of formation of the trifluorides determined by Polyachenok[14] show a similar trend. The heat of formation of rare earth fluorides was reported to be the greatest for the La compound (405 kcal mol^{-1}) and found to show a gradual decrease as the atomic number increased finally reaching a value of 370 kcal mol^{-1} for Lu. It is expected that when thermodynamic data become available for the hydrolysis of LnF_3 a gradual decrease will be found as the atomic number increases thereby showing a similar trend to that found in the thermodynamic data for the chlorides.

The volatile decomposition products detected indicate that the reactions proceed through an anhydride and decomposition to the respective acetyl and propionyl fluorides. This reaction mechanism is supported in a study by Corbett and Whittle[15] on the thermal decomposition of perfluoroacetic anhydride. They found CF_3COF, CO, and CO_2 to be the major products of decomposition in a temperature range of 216–320 °C. Roberts[9] reported the pyrolysis of Nd and La trifluoroacetates to proceed according to an overall reaction scheme as follows:

$$2Ln(C_2F_3O_2)_3 \rightarrow 2LnF_3 + 3CF_3COF + 3CO_2 + 3CO$$

The analytical data reported in this study support the equation proposed by Roberts; however, the infrared identification of the anhydride and acetyl fluoride suggest a modification of the reaction mechanism with the introduction of the anhydride intermediate as follows:

$$Ln(C_2F_3O_2)_3 \rightarrow LnF_3 + (C_2F_3O)_2O + CO_2 + CO$$

secondary decomposition of the anhydride produces

$$(C_2F_3O)_2O \rightarrow CF_3COF + COF_2 + CO$$

Hydrolysis of the anhydride in the first reaction would produce two equivalents of acid per one unit of starting product. In the second reaction path hydrolysis of the trifluoroacetyl fluoride produces two equivalents ($HF+CF_3COOH$) and an additional two equivalents from the hydrolysis of carbonyl difluoride ($COF_2+H_2O \rightarrow CO_2+2HF$) for a total of four equivalents. The number of equivalents produced if the anhydride intermediate was not considered (as in Roberts' equation) would be a 3:1 ratio. Since both anhydride and trifluoroacetyl fluoride were shown to exist simultaneously an average of the two proposed reaction paths would produce a 3:1 ratio. This is identical to the one step reaction proposed by Roberts.

Pyrolysis of the pentafluoropropionate compounds produced both trifluoroacetyl fluoride and pentafluoropropionyl fluoride suggesting a cleavage of a carbon-to-carbon bond. Since the mechanism of this reaction is unclear it is difficult to write an overall reaction scheme for these compounds. However, the presence of the anhydride suggests a similar mechanism as found in the trifluoroacetates.

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