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Note

THERMAL DECOMPOSITION OF RARE EARTH TRIFLUOROMETHANESULFONATE COMPLEXES WITH DIMETHYLFORMAMIDE (DMF)

J.E.X. DE MATOS

Universidade Federal do Ceará, Departamento de Química Orgânica e Inorgânica, C.P. 3010, CEP 60.000, Fortaleza CE (Brasil)

D.M. ARAÚJO MELO * and L.B. ZINNER

Universidade de São Paulo, Instituto de Química, Departamento de Química Fundamental, C.P. 20.780, CEP 01498, São Paulo SP (Brasil)

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INTRODUCTION

The thermal behavior of hydrated lanthanide trifluoromethanesulfonate has been investigated by Roberts and Bykowski [1]. Detailed data are not available for rare earth trifluoromethanesulfonate complexes, especially with amide ligands. Some sulfoxides [2–4] and an aminoxide [5] have recently been characterized and their thermal properties studied.

Addition compounds of lanthanide iodides [6], acetates [7], nitrates [8], perchlorates [9], chlorides [10], perrhenates [11,12], hexathiocyanate chromiates (III) [13], isothiocyanates [14], hexafluorophosphates [15] and trifluoroacetates [16] with *N,N*-dimethylformamide (DMF) have already been described.

In this paper we report on a thermoanalytical study of a new series of trifluoromethanesulfonate complexes with DMF employing the TG technique.

EXPERIMENTAL

The hydrated trifluoromethanesulfonates were treated with a small excess of DMF and the mixtures gently warmed, resulting in a series of oily products. Crystallization of the complexes was carried out using the diffu-

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* Permanent address: Departamento de Química, Universidade Federal do Rio Grande do Norte, CEP 59.000, Natal RN, Brasil.

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sion method, with chloroform as the outer solvent. The crystals were dried in air over filter paper.

The compounds were characterized by the usual microanalytical procedures, consisting of complexometric titration of the lanthanide with EDTA and C, N, H analysis via microchemical techniques.

Thermogravimetric studies were performed using a Perkin-Elmer TGA–DSC series 7 instrument set. Sample sizes were approximately 10–20 mg and two heating rates, 1 and 10 ° C min^{-1}, were used. The heatings were performed in atmospheres of air and of nitrogen.

The IR spectra of DMF and of the complexes were recorded using a Perkin-Elmer 283 spectrophotometer.

X-ray powder patterns were recorded using a Rigaku Instruments apparatus and CuKα radiation.

RESULTS AND DISCUSSION

According to the analytical results the complexes have the composition $Ln(CF_3SO_3)_3 \cdot 3DMF \cdot 6H_2O$ (Ln = La–Gd, Dy) and $Ln(CF_3SO_3)_3 \cdot DMF \cdot 6H_2O$ (Ln = Ho, Er). Strong water bands and small shifts of ν(CO) to lower frequencies (in relation to that for free DMF) indicate the presence of coordinated water and coordination of DMF through the oxygen. Bands attributed to the $CF_3SO_3^-$ species show that they are not bonded to the lanthanides. X-ray powder patterns indicate that the compounds form two isomorphous series, the first corresponding to the complex with three ligands and the second to the complexes with one DMF.

The first step in the thermal degradation process in both air and nitrogen is the loss of the water molecules. This starts at very low temperatures (~ 30 ° C) and is complete at around 200 ° C. Dehydration proceeds in two steps for the cerium complex and in one step for all the other derivatives.

The complexes $Ln(CF_3SO_3)_3 \cdot n$DMF are unstable and the loss of DMF starts at ~ 220 ° C, producing the anhydrous salt in one step; however, in the cases of Eu and Er (in air) the species $LnF(CF_3SO_3)_2$ are possibly formed instead.

For the cerium and gadolinium compounds there is some evidence for the formation of $Ln(CF_3SO_3)_3 \cdot 2DMF$.

The anhydrous lanthanoid trifluoromethanesulfonates formed around 350 ° C rapidly decompose with evolution of COF_2 and SO_2 [1], giving LnF_3 as the final product at ~ 470 ° C as identified by X-ray diffraction patterns.

Figure 1 shows the TG curves obtained for the La, Nd and Eu complexes, while Table 1 lists the thermoanalytical data.

In air, the interpretations of the TG curves are the same as for those obtained using a nitrogen atmosphere (Fig. 2) and the thermal degradation processes are essentially the same.

TABLE 1

TG data

Reaction steps	Molecular weight	Weight (%)		Temperature range (°)
		Theoretical	Experimental	
$La(CF_3SO_3)_3 \cdot 3DMF \cdot 6H_2O$	913.501	100.00	99.98	39
$La(CF_3SO_3)_2 \cdot 3DMF$	805.405	88.17	88.17	186–256
$La(CF_3SO_3)_3$	586.117	64.18	64.92	382–465
LaF_3	195.88	21.45	21.02	490–940
$Ce(CF_3SO_3)_3 \cdot 3DMF \cdot 6H_2O$	914.711	100.00	99.79	36
$Ce(CF_3SO_3)_3 \cdot 3DMF \cdot 3H_2O$	860.663	94.09	93.96	78– 80
$Ce(CF_3SO_3)_3 \cdot 3DMF$	806.615	88.18	88.19	160–256
$Ce(CF_3SO_3)_3 \cdot 2DMF$	733.519	80.19	80.22	256–258
$Ce(CF_3SO_3)_3$	587.327	64.23	66.77	356–445
CeF_3	197.09	21.55	21.34	470–938
$Pr(CF_3SO_3)_3 \cdot 3DMF \cdot 6H_2O$	915.501	100.00	99.94	28
$Pr(CF_3SO_3)_3 \cdot 3DMF$	807.405	88.19	88.92	175–244
PrF_3	197.88	21.62	21.26	460–950
$Nd(CF_3SO_3)_3 \cdot 3DMF \cdot 6H_2O$	918.831	100.00	99.94	26
$Nd(CF_3SO_3)_3 \cdot 3DMF$	810.735	88.24	88.96	175–235
NdF_3	201.21	21.91	23.33	452–802
$Sm(CF_3SO_3)_3 \cdot 3DMF \cdot 6H_2O$	924.941	100.00	99.96	30
$Sm(CF_3SO_3)_3 \cdot 3DMF$	816.845	88.32	88.33	230–232
SmF_3	207.32	22.43	22.31	445–956
$Eu(CF_3SO_3)_3 \cdot 3DMF \cdot 6H_2O$	926.551	100.00	99.91	26
$Eu(CF_3SO_3)_3 \cdot 3DMF$	818.455	88.33	88.32	224–226
$EuF(CF_3SO_3)_2$	469.089	50.64	50.77	407–408
EuF_3	208.93	22.56	22.83	456–955
$Gd(CF_3SO_3)_3 \cdot 3DMF \cdot 6H_2O$	931.841	100.00	99.94	28
$Gd(CF_3SO_3)_3 \cdot 3DMF$	823.745	88.41	88.39	190–197
$Gd(CF_3SO_3)_2 \cdot 2DMF$	750.649	80.55	80.20	220–315
GdF_3	214.22	23.00	26.14	475–900
$Dy(CF_3SO_3)_3 \cdot 3DMF \cdot 6H_2O$	937.091	100.00	99.88	29
$Dy(CF_3SO_3)_3 \cdot 3DMF$	828.995	88.47	88.48	210–212
DyF_3	219.47	23.43	23.08	445–954
$Ho(CF_3SO_3)_3 \cdot DMF \cdot 6H_2O$	793.329	100.00	99.86	30
$Ho(CF_3SO_3)_3 \cdot DMF$	685.233	86.38	87.69	108–140
$Ho(CF_3SO_3)_3$	612.137	77.16	76.80	175–384
HoF_3	221.90	27.98	27.75	470–950
$Er(CF_3SO_3)_3 \cdot DMF \cdot 6H_2O$	795.659	100.00	99.85	26
$Er(CF_3SO_3) \cdot DMF$	687.563	86.42	85.23	205–353
$ErF(CF_3SO_3)_2$	484.389	60.89	61.23	399–400
ErF_3	224.23	28.19	28.00	450–945

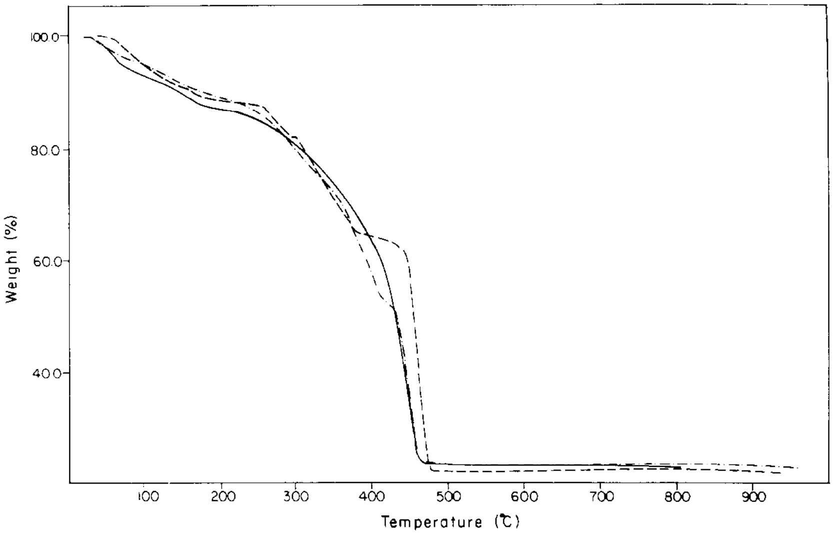

Fig. 1. Thermogravimetric curves for compounds of La (— — —), Nd (———) and Eu (·—·—·).

Isothermal studies (see Fig. 3) at 120 °C were performed with the cerium compound; these showed that anhydrous complexes $Ce(CF_3SO_3)_3 \cdot 3DMF$ can be isolated which undergo isothermal decomposition at 325 °C to the anhydrous salt $Ce(CF_3SO_3)_3$.

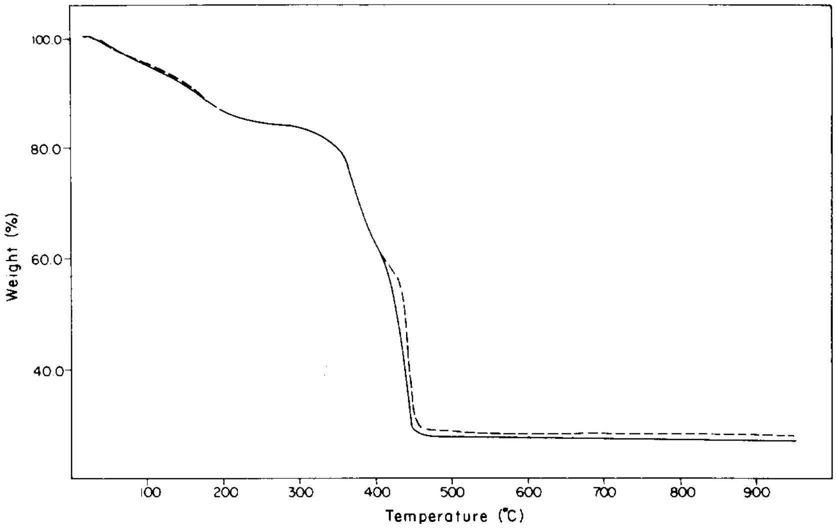

Fig. 2. TG curves for Er compounds in atmospheres of nitrogen (———) and air (— — —).

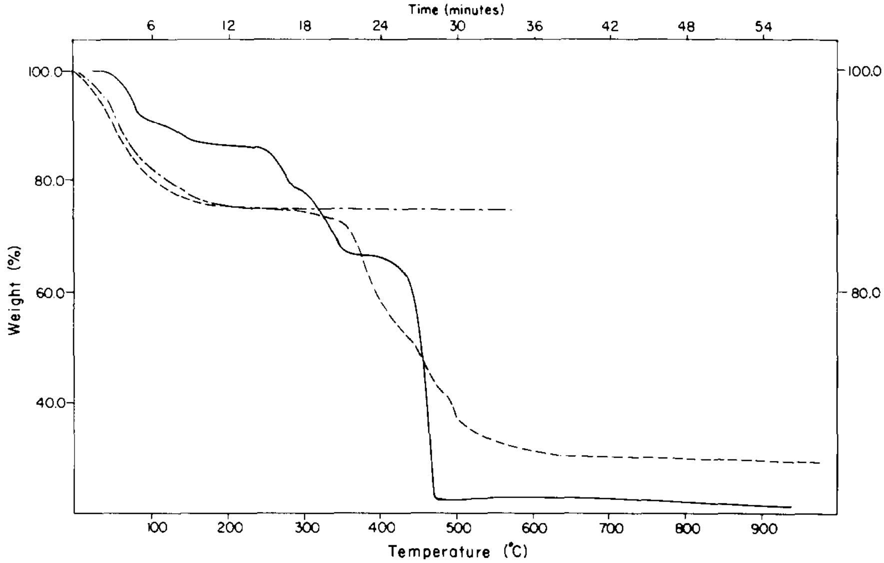

Fig. 3. TG curves for a Ce compound (———), and isothermal curves at 120 °C (·–·–·) and 325 °C (— — —) in a nitrogen atmosphere.

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