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# A THERMAL STUDY OF SOME LANTHANIDE TRIFLUOROMETHYL SULFONATES*

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## ABSTRACT

Lanthanide trifluoromethyl sulfonates, $M(SO_3CF_3)_3 \cdot 9H_2O$, have been prepared and characterized by analysis, optical properties and thermal behaviour. Dehydration proceeded in two steps for the lanthanum, cerium, praseodymium and neodymium salts and in three steps for other members of the lanthanide series. Thermal decomposition to lanthanide fluoride, carbonyl fluoride and sulfur dioxide occurred at temperatures greater than 400°C. This decomposition has been shown to be a two step process.

## INTRODUCTION

Since the preparation of trifluoromethyl sulfonic acid by Haszeldine and Kidd[1] in 1954, there have been only a few studies of its inorganic salts. Haszeldine and Kidd[1] prepared the sodium, silver and barium salts. Schmeisser et al.[2] prepared the zirconium and thorium salts as well as the more complex compounds $Cl_2Ti(SO_3CF_3)_2$, $ClTi(SO_3CF_3)_3$, $R_nSi(SO_3CF_3)_{4-n}$, $R_nSn(SO_3CF_3)_{4-n}$ and $R_3PbSO_3CF_3$ where R is $CH_3$ or $C_6H_5$. The lithium salt was reported by Bennion and Tiedmann[3] and some complex cyclopentadienyl compounds of titanium(IV) and vanadium(IV) were reported by Doyle and Tobias[4]. Dalziel and Aubke[5] prepared the compounds $I(SO_3CF_3)_3$ and $M(ISO_3CF_3)_4$ where M was K, Rb, or Cs and the iodyl and iodosyl compounds $IO_2SO_3CF_3$ and $IOSO_3CF_3$ were reported by Dalziel, Carter and Aubke[6]. Bachelor et al.[7] described the tin salts. The chromyl compound was reported by Brown and Gard[8] and the trifluoromethyl compound was reported by Noftle and Cady[9]. The only references to lanthanide trifluoromethyl sulfonates are the patent granted to Thom[10] and the preparation of the anhydrous lanthanum, samarium, europium and ytterbium compounds by Massaux and Duyckaerts[11].

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None of these studies involved detailed thermal investigations of dehydration or decomposition. Even the hydration state of many of these compounds has not been established. In view of the interesting thermal decompositions found for lanthanide salts of some other fluorinated acids[12] it was felt that a study of the lanthanide trifluoromethyl sulfonates should be undertaken.

## EXPERIMENTAL

*Reagents.* Trifluoromethyl sulfonic acid was purchased from Alfa Products (Ventron Corp.) in 25 gram ampoules packed under argon. Lanthanide oxides were from A. D. MacKay, Research Chemicals or private stock. Minimum purity was 99.9%. All other reagents were analytical reagent quality.

*Thermal methods.* Thermogravimetric curves were obtained from a Du-Pont Model 950 unit with a 40 ml min$^{-1}$ flow of dry nitrogen. Full scale and expanded scale (75–100%) modes were used with temperature ranges of ambient to 500°C (heating rate 3°C min$^{-1}$). Sample size was approximately 15 mg. For differential thermal analysis the Du-Pont Model 900 high temperature DTA cell was used with an atmosphere of dry air (100 ml min$^{-1}$), a heating rate of 15°C min$^{-1}$, an ordinate sensitivity of 0.02 mv inch$^{-1}$, 5 mg samples, and aluminum oxide as the reference material.

Pyrolysis gas chromatography was carried with a chromalytics MP 3 pyrolysis gas chromatograph. After heating the sample for 30 min at 225°C to ensure an anhydrous state, the temperature was raised to 420°C at 40°C min$^{-1}$. A helium flow of 25 ml min$^{-1}$ was used and the volatile pyrolysis products were trapped in a 1/8 in. stainless steel coil cooled in liquid nitrogen from which they were transferred to the columns. Two columns were used: (1) a 4 ft. × 1/8 inch stainless steel column packed with 80–100 mesh Poropak Q beads (Waters Associates) and (2) a 3 ft. × 1/8 inch stainless steel column packed with 5 Å molecular sieves. The thermal conductivity detector current was held at 150 mamps, while the detector temperature was programmed at 12°C min$^{-1}$. Individual peaks were trapped separately in liquid nitrogen cooled traps for subsequent IR analysis.

*IR measurements.* IR spectroscopy was accomplished with a Perkin–Elmer Model 137 spectrophotometer and a micro gas cell of 7.5 ml volume, 5 cm path length and sodium chloride or Irtran II windows (Barnes Engineering Co.).

*Microscopy.* Microscopic studies were carried out with a Vickers polarizing microscope, Model 726405, fitted with the usual polarizing optics and accessories. Cargille immersion liquids were used for refractive index measurements.

*Compound preparation.* The lanthanide salts were prepared by allowing an excess of the oxide or carbonate to stand with trifluoromethyl sulfonic acid at room temperature for several days, filtering off the excess solid and evaporating the clear solution in air or vacuum over DRIERITE or phosphoric oxide. The hydration state was established by drying in vacuum to constant weight and rehydrating over saturated aqueous NaBr · $H_2O$ (58% relative humidity) or over saturated aqueous $CaCl_2$ · $6H_2O$ (32% relative humidity).

*Analytical methods.* Lanthanides were determined gravimetrically by the usual oxalate precipitation and ignition to oxide. Carbon, hydrogen and sulfur were determined by the Office of Research Services, University of Massachusetts, Amherst. Fluorine could not be determined accurately because after Schoniger decomposition approximately 1/3 of the fluorine was tied up as lanthanide fluoride and not titratable. The other analyses, however, provide accurate characterization.

## RESULTS AND DISCUSSION

The analytical results show that all the lanthanide trifluoromethyl sulfonates form stable enneahydrates, $M(SO_3CF_3)_3 \cdot 9H_2O$. Representative analyses are shown in Tables 1 and 2. When these compounds were heated to 500–550°C they decomposed quantitatively to the metal fluoride, $MF_3$, as established by gravimetric analysis of the heated product, thus confirming the other analytical results.

Hydration–dehydration studies showed conclusively that at relative humidities of 58% and 32% the final stable compound is the enneahydrate. Dehydration in vacuum at room temperature, whether over DRIERITE or phosphoric oxide was never complete nor did it appear to result in an integral number of water molecules remaining per mole of salt, but generally the moles of water remaining when equilibrium had been established increased with atomic number from about 2 for the La–Nd end of the series to greater than 3 for the higher atomic number elements. It is clear that the water molecules are not all bonded with equal forces. This is consistent with the thermal studies which showed a temperature of 190°C necessary for complete dehydration.

The thermogravimetric curves for all members of the series were generally of similar shape exept for those portions showing dehydration steps. Representative TG dehydration curves are shown in Fig. 1 while Fig. 2 shows the DTA results. It is clear from the thermal studies that the lanthanide salts can be grouped according to the

TABLE 1

REPRESENTATIVE ELEMENTAL ANALYSIS OF SOME COMPOUNDS

| *Compound* | *% Lanthanide* | | *% Carbon* | | *% Sulfur* | | *% Hydrogen* | |
|---|---|---|---|---|---|---|---|---|
| | *Theory* | *Found* | *Theory* | *Found* | *Theory* | *Found* | *Theory* | *Found* |
| $Ce(OSO_2CF_3)_3.9H_2O$ | 18.70 | 18.73 | 4.81 | 4.79 | 12.83 | 12.78 | 2.42 | 2.37 |
| $Pr(OSO_2CF_3)_3.9H_2O$ | 18.78 | 18.84 | 4.80 | 4.74 | 12.82 | 13.00 | 2.42 | 2.41 |
| $Sm(OSO_2CF_3)_3.9H_2O$ | 19.79 | 19.82 | 4.74 | 4.75 | 12.66 | 12.79 | 2.39 | 2.34 |
| $Eu(OSO_2CF_3)_3.9H_2O$ | 19.96 | 19.94 | 4.73 | 4.53 | 12.64 | 12.62 | 2.38 | 2.29 |
| $Tb(OSO_2CF_3)_3.9H_2O$ | 20.69 | 20.92 | 4.69 | 4.86 | 12.52 | 12.53 | 2.36 | 2.40 |
| $Er(OSO_2CF_3)_3.9H_2O$ | 21.54 | 21.48 | 4.64 | 4.65 | 12.39 | 12.23 | 2.34 | 2.27 |

TABLE 2

TG DATA FOR THE LANTHANIDE TRIFLUOROMETHANE SULFONATES-9-HYDRATE

| *Cation* | *Wt. % as water* | | *Wt. % as $LnF_3$* | | *Temperature of $LnF_3$ formation* |
|---|---|---|---|---|---|
| | *Theory* | *Found* | *Theory* | *Found* | |
| La | 21.67 | 21.65 | 26.18 | 27.0 | 420°C |
| Ce | 21.63 | 21.8 | 26.30 | 27.0 | 450°C |
| Pr | 21.61 | 21.6 | 26.38 | 28.0 | 460°C |
| Nd | 21.52 | 21.7 | 26.70 | 28.5 | 440°C |
| Sm | 21.34 | 21.4 | 27.29 | 29.0 | 445°C |
| Eu | 21.30 | 21.5 | 27.48 | 29.3 | 442°C |
| Gd | 21.15 | 22.0 | 27.95 | 28.3 | 440°C |
| Tb | 21.10 | 21.1 | 28.10 | 29.0 | 432°C |
| Dy | 21.00 | 21.15 | 28.44 | 32.0 | 445°C |
| Ho | 20.94 | 21.0 | 28.44 | 30.5 | 452°C |
| Er | 20.88 | 21.0 | 28.66 | 30.0 | 450°C |
| Yb | 20.72 | 20.5 | 29.40 | 31.0 | 455°C |
| Y | 23.56 | 23.1 | 21.20 | 21.6 | 455°C |

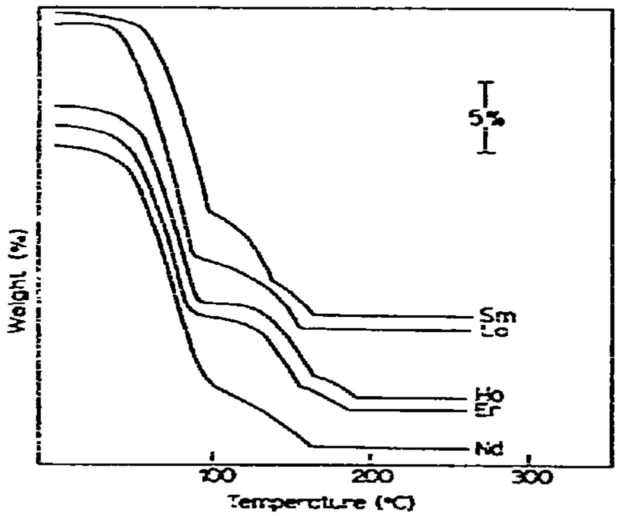

Fig. 1. Representative thermogravimetric curves for the dehydration of lanthanide trifluoromethyl sulfonates. Heating rate 3°C min$^{-1}$.

dehydration process. La, Ce, Pr and Nd salts undergo a two step dehydration from $9H_2O$ to $2H_2O$ to anhydrous. Sm, Eu, Gd, Tb, Dy and Y salts show a three step dehydration from $9H_2O$ to $3H_2O$ to $1H_2O$ to anhydrous. Ho, Er and Yb salts also show a three step dehydration but from $9H_2O$ to $3H_2O$ to $0.5H_2O$ to anhydrous. These differences are systematic with increasing atomic number. Yttrium falls in the group containing dysprosium and terbium as is usual with most of its chemical properties. Most of the salient temperatures are listed in Table 3.

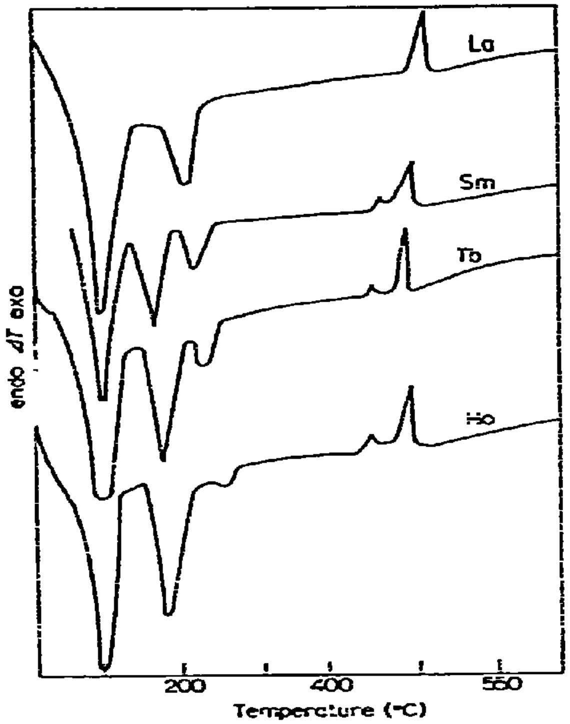

Fig. 2. Differential thermal analysis curves for representative lanthanide trifluoromethyl sulfonates. Heating rate 15°C min$^{-1}$.

TABLE 3

| Cation | TG temperatures, $T_f$ °C | | | | DTA temperatures, °C | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Dehydration | | | Decomposition to $MF_3$ | $\Delta T_{min.}$ | | | $\Delta T_{max.}$ | |
| La | 90(7)[a] | 165(2) | | 420 | 110 | 209 | | 455 | |
| Ce | 90(7) | 150(2) | | 450 | 105 | 206 | | 408 | 427 |
| Pr | 90(7) | 150(2) | | 460 | | | | 425 | 460 |
| Nd | 90(7) | 150(2) | | 435 | | | | 425 | 460 |
| Sm | 95(6) | 140(2) | 167(1) | 450 | 112 | 173 | 220 | 412 | 442 |
| Eu | 95(6) | 140(2) | 167(1) | 442 | | | | | |
| Gd | 95(6) | 140(2) | 167(1) | 440 | | | | | |
| Tb | | | | 432 | 115 | 190 | 239 | 418 | 444 |
| Dy | | | | 445 | 115 | 190 | 223 | 414 | 448 |
| Ho | 95(60) | 165(2.5) | 189(0.5) | 452 | 120 | 199 | 227 | 412 | 450 |
| Er | 95(60) | 165(2.5) | 190(0.5) | 455 | | | | | |
| Yb | 95(60) | 165(2.5) | 190(0.5) | 455 | 111 | 190 | 219 | 390 | 448 |
| Y | 95(6) | 145(2) | 170(1) | 455 | | | | | |

[a] Numbers in parentheses indicate moles of water lost.

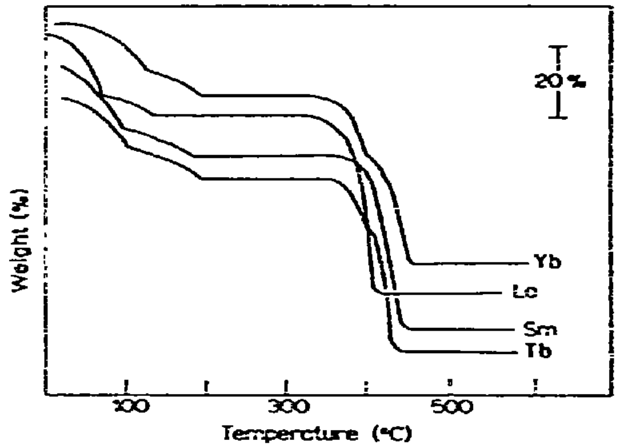

Fig. 3. Representative thermogravimetric curves for lanthanide trifluoromethyl sulfonates showing the development of the second "break" at temperatures greater than 400°C. Heating rate 10° Cmin$^{-1}$.

The DTA curve for the lanthanum salt shows only one exotherm corresponding to decomposition to $LaF_3$. With increase in atomic number of the lanthanide a second exotherm appeared and became increasingly well resolved. Close inspection of the TG curves (Fig. 3) also showed that the decomposition to the final $MF_3$ appeared to proceed in two stages, this, in part, accounting for the relatively large temperature range of decomposition. From the weight relationships shown by the TG curves, it was clear that an intermediate compound, $MF(SO_3CF_3)_2$ was formed prior to the final decomposition to $MF_3$.

Although both dry air and dry nitrogen atmospheres were used in the thermal studies, the stoichiometry and decomposition temperatures were unaffected by the atmosphere so long as it was dry. Moist atmospheres led to complications resulting from hydrolysis of the decomposition products.

In order to elucidate further the decomposition mechanism, samples were pyrolyzed and the volatile products separated by gas chromatography and examined by IR spectrophotometry. Pyrolysis at 420°C yielded volatile products which gave two well defined gas chromatograph peaks from a PORAPAK Q column. Retention times were 50 sec and 10 min 10 sec respectively. When pure sulfur dioxide was injected into the column, a single peak with a retention time of 10 min 10 sec was observed. With a column of 5 Å molecular sieve packing the pyrolyzed sample showed only one chromatographic peak with a retention time of 17 min 50 sec. A sample of pure sulfur dioxide injected into this column gave a single peak with a retention time of 17 min 46 sec.

This second chromatographic peak was examined by IR spectrophotometry resulting in the spectrum shown in Fig. 4. This established unequivocally that sulfur dioxide was one of two volatile products from the pyrolysis. As still further evidence, passage of this gas into water containing a little hydrogen peroxide yielded a solution which gave a strong test for sulfate.

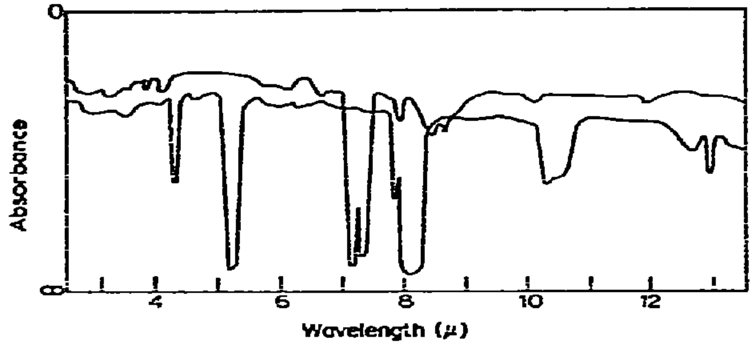

Fig. 4. IR spectra of the chromatographic peaks; upper curve, 2nd peak, identifying sulfur dioxide; lower curve 1st peak, identifying carbonyl fluoride.

Examination of the first chromatographic peak by IR spectrophotometry gave the spectrum shown in Fig. 4. This is clearly the spectrum of carbonyl fluoride[13, 14]. Passage of this gas into water yielded a solution which gave a strong test for fluoride when tested microscopically with triphenyltin chloride, the hexagonal triphenyltin fluoride crystals being a specific identification of fluoride.

From these results it can be concluded that the thermal decomposition of anhydrous lanthanide trifluoromethyl sulfonates is a step process as represented by the following equations

$$M(SO_3CF_3)_3 \rightarrow MF(SO_3CF_3)_2 + COF_2 + SO_2 \qquad (1)$$

$$MF(SO_3CF_3)_2 \rightarrow MF_3 + 2COF_2 + 2SO_2 \qquad (2)$$

While all data support this mechanism, the second step occurs so soon after the first that isolation of the intermediate compound was not possible.

The crystallography of the enneahydrates was studied microscopically. The compounds were found to be orthorhombic, optically positive, with an extremely small optic angle (2$V$), estimated at less than 5°. The refractive indices for white light and room temperature were found to be $\alpha = 1.469$, $\beta = 1.470$ and $\gamma = 1.473$. No differences out to the third decimal were measurable from one end of the series to the other. The crystal habit is shown in Fig. 5.

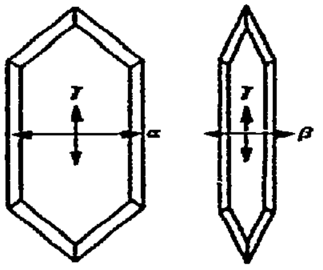

Fig. 5. Crystal habit for lanthanide trifluoromethyl sulfonate enneahydrate.

Qualitative solubilities were determined microscopically by observing rates of disappearance of birefringence. The enneahydrates are very soluble in water, methanol, 100% ethanol and acetone; appreciably soluble in diethyl ether; slightly soluble in amyl alcohol and practically insoluble in *p*-xylene, nitromethane, nitrobenzene, toluene, phenol, 1,2-dichloroethane, benzene, carbon tetrachloride and chloroform. All measurements were made at room temperature.

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## REFERENCES

1 R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, (1954) 4228; (1955) 2901.
2 M. Schmeisser, P. Sartori and B. Lippsmeier, *Chem. Ber.*, 103 (1970) 868.
3 D. N. Bennion and W. H. Tiedmann, *J. Chem. Eng. Data*, 16 (1971) 368.
4 G. Doyle and R. S. Tobias, *Inorg. Chem.*, 6 (1967) 111; 7 (1968) 2479.
5 J. R. Dalziel and F. Aubke, *Inorg. Chem.*, 12 (1973) 2707.
6 J. R. Dalziel, H. A. Carter and F. Aubke, *Inorg. Chem.*, 15 (1976) 1247.
7 R. J. Bachelor, J. N. R. Ruddick, J. R. Sams and F. Aubke, *Inorg. Chem.*, 16 (1977) 1414.
8 S. D. Brown and G. L. Gard, *Inorg. Chem.*, 14 (1975) 2273.
9 R. E. Noftle and G. Cady, *Inorg. Chem.*, 4 (1965) 1010.
10 K. F. Thom, U.S. Patent #3,723,485, 1973.
11 J. Massaux and G. Duyckaerts, *Anal. Chim. Acta*, 73 (1974) 416.
12 K. Rillings and J. E. Roberts, *Thermochim. Acta*, 10 (1974) 285.
13 A. H. Nielson, J. G. Burke, P. J. H. Woltz and E. A. Jones, *J. Chem. Phys.*, 20 (1952) 596.
14 P. J. H. Woltz and E. A. Jones, *J. Chem. Phys.*, 17 (1949) 502.