Thermal Decomposition of Lanthanum Trifluoromethanesulfonate

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Lanthanum trifluoride (LaF_3) has been obtained as the final product of the thermal decomposition of the corresponding trifluoro-methanesulfonate [$La(OTf)_3$]. The decomposition processes up to 600 °C were characterized by means of TG, DTA, XRD and MS. It was revealed that the over all reaction scheme for the decomposition proceeds as follow: $La(OTf)_3 \rightarrow LaF_3 + 3SO_2 + CO_2 + CF_3OCF_3$.

Trifluoromethanesulfonic acid [triflic acid; TfOH], which is acclaimed as one of the strongest monoprotonic acid and well recognized as precursors of both inorganic and organic shyntons,[1] was first prepared in the 1950s.[2] Until now, however, it seems that most of the interests in this acid and its derivatives have centered on the chemistry involving transition metals, and that little attention has been given to lanthanides related. Moreover, a thorough survey of the literature revealed only a few studies[3-5] on thermal decomposition of lanthanide compounds.

We have been interested in studying chemistry of metal trifluoro-methanesulfonates (triflates), especially of copper(I) and silver(I) triflates.[6] These interests as well as the aforementioned reasons motivated us to investigate lanthanide (III) triflates.

Lanthanum triflate [$La(OTf)_3$] was prepared according to the literature,[7,8] and used as it was. TG and DTA curves were obtained on heating up to 600 °C. The heating rate was 5 °C min^{-1} in a static atmosphere of air, and α-alumina was used as a thermally inert reference. The X-ray diffraction patterns were obtained by XD-610 diffractometer with Cu K_α irradiation. For identification purposes, diffraction patterns of the products were matched with relevant JCPDS cards. The volatiles were analyzed by MS in the electron impact positive ion mode.

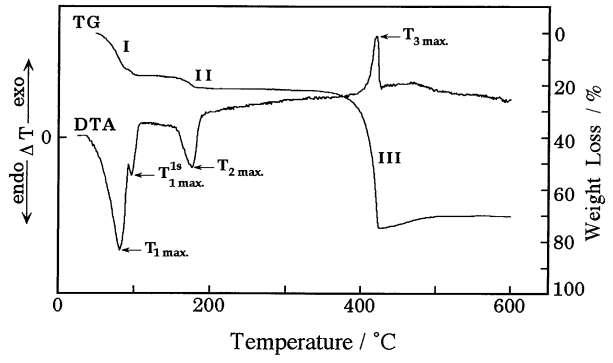

Figure 1. TG and DTA curves for lanthanum triflate.

Table 1. Thermal analysis data for $La(OTf)_3{\cdot}9H_2O$.

Step Number	Temperature / °C Range	Temperature / °C Peak	Weight Loss / % obsd.	Weight Loss / % calcd.	Dehydration Num. in each step
I	42~105	$T_{1max.}$ = 80	14.6	14.4[a]	6
		$T^{1s}_{1max.}$ = 95	16.7	16.8[a]	1
II	156~188	$T_{2max.}$ =175	21.5	21.7[a]	2
III	400~427	$T_{3max.}$ = 421	75.2	73.8[b]	

[a]As H_2O. [b]As LaF_3.

Figure 1 shows the results of the simultaneous DTA and TG of [$La(OTf)_3{\cdot}9H_2O$], and the results of thermal analysis of the triflate are summarized in Table 1. For the convenience, each weight loss (WL) steps monitored on the TG curve is designated to roman numeral, and the corresponding peak temperature on the DTA curve is denoted as $T_{1max.}$, $T_{2max.}$, and so on. The triflate began to lose water of hydration at 42 °C giving two clearly defined steps (I and II in Figure 1) in the curve prior to reaching the anhydrous state. The first step (WL=16.7%) corresponded to the loss of seven hydrated water molecules while the second step (WL=21.5%) resulted from the loss of two water molecules. However, a careful observation elucidated that the first step involves a poorly defined break around 100 °C that appeared to be the loss of one molecular of water. Consequently, the intermediates such as trihydrate and dihydrate are formed during the stepwise dehydration of the triflate. The enthalpy determined[9] for the process encountered throughout the dehydration of $La(OTf)_3{\cdot}9H_2O$ found to be 123 $kJmol^{-1}$, and this value is in good agreement within the range of characteristic dehydration process.[5] The anhydrous plateau beginning at 180 °C was not quite horizontal suggesting a slow decomposition to take place. More rapid decomposition at 427 °C resulted in a sharp weight loss (step III in Figure 1, WL=75.2%) to a horizontal plateau. After the complete thermal decomposition, the TG curve trends to increase and the weight gains, which suggests a probable oxidation of the final product. This oxidation is anticipated from a reexamination, in which when the

Table 2. A comparison of X-ray powder diffraction data of LaF_3.

h k l	Reference[a] d / Å	Reference[a] I / I$_0$	Observed d / Å	Observed I / I$_0$	Δd / Å[b]
0 0 2	3.678	50	3.687	46	0.009
1 1 0	3.596	40	3.603	31	0.007
1 1 1	3.231	100	3.237	100	0.006
1 1 2	2.570	15	2.574	9	0.004
3 0 0	2.074	55	2.078	52	0.004
1 1 3	2.024	65	2.026	59	0.002
3 0 2	1.807	40	1.808	31	0.001
2 2 1	1.745	25	1.747	20	0.002
2 2 3	1.449	18	1.450	15	0.001
3 0 4	1.376	16	1.376	11	0
1 1 5	1.389	12	1.361	7	-0.028

[a]JCPDS 32-483. [b]$\Delta d = d_{obsd.} - d_{ref.}$

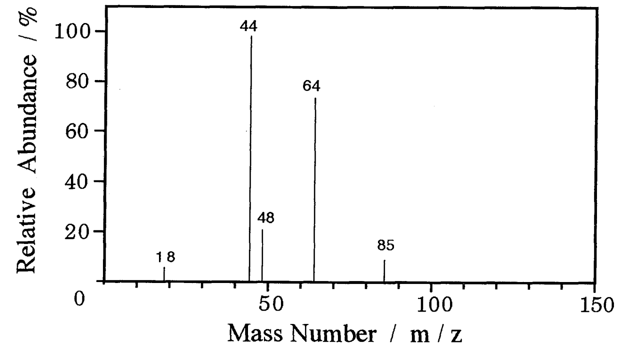

Figure 2. Mass spectra of the volatile products obtained in the pyrolysis of lanthanum triflate.

triflate was thermally analyzed in a dynamic atmosphere of N_2, the resulting final plateau on the TG curve remained quite horizontal until a temperature reached to 600 °C.

DTA study showed a rather complex curve in the temperature region at which dehydration takes place in that three strong endotherms were present. The first and most intense endotherm with a peak temperature ($T_{1max.}$) of 80 °C corresponds to the loss of 6 water molecules while the weak shoulder at $T^{1s}_{1max.}$=95 °C results from the additional loss of one water molecule. The second endotherm at $T_{2max.}$=175 °C associated with the loss of the last two water molecules. The last sharp exotherm peak at $T_{3max.}$=421 °C corresponds to the decomposition.

In an effort to confirm the products remaining after decomposition in atmosphere, the product was subjected to XRD study. As shown in Table 2, the XRD data of the sample matches very well with reference data of standard LaF_3 (JCPDS 32-483), which structure is known as a hexagonal form. In the course of the decomposition, there might be a possible formation of lanthanum oxyfluoride. However, since it is shown[4] that the decomposition of trifluoride to oxyfluoride is a hydrolysis reaction, the formation of lanthanum oxyfluoride is very little under the experimental condition in this study. Moreover, no peaks[11] concerning to the LaOF are present in the XRD pattern of the sample obtained. Therefore, the analysis elucidates that the triflate converted to the corresponding trifluoride.

On the other hand, when the triflate was pyrolyzed at slightly higher temperature of the end of decomposition, it was found that volatile products are evolved. By means of MS analysis of the gases, it was shown that three peaks at m/z 44, 64 and 85 with relatively high intensity are present in the spectra (see Figure 2). Undoubtedly the first two peaks are molecular ion peaks, and easily assigned to be CO_2 and SO_2, respectively. The peak at m/z 85 can be considered as a fragment ion peak that was generated as a result of the cleavage from the molecular ion, $[CF_3OCF_3]^{\bullet +}$, and the probable pathway can be rationalized as:

$$[CF_3OCF_3]^{\cdot +} \xrightarrow{-CF_3\cdot} [CF_3O]^+ \text{ (m/z 85)}$$

The other peaks at m/z 18 and 48 are H_2O[12] and $[SO]^+$, respectively. The later fragment ion peak is the further experimental evidence for the confirmation of SO_2. Thus, the present studies revealed the general reaction scheme for the lanthanide triflates to proceed as follows:

$$La(CF_3SO_3)_3 \longrightarrow LaF_3 + 3SO_2 + CO_2 + CF_3OCF_3$$

Current efforts are being devoted to thermal decomposition of a series of lanthanide triflates, in order to compare with and correlate to the present study.

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References and Notes

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9 Copper(II) sulfate pentahydrate was used as an external standard, since thermal properties of this compound have been well studied. The enthalpy of dehydration has been estimated by comparing the integrated endothermic areas on each DTA curve.
10 The references used for the matching for LaOF were JCPDS 5-0470, 6-0288 and 17-280.
11 There was a little water as a contaminant in the sample, since the evolved gases were collected passing through water.