Studies on Thermal Behaviour of Samarium Soaps

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ABSTRACT

Thermogravimetric analysis of Samarium laurate has been carried out in order to investigate the structure and kinetics of thermal decomposition of Samarium soap in the solid state. The results of thermal analysis show that samarium laurate decomposes in two stages. The values of the energy of activation for the first and second stage of the decomposition were in the range of 15 to 32 K Cal mol^{-1} and 1 to 9 K Cal mol^{-1} respectively.

Keywords- Samarium laurate, Energy of Activation, TGA.

I. INTRODUCTION

The studies of lanthanide and actinide soaps have not been carried out systematically, inspite of their wide applications in various industries. Several workers [1-4] prepared metal carboxylate of lanthanides and actinides by using metal oxide, hydroxide or carbonate as starting material. The method of preparation and properties of lanthanide soaps were reviewed by Mehrotra [5]. The thermal stability of rare earth metal soaps was studied by differential thermal and thermogravimetric analysis [6-8]. J.C. Grivel et al [9] investigated the thermal decomposition of lanthanum (III) butyrate in argon atmosphere while Dwivedi et al [10] studied the thermal degradation of erbium metal soaps in an inert atmosphere.

The present work has been initiated with a view to study the kinetics of thermal decomposition of Samarium laurate by thermo gravimetric analysis (TGA). The results of TGA have been used to explain the order of reaction and to evaluate the values of energy of activation for the decomposition process by using well known equations.

$$2\,[\text{Sm}\,(\text{C}_{11}\text{H}_{23}\text{COO}\,)_3] \xrightarrow{200-380^{o}\text{C}} = \text{Sm}_2\,(\text{CO}_3)_3 + 3\,(\text{C}_{11}\text{H}_{23})_2\,\text{CO}$$

Samarium laurate   **Samarium carbonate**   **Laurone**

In the second stage of decomposition, samarium carbonate changes to samarium oxycarbonate on heating up to 460°C and the intermediate oxycarbonate so

II. EXPERIMENTAL

Samarium laurate was prepared by direct metathesis of potassium laurate with slight excess of the solution of samarium acetate at 50-60°C. under vigorous stirring. The precipitated soap was filtered off and washed several times with distilled water and then with acetone. The metal soap thus obtained was first dried in an air oven at 50-60°C and the final drying of the soap was carried out under reduced pressure. The soap was purified by recrystallisation with benzene-methanol mixture. The purity of the soap was confirmed by elemental analysis and by determining its melting point. The melting point of purified samarium laurate was 94°C.

The thermogravimetric analysis of samarium soap was carried out by a Perkin - Elemer Thermogravimetric Analyser TGS-2 at constant heating rate (15° per minute) in nitrogen atmosphere and maintaining similar conditions throughout the investigations.

III. RESULTS AND DISCUSSION

Thermogravimetric Analysis:

The results of thermogravimetric analysis of samarium laurate are recorded in Table 1. The results show that the soap loses weight slowly on heating upto 200°C and this may be due to the loss of water and other volatile substances from the soap molecules. The subsequent weight losses on further heating of the soap indicate that the decomposition of samarium laurate takes place in two stages. In the first stage of decomposition between 200 and 380°C, the soap (samarium laurate) decomposes into carbonate and laurone (Ketone) which can be expressed as :

formed undergoes decomposition on heating between 460 and 820°C to samarium oxide and carbon dioxide.

$$\text{Sm}_2\,(\text{CO}_3)_3 \xrightarrow{460^{o}\text{C}} \text{Sm}_2\text{O}_3\,\text{CO}_2 + 2\text{CO}_2$$

Samarium Carbonate   **Samarium Oxycarbonate**   **Carbondi-Oxide**

$$\underset{\substack{\text{Samarium}\\\text{Oxycarbonate}}}{Sm_2O_3.CO_2} \xrightarrow{460-820^oC} \underset{\text{Samarium Oxide}}{Sm_2O_3} + CO_2$$

The net decomposition reaction of soap may be expressed as -

$$2\,[\underset{\text{Samarium laurate}}{Sm\,(C_{11}H_{23}COO\,)_3}] \longrightarrow \underset{\substack{\text{Samarium}\\\text{oxide}}}{Sm_2O_3} + \underset{\substack{\text{Carbon di-}\\\text{oxide}}}{3CO_2} + \underset{\text{Laurone}}{3\,(C_{11}H_{23})_2\,CO}$$
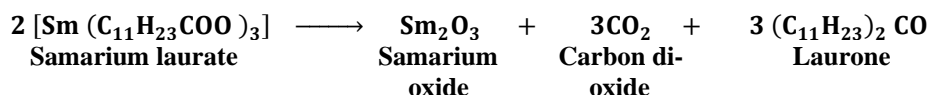
Finally the Ketone (laurone) also changes to carbon dioxide and water. The weight of residue left on heating samarium laurate is in agreement with the theoretically calculated weight of samarium oxide from the molecular formula of samarium laurate. It is also observed that some substance condenses at the cold parts of the sample tube surrounding the soap and it is identified as laurone (M.P. 69.4°C). The results are in agreement with the studies of Patil et al [11] and Edwards and Hayward [12].

The plot of loss in weight, W of samarium laurate Vs time, is shown in Fig. 1. The results of thermal decomposition of samarium soap have been explained in terms of Freeman - Carroll's, Coats Redfern's and Horowitz - Metzger's equations.

Freeman and Carroll's [13] rate expression for the thermal decomposition of the soap, when the soap disappears continuously with time and temperature and one product is gaseous, may be expressed as :

$$\frac{\Delta\,[\log\,(dw/dt)\,]}{\Delta\,(\log\,W_r\,)} = -\frac{E}{2.303\,R}\,\frac{\Delta\,(1/T)}{\Delta\,(\log\,W_r\,)} + n$$

Where,

E   =   Energy of activation,
R   =   Gas constant
n   =   Order of decomposition reaction.
T   =   Temperature on absolute scale,
W_r =   Difference between the total loss and loss in weight at time, t i.e. $W_O - W_t$, and
(dw/dt)   =   Value of rate of weight loss obtained from the plot of loss in weight Vs time.

The values of the rate of weight loss, (dw/dt) were obtained from the plot of loss in weight of soap, W Vs time, t (Fig. 1). The values of W_r were calculated from the total loss in weight of soap and the loss at predetermined time and the plot of $\Delta\,[\log\,(dw/dt)]\,/\,\Delta\,(\log\,W_r)$ Vs $[\,\Delta\,(1/T)/\,\Delta\,(\log\,W_r)$ was obtained. The treatment of the thermogravimetric result according to Freeman Carroll's equation is recorded in Table 2.

The plot of $\Delta\,[\log\,(dw/dt)]\,/\,\Delta\,(\log\,W_r\,)$ Vs $[\,\Delta\,(1/T)/\,\Delta\,(\log\,W_r)$ shows a break at a temperature of about 380°C indicating that the decomposition takes place in two stages. In the first stage, the soap decomposes on heating between 200 - 380°C into Ketone and Carbonate. In the second stage of decomposition the samarium

carbonate changes to oxycarbonate and the intermediate samarium oxycarbonate further, undergoes decomposition to give the residue (samarium oxide). The results indicate that the order of the reaction for the second stage of the thermal decomposition of samarium laurate is zero and the values of energy of activation for the first and second stage of decomposition are 15.6 K cal mol^{-1} and 9.2 K cal mol^{-1}, respectively (Table-3).

Coats and Redfern's equatiom [14] (Table-2) also provides a method for the evaluation of energy of activation for the thermal decomposition of samarium laurate. Coats and Redfern's equation for zero order reaction can be written as :

$$\log\,\left(\frac{\alpha}{T^2}\right) = \log\,\frac{AR}{aE}\,\left(1 - \frac{2RT}{E}\right) - \frac{E}{2.303\,RT}$$

Where,

α   =   Fraction of the soap decomposed,
T   =   Temperature on absolute scale,
R   =   Gas constant,
A   =   Frequency factor,
A   =   Rate of heating in °C per. minute, and
E   =   Energy of activation.

The plot of $\log\,(\alpha/T^2)$ Vs $(1/T)$ shows a break at a temperature of about 380°C indicating that the decomposition occurs in two stages. The value of energy of activation obtained from the slope of the plot of $\log\,(\alpha\,/T^2)$ Vs $(1/T)$ for the second stage of decomposition is 2.8 K cal mol^{-1}, (Table-3).

The values of energy of activation for the thermal decomposition of samarium laurate have also been determined by using Horowitz and Metzger's [15] equation which can be written as :-

$$\ln\,[\,\ln\,(1-\alpha)^{-1}\,] = \frac{E}{R\,Ts^2}\,\theta$$

Where,

α   =   Fraction of the soap decomposed,
E   =   Energy of activation,
Ts   =   Temperature on absolute scale at which the rate of decomposition is maximum, and
θ   =   T - Ts.

The plot of In [ln [ln $(1-\alpha)^{-1}$] Vs q also shows a break indicating that the decomposition occurs

in two stages. The values of energy of activation obtained from the slope of the plot for the first and second stage of decomposition are 32.1 K cal mol^{-1} and 1.5 K cal mol^{-1} respectively (Table-3).

It is, therefore, concluded that the thermal decomposition of samarium laurate occurs in two stages. In the first stage of the decomposition between 200-380°C, the soap decomposes into carbonate and ketone while in the second stage of the decomposition (above 380°C), samarium carbonate changes to oxycarbonate which further decomposes to samarium oxide and carbon dioxide. The second stage of the decomposition reaction of samarium laurate is found to be kinetically of zero order and the values of activation energy for the first and second stage of decomposition are in the range of 15 to 32 K cal mol^{-1} and 1 to 9 K cal mol^{-1}, respectively.

Table 1: Thermogravimetric Data of Samarium Laurate

S. No.	Time, t (min)	Temperature T (° K)	Weight of the Soap Decomposed W×10^5 (gm.)	[dw/dt]×10^5	W$_r$×10^5
1	4.00	333	0.000	0.000	204.31
2	6.66	373	7.050	2.650	197.26
3	9.33	416	8.810	1.653	195.26
4	16.00	513	10.568	0.881	193.74
5	18.60	553	12.330	0.845	191.98
6	20.00	573	14.090	0.881	190.22
7	21.33	593	18.500	1.068	185.81
8	22.66	613	35.230	1.888	169.08
9	23.33	623	54.599	2.825	149.72
10	24.00	633	88.077	4.404	116.24
11	24.66	643	114.490	5.542	89.92
12	25.53	653	149.710	7.019	54.60
13	26.66	673	172.610	7.617	31.70
14	28.00	693	179.652	7.485	24.66
15	29.33	713	181.410	7.162	22.90
16	30.66	733	184.490	6.937	19.37
17	32.00	753	188.461	6.731	15.85
18	33.33	773	191.985	6.546	12.33
19	34.66	793	194.620	6.348	9.69
20	36.00	813	197.260	6.164	7.05
21	37.33	833	199.030	5.972	5.28
22	38.66	853	200.791	5.793	3.52
23	41.33	893	202.550	5.426	1.76
24	48.00	993	203.430	4.623	0.88
25	54.66	1093	204.310	4.033	0.00

Table 2: Freeman-Carroll's of Thermogravimetric Data of Samarium Laurate

S. No.	Δ (1/T)×10^3	- Δ (log W$_r$)	- Δ [log dw/dt]	$-\dfrac{\Delta\,(1/T)}{\Delta\,(\log W_r)} \times 10^3$	$-\dfrac{\Delta\,[\log(dw/dt)]}{\Delta\,(\log W_r)}$
1	3.003	2.689	0.000	1.116	0.000
2	2.681	2.705	4.576	0.991	1.692
3	2.421	2.709	4.782	0.894	1.765
4	1.949	2.713	5.055	0.718	1.863
5	1.808	2.717	5.073	0.666	1.867
6	1.745	2.720	5.055	0.641	1.858
7	1.686	2.731	4.972	0.617	1.820
8	1.631	2.772	4.724	0.588	1.704
9	1.605	2.825	4.549	0.568	1.610
10	1.579	2.935	4.356	0.538	1.484

11	1.555	3.047	4.256	0.510	1.397
12	1.531	3.263	4.154	0.469	1.273
13	1.486	3.499	4.118	0.425	1.177
14	1.443	3.608	4.125	0.399	1.143
15	1.403	3.640	4.145	0.385	1.139
16	1.364	3.713	4.156	0.367	1.119
17	1.328	3.799	4.172	0.350	1.098
18	1.294	3.909	4.184	0.331	1.070
19	1.261	4.014	4.197	0.314	1.046
20	1.230	4.152	4.210	0.296	1.014
21	1.200	4.277	4.224	0.281	0.988
22	1.172	4.454	4.237	0.263	0.951
23	1.120	4.755	4.266	0.236	0.897
24	1.007	4.506	4.335	0.224	0.962
25	0.915	0.000	4.394	0.000	0.000

Table 3: Energy of Activation (K cal mol^{-1}) for the decomposition of samarium laurate by using various equation.

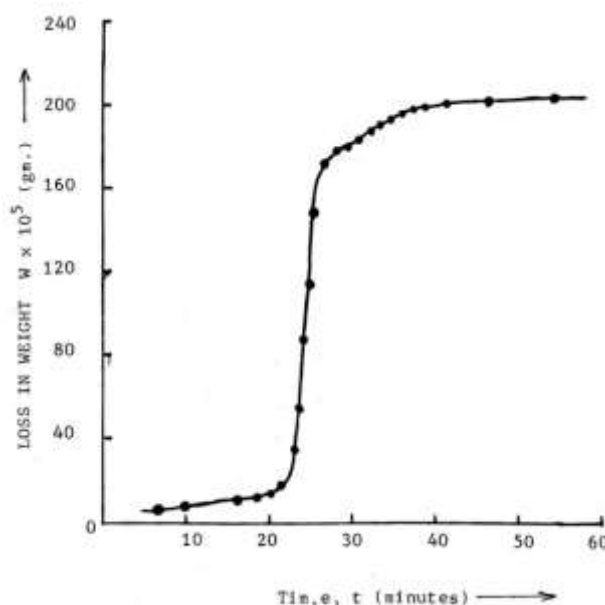| S. No.	Name of Equation	Activation Energy of First Stage	Activation Energy of Second Stage
1	Freeman and Carroll's Equation	15.6	9.2
2	Coats and Redfern's Equation	-	2.8
3	Horowitz and Metzger's Equation	32.1	1.5

Fig. 1:   Thermogram of Samarium laurate, loss in weight (W) Vs time (t)

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