THERMOGRAVIMETRIC ANALYSIS OF YTTRIUM SOAPS IN SOLID STATE

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The thermogravimetric analysis were made on Yttrium soaps (Myristate, Palmitate, and Stearate) in solid state with a view to determine the Rate of reaction, Order of reaction and Energy of activation. The result show that the order of reaction for the decomposition of Yttrium soaps is zero order and the Energy of activation lie between 7.4-9.9 k cal mol^{-1}. These results were discussed in term of some well known equation and the results were in agreement with properties.

KEYWORD: Metal soaps, order of reaction, energy of activation.

INTRODUCTION

The transition metal soaps are being widely used in industry, technology and allied sciences. The uses of metal soaps largely depend on their physical state, stability, chemical reactivity and solubility in polar and non polar solvents. These metal soaps has been a subject intense investigation in the recent past on account of its role in such diversified field as medicine, cosmetic emulsifier, lubricant, germicides and anti oxidant. The methods of preparation of potassium soaps and metal soaps were described by several workers [1-6]. The IR spectra and *X*-ray diffraction pattern of manganese and zinc soaps were studied by Upadhyaya *et al*. [7]. The thermal decomposition kinetics of nickel and manganese soaps were studied by Mehrotra *et al*. [8]. The physicochemical studies on Erbium soaps of saturated higher fatty acids in solid state studied by Rajesh *et al.* [9]. The viscometric and spectral studies of copper soap in benzene and methanol mixture were studied by Rawat [10]. The studies on miceller properties of scandium and yttrium metal soaps was studied by Khirwar [11]. The studies of ultrasonic velocity and allied properties of magnese, cobalt and copper soaps in non aqueous medium Rawat [12]. In the present work attempts have been made to determine the various physical properties (rate of reaction, order of reaction and energy of activation) of Yttrium soaps by thermogravimetric analysis.

EXPERIMENTAL

The Yttrium soaps (Myristate, Palmitate and Stearate) were synthesized by direct metathesis of corresponding potassium soaps with the required amount of aqueous solution of Yttrium nitrate at 50-55°C under vigourous stirring. The precipited soaps were washed several times with distilled water and acetone to remove the fatty acid and metal nitrate. The soaps were purified by recrystallisation, dried in an air oven at 50-60°C and the finally drying of the

soaps were carried out under reduced pressure. The purity of the soaps were checked by IR spectra and determination of their melting points. The thermogravimetric analysis of Yttrium soaps were carried out by a Perkin-Elmer thermogravimetric analyser TGS2 at constant heating rate (10° per minute) in nitrogen atmosphere.

Table 1 : Thermal decomposition data of Yttrium soaps

Sr. No.	Time, *t* (Minutes)	Temperature T°	Weight of soap decomposed $W \times 10^3$ (gms)	$\frac{dw}{dt} \times 10^6$	$W_r \times 10^3$
Yttrium Myristate					
1.	6.1	330	83.15	-	75.67
2.	9.1	362	80.84	2.39	73.36
3.	11.5	382	79.69	3.10	72.21
4.	14.0	416	79.10	2.75	71.62
5.	19.2	466	78.51	2.33	71.03
6.	23.4	501	77.38	2.47	69.90
7.	26.7	535	73.91	3.49	66.43
8.	29.3	569	71.60	3.76	64.12
Yttrium Palmitate					
1.	6.1	330	83.24	-	72.37
2.	7.4	348	81.23	7.75	70.36
3.	9.3	364	78.80	8.89	67.93
4.	12.3	401	78.21	7.20	66.34
5.	14.3	416	77.61	6.58	66.74
6.	16.0	433	77.40	6.00	66.53
7.	20.1	471	77.00	5.05	66.38
8.	24.2	512	76.38	4.41	64.51
Yttrium Strearate					
1.	6.1	330	114.04	-	82.42
2.	8.4	351	112.43	1.952	80.26
3.	10.1	373	110.88	3.062	79.66
4.	23.4	501	109.28	2.051	77.71
5.	25.1	523	105.33	3.441	73.30
6.	27.2	543	102.92	4.048	71.74
7.	29.4	566	101.36	4.281	69.38
8.	31.2	588	99.00	4.748	67.60

Result and discussion

The results of thermogravimetric analysis of Yttrium soaps (Myristate, Palmitate and Strearate) and the treatment of the data recorded in (table 1-3). The final residue on thermal

decomposition of Yttrium soap is Yttrium oxide. This conclusion is in harmony with the fact that the weight of residue is in agreement with theoretically calculated weight of Yttrium oxide from the molecular formula of the corresponding soap. It may be pointed out that some white crystalline powder is found condensed at the cold part of the sample tube surrounding the soap and it is identified by the determination of M.P. Myristone (79.0°C), Plamitone (84.8°C) and stearone (89.6°C) for Yttrium soaps of Myristate, Palmitate and Stearate, respectively. The thermal decomposition of Yttrium soaps can be expressed as-

$$\underset{\text{Metal soap}}{2(RCOO)_3M} \longrightarrow \underset{\text{Ketone}}{3R.CO.R} + \underset{\text{Metal oxide}}{M_2O_3} + \underset{\text{Carbondioxide}}{3CO_2}$$

where M is Yttrium metal, R is $C_{13}H_{27}$, $C_{15}H_{31}$ and $C_{17}H_{35}$ for Myristate, Palmitate and Stearate, respectively.

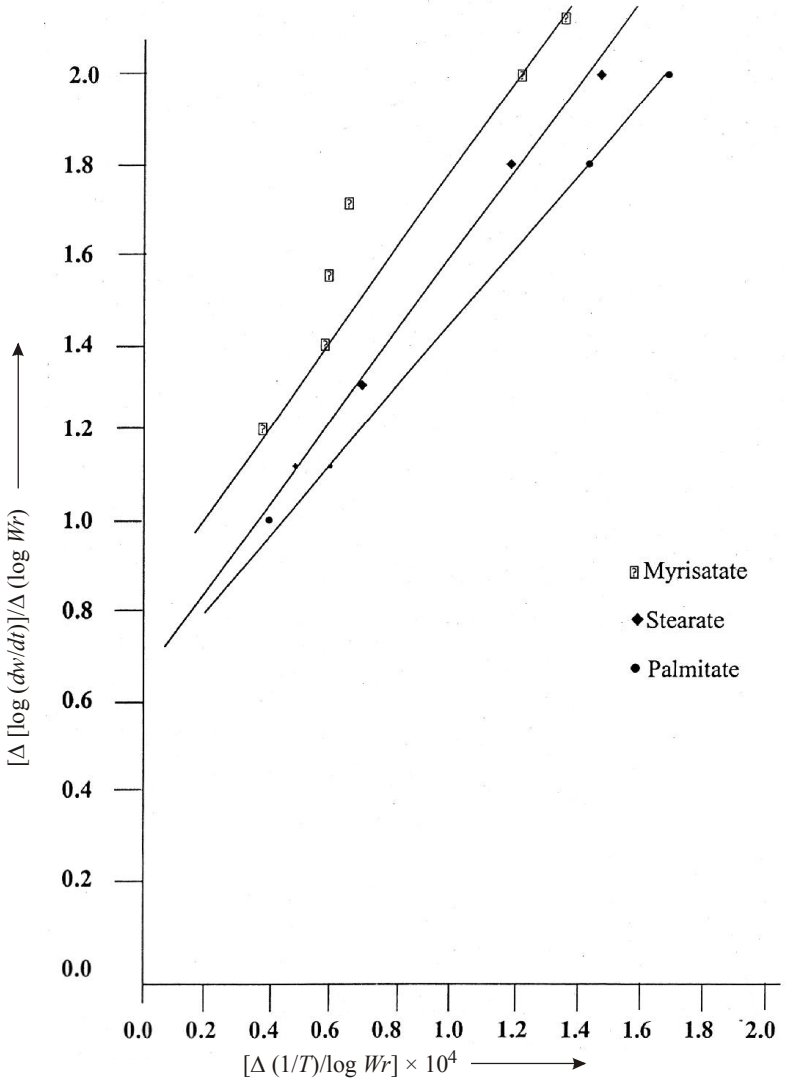

Fig. 1. Freeman-Carboll's Type Plots

Table 2 : Freeman Carroll's treatment of thermogravimetric data of Yttrium soaps.

Sr. No.	$\frac{1}{T} \times 10^5$	$-\Delta$ (log w_r)	$-\Delta$ {log (dw/dt)}	$\frac{-\Delta \log(1/T)}{\log W_r \times 10^4}$	$\frac{-\Delta \log(dw/dt)}{\Delta \log W_r}$
Yttrium Myristate					
1.	303.03	2.121	-	1.428	-
2.	287.35	2.124	5.142	1.352	2.420
3.	276.24	2.134	4.621	1.294	2.165
4.	261.78	2.141	4.508	1.222	2.105
5.	240.38	2.144	4.560	1.121	2.126
6.	214.59	2.148	4.632	0.999	2.156
7.	199.60	2.155	4.607	0.926	2.137
8.	193.05	2.170	4.489	0.889	2.068
Yttrium Palmitate					
1.	303.03	2.140	-	1.416	-
2.	287.35	2.152	4.110	1.335	1.909
3.	274.72	2.171	4.051	1.267	1.869
4.	249.37	2.175	4.142	1.114	1.904
5.	240.38	2.176	1.181	1.105	1.922
6.	230.94	2.179	4.221	1.061	1.939
7.	212.31	2.190	4.296	0.974	1.98
8.	195.31	2.187	4.355	0.891	1.988
Yttrium Strearate					
1.	303.03	2.083	-	1.454	-
2.	284.90	2.092	4.709	1.632	2.250
3.	268.09	2.100	4.513	1.276	2.149
4.	199.60	2.109	4.688	0.946	2.222
5.	191.20	2.132	4.463	0.896	2.093
6.	184.16	2.146	4.392	0.858	2.046
7.	176.67	2.15	4.368	0.819	2.025
8.	170.06	2.171	4.323	0.783	1.991

Freeman and Carroll's [13] expression for the thermal decomposition of Yttrium soaps where the soap disappears continuously with time and temperature and one product is gaseous can be expressed as-

$$\frac{\log (dw/dt)}{\Delta(\log W_r)} = \frac{-E}{2.303RT} \cdot \frac{\Delta t(1/T)}{\Delta(\log W_r)} + n$$

were E, n, T, W_r and dw/dt are Energy of activation, Order of reaction, Temperature on absolute scale, Difference between the total loss in weight and the loss in weight at time t, and Rate of weight loss obtained from the loss in weight *vs* time curves at appropriate times, respectively.

The plots of the loss in weight of the soap, W against time t, and values of (dw/dt) are obtained from the curves by drawing tangents at appropriate times. The values of W_r have been calculated from the total loss in weight of the soap and the loss at predetermined time (table : 1) and the plots of $\Delta\{\log (dw/dt)\}/\Delta (\log w_r)$ against $\Delta(1/T)/\Delta (\log w_r)$ are obtained (fig. 1-2). The treatment of the thermogravimetric data according to Freeman-Carroll's equation is given in (table 2).

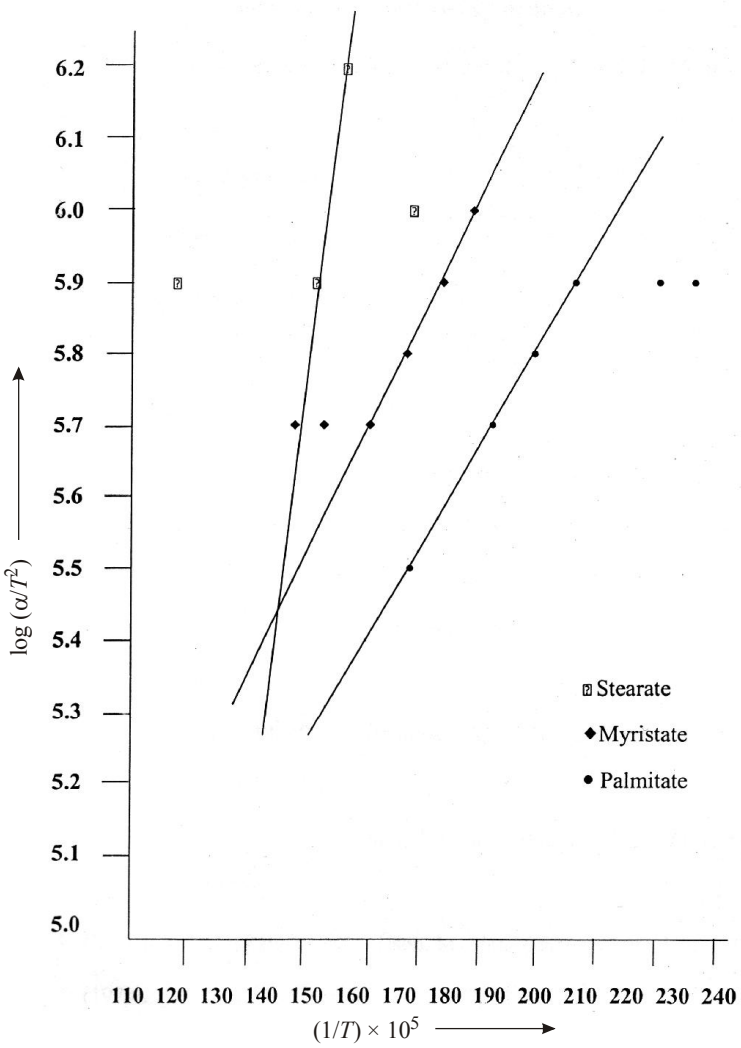

Fig. 2. Coats and Redfern's Type plots

The results indicate that the order of reaction for decomposition of Yttrium soaps is zero order and the values of energy of activation lie between 7.4-9.9 k cal mol^{-1} (table 4).

It is suggested that the surface of the soap molecules remains completely covered all the time by the molecules of the gaseous product as the decomposition is fast so that rate of the decomposition becomes constant and process is kinetically of zero order.

Table 3 : Coats-Redfern's treatment of thermogravimetric data of Yttrium soaps

Sr. No.	Temperature T	$\frac{1}{T} \times 10^5$	α	$\alpha/10^7$	$-[\log(\alpha/T^2)]$
Yttrium Myristate					
1.	330	303.03	0.083	7.62	6.117
2.	348	287.35	0.096	7.92	6.100
3.	362	276.24	0.103	7.85	6.104
4.	382	261.78	0.122	8.36	6.077
5.	416	240.38	0.154	8.89	6.050
6.	46	214.59	0.187	8.61	6.064
7.	501	199.60	0.219	8.64	6.059
8.	518	193.05	0.232	8.55	6.063
Yttrium Palmitate					
1.	330	303.03	0.133	12.21	5.913
2.	345	287.35	0.146	12.26	5.911
3.	364	274.72	0.158	11.92	5.923
4.	401	249.37	0.171	10.63	5.973
5.	416	240.38	0.210	12.13	5.915
6.	433	230.94	0.235	12.53	5.901
7.	471	212.31	0.343	15.46	5.810
8.	512	195.31	0.509	19.41	5.711
Yttrium Strearate					
1.	330	303.03	0.214	19.65	5.706
2.	351	284.90	0.224	18.18	5.740
3.	373	268.09	0.240	17.25	5.763
4.	501	199.60	0.255	10.15	5.993
5.	523	191.20	0.265	9.68	6.013
6.	543	184.16	0.280	9.49	6.022
7.	566	176.67	0.291	9.08	6.041
8.	588	170.06	0.306	8.85	6.053

The values of the energy of activation for the thermal decomposition of Yttrium soaps have also been calculated by using coats and Redfern's [14] equation which can be expressed as-

$$\log\left[\frac{1-(1-\propto)^{1-n}}{T^2(1-n)}\right] = log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT}$$

where *α, T, R, A, a, E* and *n* are Fraction of the soap decomposed, Temperature on absolute scales, Gas constant, Frequency factor, Rate of heating in °C per minute, Energy of activation, and Order of the reaction, respectively.

The equation for zero order reaction can be written as-

$$\log\left[\frac{\propto}{T^2}\right] = \log\frac{AR}{aE}\left[1 - \frac{2RT}{E}\right] - \frac{E}{2.303RT}$$

The plot of log (α/T^2) against ($1/T$) should be a straight line with its slope equal to [$-E/2.303R$]. The values of the energy of activation obtained from these plots (fig. 2) lie between 7.4-9.9 k cal mol^{-1} and are in agreement with values obtained from Freeman-Carroll's equation (table 4).

It is therefore, concluded that the rate of decomposition of Yttrium soaps is kinetically zero order and the energy of activation for the process lies in the range of 7.4-9.9 k cal mol^{-1}.

Table : 4. Energy of activation (k cal mol^{-1}) for the decomposition of Yttrium soaps by various equations

Sr. No.	Name of soaps	Freeman-Carroll's equation	Coats-Redfern's equation
1.	Yttrium Myristate	7.4	8.4
2.	Yttrium Palmitate	9.6	9.9
3.	Yttrium Strearate	8.4	7.9

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