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Thermogravimetric Analysis of Cadmium Soaps by Using Freeman-Carroll's and Coats-Redfern's Equations

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Abstract

In this presentation, we studied the thermogravimetric analysis of cadmium soaps (caproate, caprylate, caprate, laurate and myristate) by using Freeman-Carroll's and Coats-Redfern's equations. The thermogravimetric analysis of cadmium soaps were carried out by a Perkin-Elmer (Pyris diamond) thermogravimetric analyser at constant heating rate (10^0 per minute) in nitrogen atmosphere and maintaining similar conditions throughout the investigations. These soaps were prepared by metathesis of corresponding sodium soap with an aqueous solution of metallic salt [(1-6)] Blachford[(7)] prepared the transition metal soaps of low free acid content in molten state by agitating and heating the suspension of oxide of zinc or hydroxide of cobalt, manganese or zinc in a mixture of water and glyceryl ester. The result shows that, the decomposition reaction for metal soaps is found kinetically of zero orderand the values of the energy of activation for the decomposition of Be soaps increases with increasing chainlength of soap molecules and lie in the range of 5.73-21.76 kCal mol^{-1}.

INTRODUCTION

The soaps of the heavy metals have important applications in the manufacture of greases, paints or inks, plastics, cosmetics, textiles, pharmaceuticals, etc, in which they are employed as lubricants[1], driers[2], catalysts[3], wetting agents[4], thickening agents[5], stabilizers[6], waterproofing agents[7], fungicides and pesticides.[8-9] Metallic soaps have been described as alkaline-earth or heavy-metal long-chain carboxylates, which are insoluble in water, but soluble in non-aqueous solvents. They have the general formula (RCOO)2M, where M is a metal such as Zn, Cd, Pb, Ba, Ca, Co, Cu, Al, Fe, etc and R is a linear or branched alkyl group.Thermogravimetric analysis measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, other gas, or in vacuum. Thermogravimetric analysis shows that the decomposition reaction of the alkali metal soaps is kinetically of zero order and the activation energy for the process lies in the range of 2 to 6 kcal/mol. We studied the thermogravimetric analysis of cadmium soaps (caproate, caprylate, caprate, laurate and myristate).

EXPERIMENTAL

Potassium soaps (caproate, caprylate, caprate, laurate and myristate) were prepared by refluxing equivalent amount of corresponding fatty acid and aqueous solution of potassium hydroxide for 8-10 hours on a water bath. The soap were purified by recrystallization. The cadmium soaps were prepared by direct metathesis with corresponding potassium soap (caproate, caprylate, caprate, laurate and myristate) with slight excess of the solution of cadmium nitrate at 50–55ºC under vigorous stirring. The precipitated soaps were washed several times with conductivity water and acetone. The metal soaps thus obtianed were first dried in an air ovan at 50-60ºC and the final drying of the soaps was carried out under reduced pressure. The soaps were purified by recrystallization with benzene. The purity of the soaps was confirmed by the determination of their melting points and the absence of hydroxyl group in the soaps was confirmed by studying their infrared absorption spectra. The thermogravimetric analysis of cadmium soaps were carried out by a Perkin-Elmer (Pyris diamond) Thermogravimetric Analyser at constant heating rate (10º per minute) in nitrogen atmosphere and maintaining similar conditions throughout the investigations.

MATARIAL AND METHODS

The data show that the decomposition is initially slow due to the removal of water and carbon dioxide molecules and then fast due to the removal of ketone molecules and finally constant due to the formation of cadmium oxide. The final residue on thermal decomposition of cadmium soaps is cadmium oxide. This conclusion is in harmony with the fact that the weight of residue is in agreement with theoretically calculated weight of cadmium oxide. 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 as caprone (b.p. : 228.0ºC), caprylone (m.p. : 39.0ºC), caprinone (m.p. : 58.0ºC), laurone (m.p. : 69.4ºC) and myristone (m.p. : 78.0ºC) in case of caproate, caprylate, caprate, laurate and myristate, respectively. The thermal decomposition of cadmium soaps can be expressed as:

$$(RCOO)_2\,M \rightarrow R.CO.R. + MO + CO_2$$

Soap Ketone Metal

Where M is metal (cadmium), R is C_5H_{11}, C_7H_{15}, C_9H_{19}, $C_{11}H_{23}$ and $C_{13}H_{27}$ for caproate, caprylate, caprate, laurate and myristate, respectively. The results of thermal decomposition of Cd soaps have been explained in the terms of various equations. Freeman and Carroll's rate[10] expression for the thermal decomposition of metal soaps, where the soap disappears continuously with time and temperature and one of the product is gaseous can be expressed as:

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

where E = Energy of activation,

n = Order of reaction,

T = Temperature on absolute scale,

W_r = Difference between the total loss in weight and the loss in weight at time t, i.e. w_0–w_t and

dw/dt = Rate of weight loss obtained from the loss in weight Vs. time curves at appropriate times.

RESULTS AND DISCUSSION

We studied the thermogravimetric analysis of cadmium soaps (caproate, caprylate, caprate, laurate and myristate) and the treatment of data are recorded in Tables 1–3. The treatment of the thermogravimetric data according to Freeman Carroll's equation is given in Tables 2, 5, 8, 11, 14. The plots of the loss in weight of the soap, w against time, t are shown in Figs. 1 and the 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 (Tables 1, 4, 7. 10, 13) and the plots of □[log (dw/dt))/□(log W_r)] against □(1/T)/□(log W_r) are obtained (Figs. 2). The results indicate that the order of reaction for decomposition of cadmium soaps is zero and the values of energy of activation increases with increasing chain length of soap molecules and lie between 11.66–21.76 kCal mol^{-1} (Table 16).

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 and so the rate of the decomposition becomes constant and the process is kinetically of zero order.

The values of the energy of activation for the thermal decomposition of cadmium soaps have also been calculated by using Coats and Redfern's[11] equation which can be expressed as:

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

where, α = Fraction of the soap decomposed,

T = Temperature on absolute scales,

R = Gas constant,

A = Frequency factor,

a = Rate of heating in ºC per minute,

E =Energy of activation and

n = Order of the reaction

The equation for zero order reaction can be written as

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

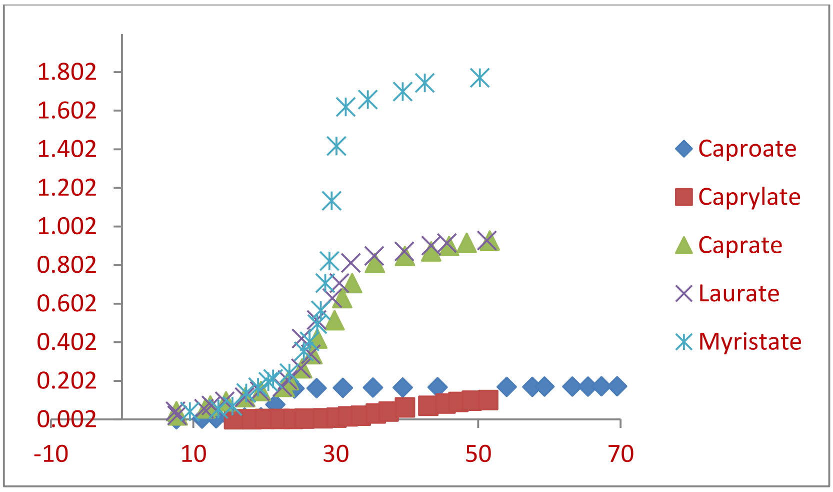
The plot of log (α/T^2) against (1/T) should be a straight line with its slope equal to [–E/2.303R]. The values of the energy of activation obtained from these plots (Figs. 3) lie between 5.75–18.32 kCal.mol^{-1} (Table 16).

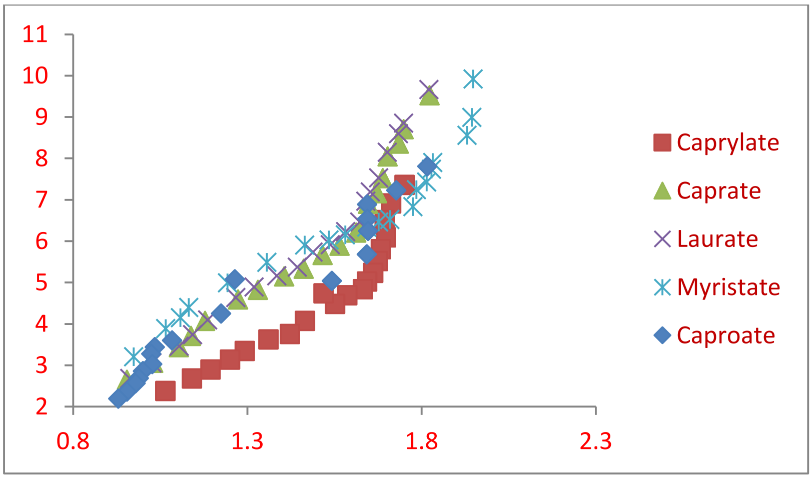
It is, therefore, concluded that the decomposition reaction of cadmium soaps is kinetically of zero order and the energy of activation for the process lie in the range of 5.73-21.76 kCal.mol–1.

Table 1 : Thermal decomposition of Cadmium Caproate

Time, t (minutes)	Weight of the soap decomposed W x 10^3 (gms)
4.0	-
7.6	0.0022
11.2	0.0061
13.2	0.0072
13.2	0.0082
15.1	0.0086
17.2	0.0107
19.5	0.0125
21.5	0.0780
24.2	0.1612
27.3	0.1640

31.0	0.1650
35.2	0.1664
39.4	0.1670
44.3	0.1675
54.0	0.1692
57.6	0.1704
59.3	0.1710
63.2	0.1717
65.4	0.1722
67.3	0.1727
69.5	0.1732





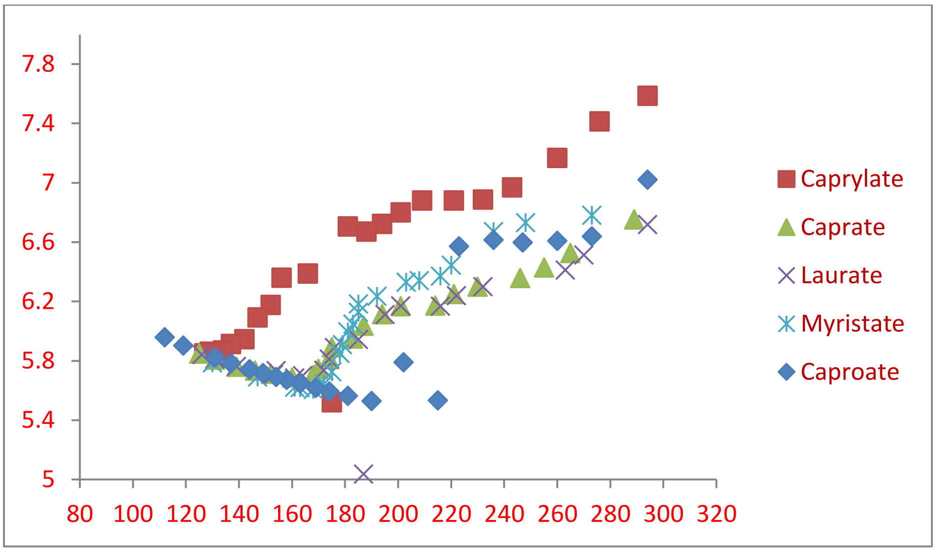


Fig. 1 : Loss in weight Vs Time

Table 16: Energy of activation (KCal Mol^{-1}) for the decomposition of metal soaps by using various equations

S.No.	Name of the soap	Freeman and Carroll's Equations	Coats and Redfern's Equations
1.	Cadmium Caproate	11.66	5.75
2.	Cadmium Caprylate	13.25	6.89
3.	Cadmium Caprate	16.68	9.32
4.	Cadmium Laurate	18.93	12.65
5.	Cadmium Myristate	21.76	18.32

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