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Thermal, Spectral and Structural Studies on Dysprosium Carboxylates

Amit K. Agarawal

Department of chemistry, Agra College, Agra, **INDIA**

Email: akagarwal.chem@gmail.com

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ABSTRACT

The structural and thermal studies of carboxylates of dysprosium (palmitate and stearate) have been investigated by IR, X-Ray and TGA measurements. The IR spectra results shows that the fatty acid exist dimeric state through hydrogen bonding and these carboxylates possess partial ionic character. The X-Ray results confirmed the single layer structure of these carboxylates. The decomposition reaction has been found kinetically zero order and the value of energy of activation for the decomposition process found to be in the range of 7.68-18.45 Kcal mol-^{1}.

Keywords: Dysprosium carboxylates, IR spectra and thermal decomposition.

INTRODUCTION

Dysprosium carboxylates serve a wide range of industrial applications as water proofing agent, emulsifier, hardener, lubricant stabilizer, plasticizer, antioxidant, fungicide, germicide, antiseptic, and in Textile, Paper, Pharmaceutical industries. The studies on the nature and structure of dysprosium carboxylates are of great importance for their uses in industries and for explaining their characterization under different conditions. Many metal carboxylates have been prepared by fusion and metathesis methods. Their X-ray, Thermal, Spectroscopic and Acoustic behaviour were investigated by several workers [1-7]. The structure of the compound has been studied by IR and X-ray diffraction analysis and their thermal behavior have also been investigated by Thermogravimetric analysis.

MATERIALS AND METHODS

Preparation of carboxylates: The chemicals used for present research were of AR/GR grade. Dysprosium carboxylates (palmitate and stearate) have been prepared by direct metathesis of the Corresponding Potassium carboxylate with slight excess of solutions of Dysprosium Nitrate at 50 – 55ºC under vigorous stirring. The precipitated carboxylates have been filtered and washed with distilled water and acetone to remove the excess of metal ions and unreacted potassium carboxylates. The main advantage of this method is the possibility of getting directly anhydrous samples of metal carboxylates, since attempts to remove the water of hydration from carboxylates isolated from an aqueous medium often yield hydrolyzed products.

The carboxylates were purified by recrystallisation with a mixture of benzene and methanol and dried under reduced pressure. The purity of these carboxylates were confirmed by determination of their melting point.

Measurements: The IR spectra were obtained with Perkin Elmer "577 Model" Grating spectrophotometer in the region of 4000 – 200 cm^{-1} using potassium bromide disc method.

The XRD powder patterns of Dysprosium carboxylates have been measured with Rich Siemens "2002 D" Iso Debyeflex Diffractometer using Cu-Kα radiations filtered by a nickel foil over the range of diffraction angle 2θ = 6º to 40º (where θ is Bragg's angle).

The X-Ray Diffraction curved were recorded under the applied voltage of 45 KV using scanning speed 1° per minute and chart speed of 1 cm per minute. The wave length of the radiation has been taken as 1.542Å. The Thermogravimetric analysis of Dysprosium carboxylates have been carried out by Perkin-Elmer Thermogravimetric analyzer 'TG-S-2' at constant heating rate (10° Per minute) in nitrogen atmosphere and maintaining similar conditions throughout the investigations.

RESULTS AND DISCUSSION

The spectra of dysprosium carboxylates (palmitate and stearate) have been recorded and compared with the results of the corresponding fatty acids (Table-1). The absorption bands observed near 2660, 1700, 1440, 950, 690 and 550 cm^{-1} in the spectra of fatty acids are associated with the localized (COOH) carboxyl group of the acid molecules in the dimeric state and confirmed the existence of hydrogen bonding between two molecules of carboxylic acids.

Table 1. Infrared Absorption frequencies (cm^{-1}) together with their assignments

S. No.	Absorption	Dysprosium	
		Palmitate	stearate
1.	CH_3, C-H asymmetrical stretching	2955	2954
2.	CH_2, C–H asymmetrical stretching	2918	2917
3.	CH_2, C–H symmetrical stretching	2855	2857
4.	OH, stretching	—	—
5.	C=O stretching	—	—
6.	COO^-, C–O asymmetrical stretching	1542	1540
7.	CH_2 deformation	1466	1465
8.	COO^-, C–O symmetrical stretching	1418	1419
9.	CH_2, (adjacent to COOH group) deformation	—	—
10.	CH_3, asymmetrical deformation	1351	1352
11.	Progressive bonds (CH_2 twisting and wagging)	1315-1196	1317-1197

12.	CH_3, rocking	1106	1107
13.	OH, out of plane deformation	—	—
14.	CH_2, rocking	720	721
15.	COOH bending Mode	—	—
16.	COOH wagging Mode	—	—
17.	M—O bond	441	442

The appearance of two carboxyl bonds corresponding to the symmetric and asymmetric stretching of the carboxylate ion near 1405,1435, 1440, 1550,1560 and 1580 cm^{-1} respectively, in the spectra of dysprosium carboxylates (palmitate and stearate) instead of one bond of carboxyl frequency near 1700cm^{-1} confirms that these carboxylates posses ionized structure and the metal to oxygen bond in these carboxylates have an ionic character.

The result confirms that the fatty acid exists with dimeric structure through intermolecular hydrogen bonding between carboxyl groups of two acid molecules, whereas potassium, dysprosium carboxylates are ionic in nature and the metal – to –oxygen bond the carboxylate has an ionic character. The IR spectra in the region of 3500-3300 cm^{-1} of dysprosium carboxylates donot show any absorption maxima which confirms the absence of any coordinated water molecule in these carboxylates.

X-Ray Diffraction Analysis: The X-ray diffraction pattern of Dysprosium carboxylates (palmitate and stearate) have been investigated in order to characterize their structure and the intensities of diffracted X-ray as a function of diffraction angle, 2θ are measured in the range of 6° to 40° with the help of X-ray spectrophotometer and the calculated interplanar spacing together with the relative intermediate are recorded (table 2 – 3). Bragg's equation has been used to calculate the interplanar spacing, d from position of intense peaks.

$$n\lambda = 2\, d \sin\theta$$

Where λ = wave length of radiation

The appearance of diffraction for palmitate and stearate upto 11th and 10th for dysprosium suggested good crystallinity for these carboxylates.

It is, therefore, concluded that the molecular axes of these carboxylate molecules are somewhat inclined to the basal planes. The metal ions Dy^{+3} fit into spaces between oxygen atoms of the ionized carboxyl groups without a large strain of the bond.

On the basis of long and short spacing, it is suggested that the metal ions in metal carboxylates are arranged in parallel plane, i.e., a basal plane equally spaced in the crystal of carboxylates with fully extended zig-zag chains of the fatty acid radical on both sides of each basal plane and the carboxylates possess single layer structure with molecular axes somewhat inclined to the basal planes.

Table 2. X-ray diffraction Analysis of Dysprosium palmitate

S. No.	2θ	D	d(Å)	n
1.	7.96	5.5510	11.1020	2
2.	8.89	2.9821	8.9464	3

3.	14.08	1.5728	6.2914	4
4	16.30	1.0873	5.4368	5
5.	17.82	0.8294	4.9769	6
6.	21.91	0.5794	4.0564	7
7.	23.94	0.4647	7.7178	8
8.	29.04	0.3416	3.0752	9
9.	38.85	0.2107	2.3178	11

Average value of d = 5.5467 (Å)

Table 3. X-ray diffraction Analysis of Dysprosium stearate

S. No.	**2θ**	**D**	**d(Å)**	**n**
1.	6.42	6.8848	13.7696	2
2.	8.23	3.5790	10.7372	3
3.	10.03	2.2046	8.8187	4
4	11.97	1.4792	7.3963	5
5.	16.77	0.8809	5.2854	6
6.	19.19	0.6607	4.6255	7
7.	21.78	0.5100	4.0802	8
8.	23.46	0.3792	3.7924	10

Average value of d = 7.3131 (Å)

Thermogravimetric Analysis: On thermal decomposition the final residue of Dysprosium oxide. This conclusion is in harmony with theoretically calculated weight of Dysprosium Oxide from the molecular formula of the corresponding carboxylates. Some white crystalline powder condensed at the cold part of the sample tube and it is identified as palmitone (82.2°C) and stearone (88.4°C) for (palmitate and stearate) respectively.

The thermal decomposition of Dysprosium carboxylates can be expressed as–

$$\underset{\text{Metal Carboxylate}}{2(RCOO)_3M} = \underset{\text{Ketone}}{3R.CO.R.} + \underset{\text{Metal Oxide}}{M_2O_3} + \underset{\text{Carbon Dioxide}}{3CO_2}$$

Where M is Dysprosium, R is $C_{11}H_{23}$, $C_{13}H_{27}$ and $C_{15}H_{31}$ for Palmitate and stearate respectively. The plots of the loss in weight, w of the carboxylates vs time, t (Fig.1) for dysprosium. carboxylate have been explained in terms of equations proposed by Freeman- Carroll's [8] and Coats – Redfern's [9].

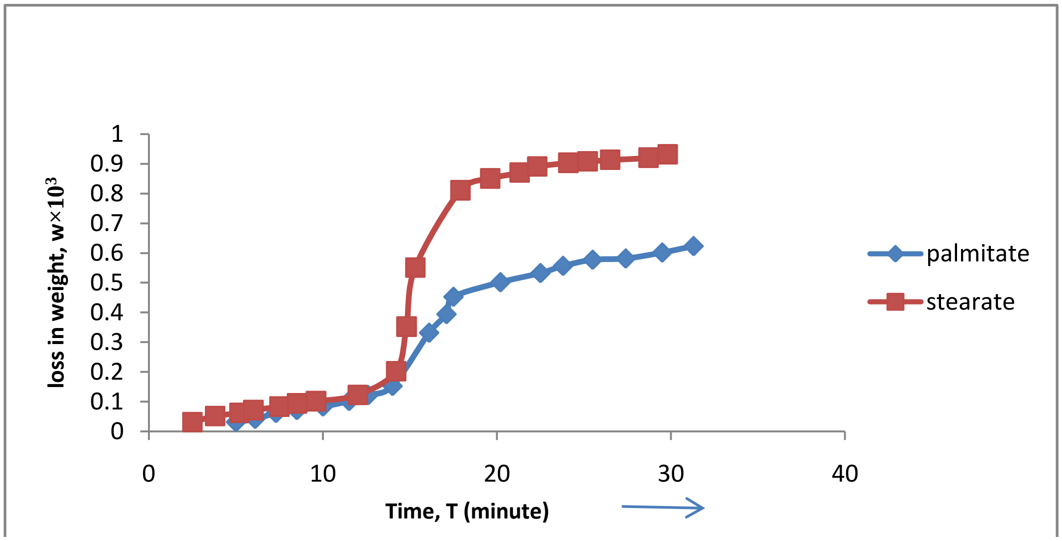

Fig 1. Loss in Weight Vs Time

Freeman and Carroll's rate expression for the thermal decomposition of carboxylates where the carboxylates disappears continuously with time and temperature and one product is gaseous may be expressed as –

$$\frac{\Delta\left[\log\left(dw/dt\right)\right]}{\Delta\left(\log Wr\right)} = \frac{-E}{2.303R} \quad \frac{\Delta\left(1/T\right)}{\Delta\left(\log Wr\right)} + n$$

Where E = Energy of activation, n = Order of decomposition reaction, T = Temperature on absolute scale. R = Gas constant, W = Difference between the total loss in weight and the loss in weight at time, t i.e. w_0-w_t and (dw/dt) = value of rate of weight loss obtained from the loss in weight vs time curves at appropriate times.

The plots ofΔlog [(dw/dt)] / (Δlog w_r) against Δ (1/T/Δlog Wr) (Fig.2) have been found to the linear with an intercept equal to Zero. It is, therefore, concluded that the reaction of thermal decomposition of Dysprosium carboxylates zero order and the values of energy of activation lie between 7.68-8.67 k. cal. mol^{-1} (Table 4)

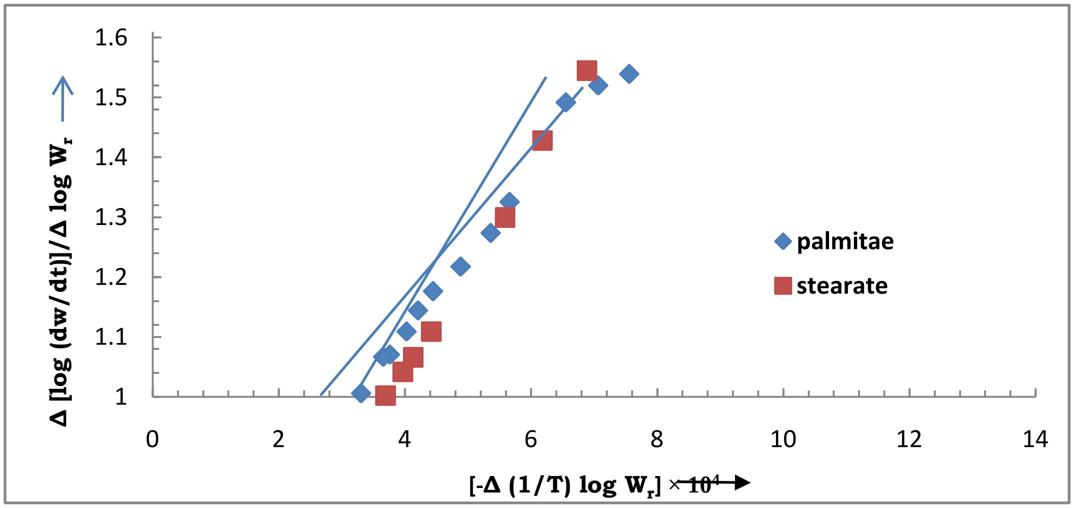

Fig 2. Freeman Carroll's Type plots

The values of energy of activation for the thermal decomposition of Dysprosium carboxylate have also been calculated by using Coats and Redfern's equation, which may be written as –

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

Where α= Fraction of the Carboxylate decomposed, T = Temperature on absolute scale, R = Gas constant. A = Frequency factor, a = Rate of heating in ºC per minutes, 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 the plots (Fig. 3) lie, between 12.33 – 18.45 kcal mol^{-1} and are in agreement with the values obtained from Freeman-Carroll's equation.

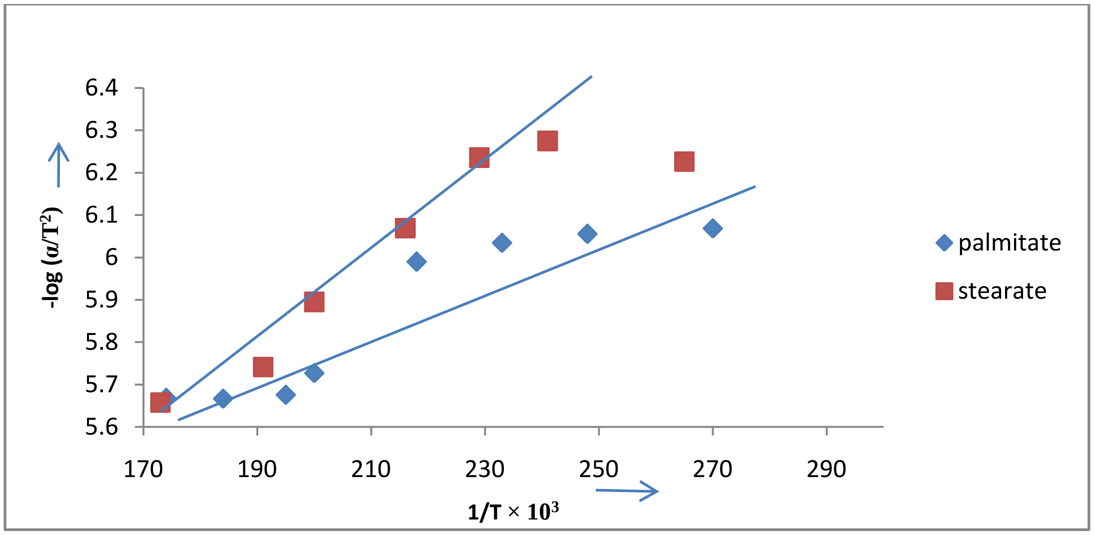

Fig 3. Coats and Redfern's Type plots

It is concluded that the decomposition reaction of Dysprosium carboxylates is kinetically of zero order and the energy of activation for the process lie in the range of 7.68 to 18.45k.cal.mol^{-1}.

Table 4. Energy of activation (KCal Mol^{-1}) for the decomposition of dysprosium carboxylates by using various equations

S. No.	**Name of the Carboxylates**	**Freeman and Carroll's equation**	**Coats and Redfern's Equation**
1.	Dysprosium palmitate	7.68	12.33
2.	Dysprosium stearate	8.67	18.45

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AUTHOR ADDRESS

1. **Amit K. Agarawal**
Department of chemistry,
Agra College, Agra, India
Email: akagarwal.chem@gmail.com,
Mob No: 9412064362