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Spectral and Thermal Behaviour of Copper Carboxylates

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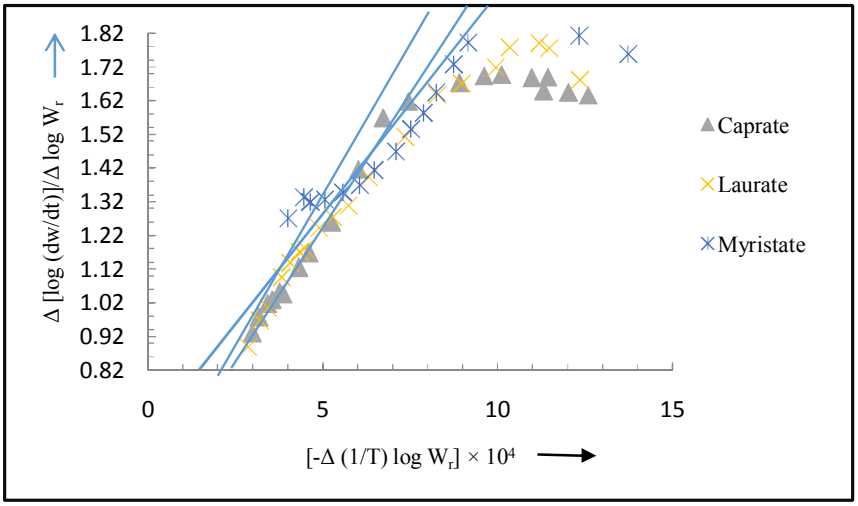
ABSTRACT

Copper carboxylates of fatty acids (capric, lauric and myristic) have been prepared by direct metathesis. The IR spectra of the carboxylates were characterized by two asymmetric and two symmetric vibration of carboxylic group and results reveals that the fatty acids exist dimeric structure through intermolecular Hydrogen bonding and copper carboxylates are ionic in nature. The double layer structure with long spacing confirmed by X-ray diffraction reaction decomposition reaction has been found kinetically zero order with energy of activation for copper lies in the range from 2.15 to 17.15 kcal.mol^{-1}.

Graphical Abstract



Freeman Caroll's type plot

Keywords: Copper carboxylates, IR, Powder diffraction and Thermal decomposition.

INTRODUCTION

Metal carboxylates are salts of long-chain fatty acids with alkaline and other metals which are insoluble in water but soluble in non-aqueous solvents. The physical properties of metal carboxylates

vary considerably due to variation in the valency of the fatty acids. Many researchers [1-4] used different techniques for the preparation of metal carboxylates. Metal carboxylates have many applications in industries and in our daily life. Silver carboxylates were used as the source of silver in thermographic and photographic materials [5]. Electrical properties of lanthanide carboxylates has been reported by several workers [6, 7].

Upadhyaya *et al*., [8] studied thermal infrared and X-ray diffraction analysis of manganese and zinc carboxylates. The thermal behavior of chromium–cadmium carboxylates were studied by several workers [9, 10]. Sharma *et al*., [11] investigated thermogravimetric analysis of gadolinium carboxylates.

In present manuscript, we report on the structural and Thermal behaviour of copper carboxylates. The structure of the compound has been studied by IR and X-ray diffraction analysis and their thermal behaviour have also been investigated by Thermogravimetric analysis.

MATERIALS AND METHODS

Preparation of carboxylates: Copper carboxylates (caprate, laurate and myristate) were synthesized by metathesis of the corresponding potassium carboxylates with the required amount of aqueous solution of copper nitrate. Purity of metal carboxylates was checked by melting point, elemental analysis and IR spectra. The advantage of 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.

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 copper 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° min^{-1} and chart speed of 1 cm per min. The wave length of the radiation has been taken as 1.542Å.The Thermogravimetric analysis of Copper carboxylates have been carried out by Perkin-Elmer Thermogravimetric analyzer 'TG-S-2' at constant heating rate (10° min^{-1}) in nitrogen atmosphere and maintaining similar conditions throughout the investigations.

RESULTS AND DISCUSSION

The spectra of copper carboxylates (caprate, laurate and myristate) have been recorded and compared with the results of the corresponding fatty acids (Table 1). The absorption bands observed near 2645-2660, 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.

The appearance of one bond of carboxyl frequency near 1700cm^{-1} confirms that these carboxylates possess ionized structure and 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, copper 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 copper carboxylates donot show any absorption maxima which confirm the absence of any coordinated water molecule in these carboxylates.

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

S.No.	Absorption	Copper		
		caprate	laurate	myristate
1.	CH_3, C-H asymmetrical stretching	2942	2940	2948
2.	CH_2, C–H asymmetrical stretching	2920	2918	2918
3.	CH_2, C–H symmetrical stretching	2842	2850	2850
4.	OH, stretching	-	-	-
5.	C=O stretching	-	-	-
6.	COO^-, C–O asymmetrical stretching	1525	1528	1520
7.	CH_2 deformation	1470	1470	1470
8.	COO^-, C–O symmetrical stretching	1440	1442	1444
9.	CH_2, (adjacent to COOH group) deformation	1368	1406	1406
10.	CH_3, asymmetrical deformation	-	1315	-
11.	Progressive bonds (CH_2 twisting and wagging)	-	-	1298
12.	CH_3, rocking	998	1114	1092
		-	1084	1115
13.	OH, out of plane deformation	-	-	935
14.	CH_2, rocking	919	721	718
15.	COOH bending Mode	-	-	-
16.	COOH wagging Mode	515	525	525
17.	Cu—O bond	435	432	440

X-ray Diffraction analysis: The X-ray diffraction pattern of Copper carboxylates (caprate, laurate and myristate) 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 2° to 38° with the help of X-ray spectrophotometer and the calculated interplanar spacing together with the relative intermediate are recorded (Tables 2–4). 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 caprate, laurate and myristate upto 18^{th} and 21^{st} for copper suggested as good crystallinity for these carboxylates.

Table 2. X-ray Diffraction analysis of copper caprate

S.No.	2θ	θ	Sin θ	D	d (Å)	n
1.	2.8983	1.449	0.0252	16.0888	32.1777	2
2.	4.6734	2.336	0.0407	15.9298	31.8596	4
3.	7.8097	3.904	0.0689	6.4450	32.2254	5
4.	10.5713	5.285	0.0921	5.2295	31.3774	6
5.	13.2114	6.605	0.1150	3.8348	30.6785	8
6.	17.8017	8.900	0.1547	3.1935	31.9354	10
7.	20.0832	10.041	0.01743	2.8385	31.2245	11
8.	23.6381	11.819	0.2048	2.7074	32.4897	12
9.	25.2243	12.612	0.2183	2.3575	33.0056	14
10.	28.8981	14.449	0.2495	2.1926	32.8892	15
11.	31.1983	15.599	0.2689	2.0692	33.1083	16
12.	33.0074	16.503	0.2840	1.7643	31.7581	18

Average Value of d (Å) = 32.0607

It is, therefore, concluded that the molecular axes of these carboxylate molecules are somewhat inclined to the basal planes. The metal ions Cu^{+2} fit into spaces between oxygen atoms of the ionized carboxyl groups without a large strain of the bond.

Table 3. X-ray Diffraction analysis of copper laurate.

S.No.	2θ	θ	Sin θ	D	d (Å)	n
1.	4.7893	2.394	0.0417	36.7347	36.7347	1
2.	5.6217	2.810	0.0490	12.9473	38.8421	3
3.	8.0794	4.039	0.0704	7.4815	37.4076	5
4.	9.1563	4.578	0.0798	5.3888	37.7216	7
5.	12.4708	6.235	0.1086	4.2701	38.4313	9
6.	15.2116	7.605	0.1323	3.72261	37.2261	10
7.	18.3214	9.160	0.1592	3.0678	36.8139	12
8.	23.7052	11.852	0.2053	2.8287	36.7743	13
9.	27.1635	13.581	0.2348	2.3905	38.2489	16
10.	29.8419	14.920	0.2574	2.3175	39.3988	17
11.	33.8213	16.910	0.2908	2.1242	38.2367	18
12.	34.5317	17.265	0.2968	1.9131	36.3498	19

Average Value of d (Å) = 37.6821

Table 4. X-ray Diffraction Analysis of copper myristate

S.No.	2θ	θ	Sin θ	D	d (Å)	n
1.	5.3217	2.660	0.0464	21.0049	42.0098	2
2.	6.8984	3.449	0.0601	13.8895	41.6685	3
3.	9.0172	4.508	0.0786	8.2643	41.3219	5
4.	13.8375	6.918	0.1204	6.8143	40.8859	6
5.	17.6218	8.810	0.1531	5.9036	41.3252	7
6.	22.2429	11.121	0.1928	4.6322	41.6898	9
7.	23.4032	11.701	0.2028	3.7632	41.3954	11
8.	26.3327	13.166	0.2277	3.1452	40.8877	13
9.	28.8342	14.417	0.2489	2.9827	41.7582	14
10.	31.6913	15.845	0.2730	2.6043	41.6698	16
11.	34.2084	17.104	0.2941	2.2236	42.2493	19
12.	37.3418	18.670	0.3201	2.0630	43.3247	21

Average Value of d (Å) = 41.682

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.

Thermogravimetric analysis: On thermal decomposition the final residue of Copper oxide. This conclusion is in harmony with theoretically calculated weight of Copper 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 caprinone (M.P.58°C), laurone (M.P.69.4°C), myristone (M.P.78.0°C) for (caprate, laurate and myristate) respectively.

The thermal decomposition of Copper carboxylates can be expressed as

$$2(RCOO)_2Cu \;=\; 2R.CO.R. \;+ Cu_2O_2 \;+\; 2CO_2$$

Copper carboxylate — Ketone — Copper oxide — Carbon dioxide

Where R is C_9H_{19}, $C_{11}H_{23}$ and $C_{13}H_{27}$ for Caprate, laurate and myristate respectively.

The plots of the loss in weight, w of the carboxylates vs time, t (Fig.1) for copper carboxylate have been explained in terms of equations proposed by Freeman- Carroll's [12] and Coats – Redfern's [13].

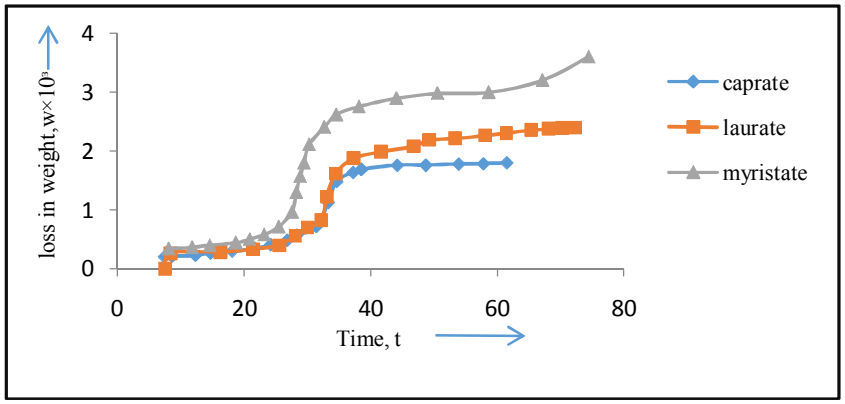


Figure 1. Loss in weight versus time

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 of Δlog [(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 Copper carboxylates zero order and the values of energy of activation lie between 4.82-7.33 kcal.mol^{-1} (Table 5).

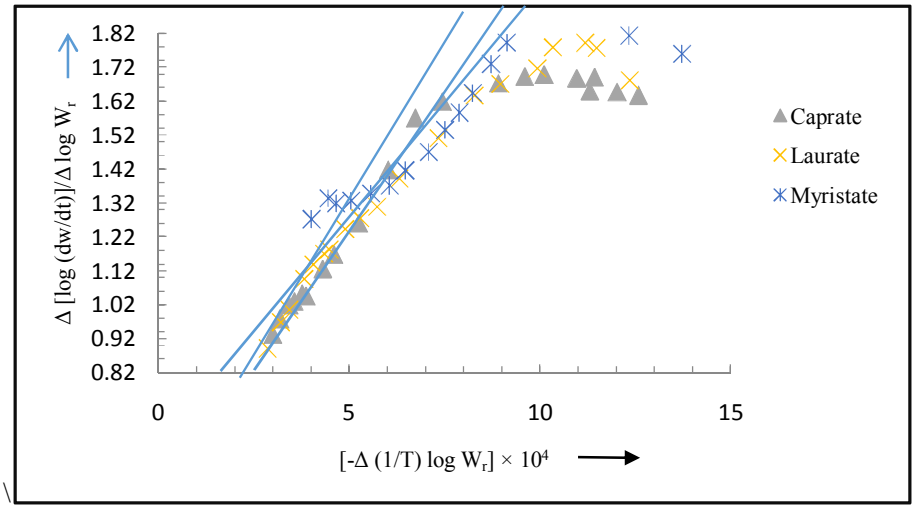


Figure 2. Freeman caroll's type plot

The values of energy of activation for the thermal decomposition of copper 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.

Table 5. Energy of activation (k.cal.mol^{-1}) for the decomposition of copper carboxylates by using various equations

S.No.	Name of the Carboxylates	Freeman and Carroll's equation	Coats and Redfern's Equation
1.	Coppercaprate	4.82	9.37
2.	Copperlaurate	5.98	11.29
3.	Copper myristate	7.33	17.15

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 lie, between 9.37-17.15 kcal.mol^{-1} and are in agreement with the values obtained from Freeman-Carroll's equation.

CONCLUSIONS

It is concluded that the decomposition reaction of copper carboxylates is kinetically of zero order and the energy of activation for the process lie in the range from 4.82-17.15 kcal.mol^{-1}.

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