

## Thermal Decomposition Kinetics of Nano-Sized Chromium(III) Carboxylates

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The kinetics of thermal decomposition of a few nano-sized trinuclear oxo-centered, carboxylato bridged chromium(III) complexes has been reported on the basis of TG, DSC and DTG studies. It is found that the decomposition occurs in two steps. Following the experimental results a thermal decomposition scheme along with thermal stability order of the complexes under investigation is proposed. The kinetic parameters like activation energy ( $E_a$ ), pre-exponential factor (A) and activation entropy ( $\Delta S^\ddagger$ ) have been evaluated for each step. Powder XRD data were used to find out the particle size of the complexes which indicated them to be of nano-size.

**Key Words:** Activation energy, Carboxylate complexes, Chromium(III), Nano-size, Oxo-centered, TG-DTG-DSC.

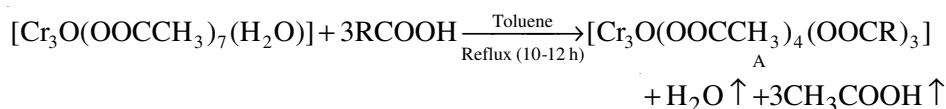
### INTRODUCTION

Many theories of magnetic and electronic coupling between trivalent 3d-metal ions<sup>1-4</sup> were tested by preparing model compounds with trinuclear, oxo-bridged assemblies. These compounds are valuable precursors for the synthesis of higher nuclearity clusters for single molecule magnets<sup>5</sup>. Among these, chromium(III) complexes exhibited valuable biological properties, *e.g.*, control over cholesterol and triglycerides in rats, treatment for type 2 diabetes and hyperlipidemia *etc.*<sup>6,7</sup>. The most interesting feature in such complexes is the existence of  $\mu_3$ -O moiety which is the active sites of numerous non-heme iron and manganese metalloproteins<sup>8</sup>. However, literature revealed that almost no work has been done on the thermal properties of such complexes. In view of this, we report here the details of thermal behaviour of some oxo-centered chromium(III) complexes. The kinetics of their thermal decomposition has been discussed on the basis of TG, DTG and DSC studies. The other interesting part of this communication is the measurement of particle size of the complexes which is obtained in the nano range.

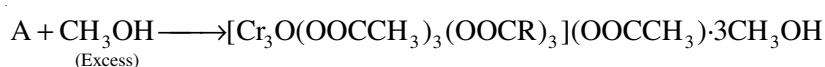
### EXPERIMENTAL

The complexes were synthesized by substitutions of acetate ions of  $[\text{Cr}_3\text{O}(\text{OOCCH}_3)_7(\text{H}_2\text{O})]$  with straight chain fatty acids in 1:3 molar ratios under reflux, using toluene as a solvent. The liberated water and acetic acid were slowly

and continuously fractionated out with toluene in the form of an azeotrope. The complexes were isolated by removing excess solvent *in vacuo*. These were purified by reprecipitation from their benzene solution by adding an excess of methanol<sup>9</sup>. The reaction **Scheme-I** is given below.



(where R = C<sub>13</sub>H<sub>27</sub>, **1**; C<sub>15</sub>H<sub>31</sub>, **2** or C<sub>17</sub>H<sub>35</sub>, **3**).



**Scheme-I:** Synthesis of the complexes

The thermograms (TG, DTG and DSC) of all the complexes were recorded on Netzsch STA 409 PG/PC by heating the sample from 32-660 °C at the rate of 10 °C/min under dynamic nitrogen atmosphere. Powder X-ray diffraction data were collected on a PW 1710 diffractometer.

The kinetic parameters like E<sub>a</sub>, A and ΔS<sup>#</sup> have been calculated for each step of decomposition of complexes from the thermograms using Doyle's equation<sup>10</sup> and the results are summarized in Table-1.

TABLE-1  
KINETIC PARAMETERS OF CHROMIUM(III)  
COMPLEXES USING DOYLE'S EQUATION

Complex	Step	Activation energy (E <sub>a</sub> ) (kJ mol <sup>-1</sup> )	Pre-exponential factor (A) (s <sup>-1</sup> )	Activation entropy (ΔS <sup>#</sup> ) (J K <sup>-1</sup> mol <sup>-1</sup> )
<b>1</b>	1	293.00	1258.22	-25.21
	2	6000.00	2.13	-29.93
<b>2</b>	1	366.66	794.43	-23.73
	2	6516.66	0.95	-30.57
<b>3</b>	1	383.33	1288.25	-23.45
	2	7027.77	1.05	-30.57

$$\log \rho T/W = E_a/4.6T + \log A/RH \quad (1)$$

where ρT = t/RH, -dw/dt the fraction decomposed at time 't', R = gas constant, H = the heating rate, W = the weight of sample at time 't', E<sub>a</sub> = the activation energy, A = pre-exponential factor or the frequency factor and T = the temperature in Kelvin.

The entropy of the activation (ΔS<sup>#</sup>) was obtained from the following equation:

$$A = kT_s/h \exp(\Delta S^{\#}/R) \quad (2)$$

where, k = the Boltzmann constant, h = the Planck's constant, T<sub>s</sub> = the DTG peak temperature and ΔS<sup>#</sup> = the activation entropy.

## RESULTS AND DISCUSSION

The first step of decomposition was in the temperature range of 70-440, 74-410 and 80-410 °C for complexes **1**, **2** and **3**, respectively, which corresponded to the

loss of three methanol molecules and an acetate ion lying outside the coordination sphere. The second step of the decomposition for complexes **1**, **2** and **3** was in the temperature range 440-550, 410-520 and 410-520 °C, respectively, which corresponded to the decomposition of three acetate ions and three fatty acid anions into ketones and carbon dioxide<sup>11,12</sup>. These products were volatile and the residue left was chromium(III) oxide. This was confirmed by analysis of chromium and infrared spectrum. The endothermic and exothermic peaks observed in their DSC supported the two steps decomposition pattern of the complexes as suggested by TG.

Powder X-ray diffraction were done for all the complexes and one spectrum along with its crystal data for  $[\text{Cr}_3\text{O}(\text{OOCCH}_3)_3(\text{OOC}_{15}\text{H}_{31})_3](\text{OOCCH}_3)\cdot 3\text{CH}_3\text{OH}$  is given in Fig. 1 (Table-2). Particle size of this complex was calculated using the standard equation of Scherrer<sup>13</sup>.

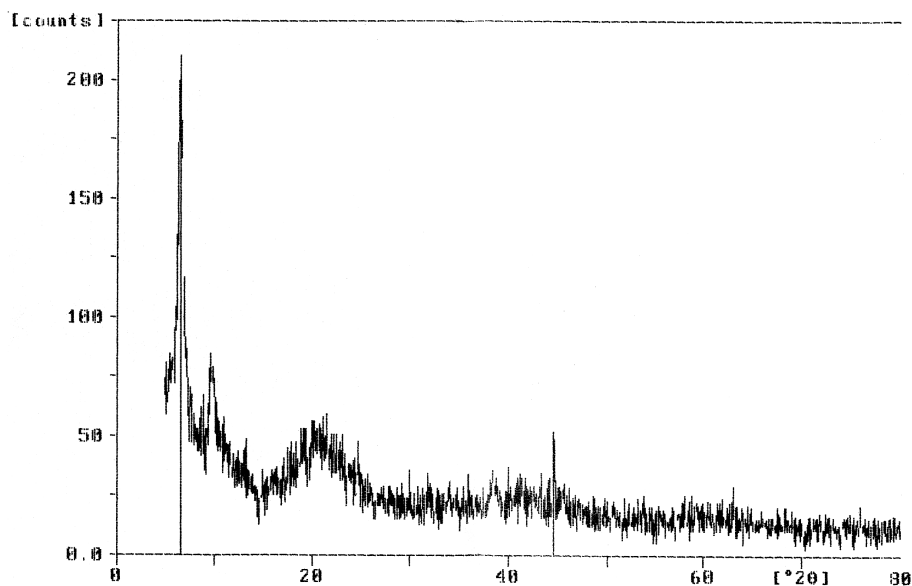


Fig. 1. Powder XRD spectrum of  $[\text{Cr}_3\text{O}(\text{OOCCH}_3)_3(\text{OOC}_{15}\text{H}_{31})_3](\text{OOCCH}_3)\cdot 3\text{CH}_3\text{OH}$

$$D = K\lambda/(\beta \cos \theta) \quad (3)$$

where, D is the particle size of the crystal grain; K is constant (= 0.94 for Cu grid);  $\lambda$  is X-ray wavelength (= 1.5406 Å);  $\theta$  is Bragg diffraction angle;  $\beta$  is integral peak width of the diffraction peak which was converted into radian. The particle size was calculated using the highest value of intensity along with all the observed data. The particle size for the complex thus obtained was 22 nm from the data. This clearly indicated the nano-size for this complex.

A two steps thermal decomposition pattern was observed in all the three complexes and a possible fragmentation pattern is given in **Scheme-II** from the thermal data (Table-3, Fig. 2).

TABLE-2  
POWDER XRD DATA OF  $[\text{Cr}_3\text{O}(\text{OOCCH}_3)_3(\text{OCC}_{15}\text{H}_{31})_3](\text{OOCCH}_3)\cdot 3\text{CH}_3\text{OH}$

Angle [ $2\theta$ ]	d-value [1]	d-value [2]	Peak width [ $2\theta$ ]	Peak int [counts]	Back int [counts]	Rel. int [x]	Signif.
6.590	13.4019	13.4349	0.400	135	59	100.0	2.31
9.795	9.0227	9.0449	0.500	31	48	23.3	1.40
38.420	2.3411	2.3469	0.600	11	20	8.1	1.09
44.505	2.0341	2.0391	0.300	27	19	20.1	2.21

TABLE-3  
THERMOANALYTICAL RESULTS OF CHROMIUM(III) COMPLEXES

Complex	Step	Decomp. Temp. ( $^{\circ}\text{C}$ )	TG Weight loss (%)		Total (%) weight loss		Residue (%)		DTG		DSC		Inference
			Found	Calcd	Found	Calcd	Found	Calcd	Peak temp. ( $^{\circ}\text{C}$ )	React.	Temp. ( $^{\circ}\text{C}$ )	Peak	
<b>1</b>	1	70-440	13.84	13.07	86.24	87.19			440	Decomp.	72	Endo*	Liberation of three $\text{CH}_3\text{OH}$ and $\text{OOCCH}_3$ moities
	2	440-550 > 550	72.40	74.12			13.65	12.81	550	"	518.5	Exo**	Liberation of three $\text{OOCCH}_3$ and $\text{OCC}_{13}\text{H}_{27}$ groups $\text{Cr}_2\text{O}_3$ as residue
<b>2</b>	1	74-410	12.51	12.20	87.74	88.04			410	"	75	Endo*	Liberation of three $\text{CH}_3\text{OH}$ and $\text{OOCCH}_3$ moities
	2	410-520 > 520	75.23	75.84			12.18	11.96	520	"	481.2	Exo**	Liberation of three $\text{OOCCH}_3$ and $\text{OCC}_{15}\text{H}_{31}$ groups $\text{Cr}_2\text{O}_3$ as residue
<b>3</b>	1	80-410	11.97	11.44	86.79	88.79			410	"	82	Endo*	Liberation of three $\text{CH}_3\text{OH}$ and $\text{OOCCH}_3$ moities
	2	410-520 > 520	75.82	77.35			11.78	11.21	520	"	525.6	Exo**	Liberation of three $\text{OOCCH}_3$ and $\text{OCC}_{17}\text{H}_{35}$ groups $\text{Cr}_2\text{O}_3$ as residue

Note: (-) \*endo (endothermic); (+) \*\*exo (exothermic); calcd.= calculated; temp.= temperature; decomp. = decomposition; react. = reaction.

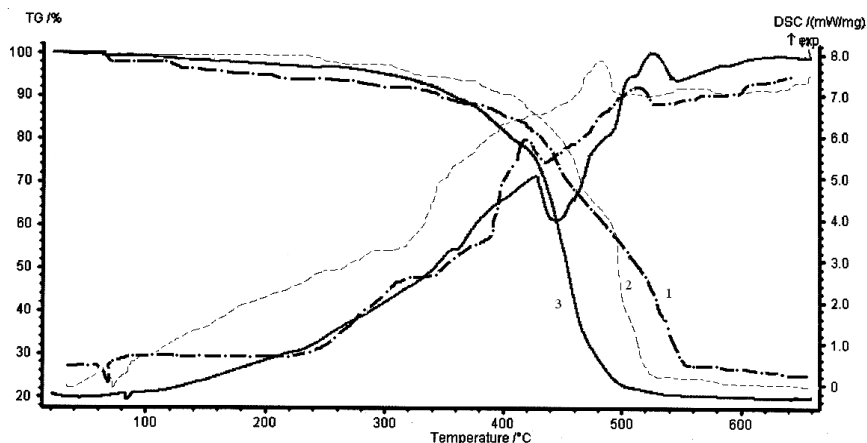
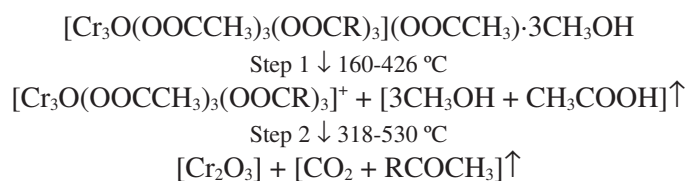
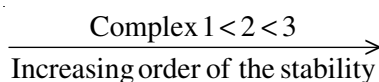


Fig. 2. TG-DSC thermograms of complexes **1**, **2** and **3**



**Scheme-II:** A possible fragmentation pattern of the complexes

This work demonstrates the kinetics of thermal decomposition of chromium(III) oxo-centered carboxylato complexes on the basis of thermoanalytical data. A possible two steps fragmentation pattern is given in all the cases and the end product was  $\text{Cr}_2\text{O}_3$ . In the thermograms, no peak was observed for melting the complexes. The values of calculated activation energy were found 293, 366.66 and 383.33  $\text{kJ mol}^{-1}$ , for step 1 of complexes **1**, **2** and **3** while for the step 2 the values were 6000.00, 6516.66 and 7027.77  $\text{kJ mol}^{-1}$ , respectively. There is a large difference in the values of activation energy of step 1 and 2 for all the complexes. This is due to the fact that in step 1 the weight loss is very low about 11-14 % while in step 2 the weight loss is very high about 72-76 %. The negative entropy of activation values for all degradation stages showed that the complexes were more ordered in the activated state. The negative entropy of activation values were compensated by the values of the energies of activation. The decrease in value of entropy of activation from first step to the second step indicated that the rate of decomposition increases in stepwise reactions<sup>14</sup>. On the basis of initial temperature of decomposition for complexes from TG-DTG and DSC curves, the following sequence of increasing thermal stability is given:



X-ray diffraction data indicated the complexes are nano-sized.

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