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Synthesis, characterization and thermal investigation of $M[M(C_2O_4)_3] \cdot xH_2O$ ($x=4$ for $M=Cr(III)$; $x=2$ for $M=Sb(III)$ and $x=9$ for $M=La(III)$)

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Abstract

The complexes, $M[M(C_2O_4)_3] \cdot xH_2O$, where $x=4$ for $M=Cr(III)$, $x=2$ for $M=Sb(III)$ and $x=9$ for $M=La(III)$ have been synthesized and their thermal stability was investigated. The complexes were characterized by elemental analysis, IR and electronic spectral data, conductivity measurement and powder X-ray diffraction (XRD) studies. The chromium(III)tris(oxalato)chromate(III)tetrahydrate (COT), $Cr[Cr(C_2O_4)_3] \cdot 4H_2O$, released water in a stepwise fashion. Removal of the last trace of water was accompanied by a partial decomposition of the oxalate group. Thermal investigation using TG, DTG and DTA techniques in air produced Cr_2O_3 at $\sim 858^\circ C$ through the intermediate formation of Cr_2O_3 and CrC_2O_4 at around $460^\circ C$. While DSC study in nitrogen up to $670^\circ C$ produced a mixture of Cr_2O_3 and CrC_2O_4 . In antimony(III)tris(oxalato)antimonate(III)-dihydrate (AOD), $Sb[Sb(C_2O_4)_3] \cdot 3H_2O$ the dehydration took place during the decomposition of precursor at 170 – $290^\circ C$ and finally at ca. $610^\circ C$ Sb_2O_5 along with trace amounts of Sb_2O_4 were produced. Trace amount of Sb_2O_3 and Sb along with Sb_2O is proposed as the end product at $670^\circ C$ of AOD in nitrogen. The oxide La_2O_3 is formed at $\sim 838^\circ C$ from the study with TG, DTG and DTA in air of lanthanum(III)tris(oxalato)lanthanum(III)nonahydrate (LON), $La[La(C_2O_4)_3] \cdot 9H_2O$. Intermediate dioxycarbonate, $La_2O_2CO_3$ was generated at $\sim 526^\circ C$ prior to its decomposition to lanthanum oxide in air; whereas in N_2 the formation of $La_2(CO_3)_3$ at $\sim 651^\circ C$ was proposed. The thermal parameters have been evaluated for each step of the dehydration and decomposition of COT, AOD and LON using five non-mechanistic equations i.e. Flynn and Wall, Freeman and Carroll, Modified Freeman and Carroll, Coats–Redfern and MacCallum–Tanner equations. Kinetic parameters, such as, E^* , k_o , ΔH^* , ΔS^* etc. were also supplemented by DSC studies in nitrogen for all the three complexes. Some of the intermediate species have been identified by analytical and powder XRD studies. Tentative schemes has been proposed for the decomposition of all three compounds in air and nitrogen. © 1998 Elsevier Science B.V.

Keywords: Oxalato; Thermal decomposition; Kinetic parameter; X-ray diffraction

1. Introduction

Several studies [1–7] have been carried out on the oxalato complexes of transition and non-transition

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metals. A comprehensive review of the chemistry of the metal oxalato complexes has been well documented by Krishnamurthy and Harris [8]. We have reported [9–18] exhaustive studies on a series of oxalato complexes of type $M[M(C_2O_4)_2] \cdot xH_2O$, where M is same bivalent metal. One of us [19] has synthesized the compound $Fe[Fe(C_2O_4)_3] \cdot 4H_2O$ by a

novel method. It decomposes by reduction of the inner Fe(III) and finally ferric oxide is formed as an end product. Interesting results from the bivalent metals as well as iron compound motivate us to study similar compounds of trivalent metals (Cr(III), Sb(III), La(III)) for investigating their decomposition kinetics and mechanism. Different studies on various oxalato complexes of chromium, antimony and lanthanum are to be found in the literature. Palmer and Kelm [20] have studied the influence of pressure on the rate of acid hydrolysis of $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ at 50°C using spectrophotometry and the activation parameters for the reaction were evaluated. Nagase [21] investigated the phase transition of anhydrous $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ from amorphous to crystalline solid state. A hexagonal structure was observed at 270°C . Enthalpy changes associated with the phase transition were also reported. Later the same author studied [22] the decomposition in helium of $\text{K}_3[\text{Cr}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ along with other trivalent metals by gas analysis. Medium effects in the hydration of $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ was studied [23]. $(\text{NH}_4)_3[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$, was decomposed [24] to a crystalline form of Cr_2O_3 and the solid solution of the iron analogue of the parent compound led to a mixed oxide, $(\text{Fe}_{2-x}\text{Cr}_x)\text{O}_3$ at high temperature through the formation of metastable oxide. The preparative method of $\text{Sb}(\text{III})(\text{C}_2\text{O}_4)\text{OH}$ was reported [25] a long time ago and Ambe [26] reported the formation of the oxide, Sb_2O_3 at 290°C from the thermal decomposition of this compound. Dollimore et al. [1] reported the thermal decomposition of $(\text{SbO})_2\text{C}_2\text{O}_4$ and that Sb_2O_3 was formed at 270°C in air, but in nitrogen Sb_2O was produced which is assumed to be a mixture of Sb and SbO . In the same study they reported that Cr_2O_3 was produced both in air and N_2 from the thermal decomposition of $\text{Cr}_2(\text{C}_2\text{O}_4)_3\cdot 6\text{H}_2\text{O}$. The bonding of the water in hydrated d-elements of $\text{La}_2(\text{C}_2\text{O}_4)_3\cdot n\text{H}_2\text{O}$ has been examined by proton NMR [28] and the effect of the cation and the crystal structure measured. The thermal decomposition of the mixed metal oxalate, $\text{LaCo}(\text{C}_2\text{O}_4)_3\cdot 9\text{H}_2\text{O}$ in air produced [29] LaCoO_3 through the formation of an intermediate $\text{LaCoO}_{3-x}(\text{CO}_3)_x$. Nag and Roy [30] reported the preparation of the rare earth cobaltites, LaCoO_3 below 800°C from the precursor $\text{LaCo}(\text{C}_2\text{O}_4)_3\cdot 9\text{H}_2\text{O}$. They mixed $\text{La}_2(\text{C}_2\text{O}_4)_3\cdot 10\text{H}_2\text{O}$ and $\text{CoC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ and on decomposition at 900°C , it was confirmed that the

residue contained mainly La_2O_3 and Co_3O_4 , and also a trace amount of LaCoO_3 . Although a few oxalato complexes of Cr(III), Sb(III) and La(III) are known, compounds of bimetallic trivalent oxalato complexes of the type $\text{M}(\text{III})[\text{M}(\text{III})(\text{C}_2\text{O}_4)_3]\cdot x\text{H}_2\text{O}$, (where $\text{M}(\text{III})$ =same metal) were not reported. Therefore, we have studied compounds of the type $\text{M}[\text{M}(\text{C}_2\text{O}_4)_3]\cdot n\text{H}_2\text{O}$ with Cr(III), Sb(III) and La(III). This paper describes the synthesis, characterization and the thermal decomposition of $\text{Cr}[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 4\text{H}_2\text{O}$, $\text{Sb}[\text{Sb}(\text{C}_2\text{O}_4)_3]\cdot 2\text{H}_2\text{O}$ and $\text{La}[\text{La}(\text{C}_2\text{O}_4)_3]\cdot 9\text{H}_2\text{O}$ in air and nitrogen. Kinetic parameters of the dehydration and decomposition have been investigated using different non-mechanistic equations and compared with a study of the decomposition by DSC. A tentative mechanism of the decomposition is postulated.

2. Experimental

Chromium hydroxide and antimony hydroxide prepared from their respective chlorides (AR grade) were made free of chloride by washing repeatedly with distilled water. Lanthanum nitrate was converted to chloride by repeatedly digesting with concentrated hydrochloric acid. The chloride free hydroxide was then produced. The metal hydroxide were dissolved in glacial acetic acid, heating on a steam bath. Compounds of antimony and lanthanum were precipitated by dropwise addition of saturated solution of oxalic acid (AR grade). The white compounds separated from solution were removed by filtration, washed several times with distilled water and dried in a desiccator. The chromium compound was obtained as light greenish white crystals after refluxing for several hours. The compound was stored in a desiccator over calcium chloride. The water content was estimated thermogravimetrically. Chromium, antimony and lanthanum contents were determined using standard methods [31]. Carbon and hydrogen contents were determined with a Carlo Erba 1108 elemental analyser. The electrical conductivity was measured at 1 kHz with an Aplab (India) LCR-Q meter (model no. 4910).

IR spectra of the compounds and their intermediates were measured ($4000\text{--}200\text{ cm}^{-1}$) using Perkin-Elmer IR 883 spectrophotometer. Diffuse reflectance spectra were recorded with Shimadzu UV-240 spectrophot-

ometer using BaSO₄ as the reference material. TG and DTG up to 1000°C and DTA up to 700°C were carried out at 10°C min⁻¹ using Shimadzu DT 30B instrument. DSC curves were recorded on Perkin-Elmer DSC-7 at 10°C min⁻¹ in a dynamic nitrogen atmosphere. The kinetic parameters of the processes were determined after integration of the peaks. Powder X-ray diffraction (XRD) pattern of the compounds as well as their decomposition products were obtained using a Geigerflex Microprocessor controlled automated Rigaku (Japan) X-ray diffractometer system D/Max IIC with SASG accessory. A JDX-11P3A JEOL diffractometer was also used with Ni filter and Cu-K_α radiation at 35 kV and 10 mA to record the XRD patterns of samples.

3. The kinetics of decomposition

Kinetic parameters, such as, activation energy (E^*), pre-exponential factor (k_0), activation entropy (ΔS^*) and the order of the reaction (n) were calculated from non-isothermal TG curves using differential and integral rate equations, such as

The Freeman and Carroll equation [32],

$$\frac{(-E^*/2.3R)\Delta T^{-1}}{\Delta \log W_r} = -X + \frac{\Delta \log(dw/dt)}{\Delta \log W_r} \quad (1)$$

The terms have their usual meaning. This is a differential rate equation.

A Modified Freeman and Carroll equation [33]

When the order of the reaction in weight change is close to unity in the above analysis, then E^* and ΔS^* can be determined using the following equations.

$$\log \left[\frac{(dw/dt)}{W_r} \right] = -\frac{E^*}{2.3RT} + \log Z \text{ and} \\ Z = \frac{KT_s}{h} \exp \left(\frac{\Delta S^*}{R} \right) \quad (2)$$

where the terms have their usual meaning.

The Flynn and Wall equation [34]

$$\log \frac{dw_t/dT}{(W_o - W_t)^n} = \log(A/B) - \frac{E^*}{2.3RT} \quad (3)$$

This is also a differential rate expression and weight loss–time equation. Curves can be drawn for different values of n in the range of 0–2 and the E^* were fixed from the value of n which gave best fit line.

The Coats–Redfern equation [35]

$$\ln \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2} = \ln \left[\frac{AR}{\phi E^*} \left(1 - \frac{2RT}{E^*} \right) \right] - \frac{E^*}{RT} \quad (4)$$

This is an integral rate expression.

The MacCallum–Tanner equation [36]

$$\log_{10} \frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \log_{10} \frac{AE^*}{\phi R} \\ - 0.485 E^{0.435} - \frac{(0.449 + 0.217 E^*) \times 10^3}{T} \quad (5)$$

This is also an integral method and is known as an exact equation. In Eqs. (4) and (5) the terms have their usual meaning. Values of n in the above two equations were calculated by Eq. (1).

4. Results and discussion

The light greenish white compound, Cr[Cr(C₂O₄)₃]·4H₂O (COT) and the white compounds Sb[Sb(C₂O₄)₃]·2H₂O (AOD) and La[La(C₂O₄)₃]·9H₂O (LON) were insoluble in water. However, they decomposed in the presence of strong acid or alkali. Analytical and microanalytical results were consistent with the proposed formula of the compounds. Analysis: calculated for Cr[Cr(C₂O₄)₃]·4H₂O: Cr, 23.61%; C, 16.36%; H, 1.83%; H₂O, 16.36%; found: Cr, 24.27%; C, 16.23%; H, 1.79% and H₂O, 16.00%; calculated for Sb[Sb(C₂O₄)₃]·2H₂O: Sb, 44.77%; C, 13.25%; H, 0.74%; H₂O, 6.63%; found; Sb, 44.41%; C, 13.12%; H, 0.71%; calculated for La[La(C₂O₄)₃]·9H₂O: La, 39.46%; C, 10.24%; H, 2.58%; H₂O, 23.03%; found: La, 40.08%; C, 10.34%; H, 2.61% and H₂O, 23.00%. The low value of the electrical conductivity $1.413 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ at 1 kHz for LON suggests that it is a poor conductor. Powder XRD pattern (Table 4) of all three compounds differed from one other and suggested that they were not isomorphous. The chelating character of the oxalato group as well as the presence of coordinated and water of crystallisation have been concluded on the basis of earlier studies [17,18,37]. The assignments of the bands are shown in Table 1. Due to the presence of only two water molecules in AOD, the bands due to $\nu_{\text{sy}}(\text{O-H})$ and $\nu_{\text{asy}}(\text{O-H})$ are weak compared to COT and LON. In COT, the band $\nu_{\text{Cr-O}}$ was not observed in

Table 1

Selected bands in the IR spectra of Cr[Cr(C₂O₄)₃].4H₂O (COT), Sb[Sb(C₂O₄)₃].2H₂O (AOD), and La[La(C₂O₄)₃].9H₂O (LON)

COT	AOD	LON	Band assignments
310 sw	290 sw	–	π (out-of-plane bending)
400 w	375 m	360 m	δ (O–C=O)
480 m	460 m	460 m	δ (O–C=O) and/or ring deformation
–	515 m, 545 m	540 m	ν (M–O) and/or ν (C–C)
600 m	610 S	610 s	Crystal water
660 m	–	730 s	Co-ordinated water
790 S	800 S	800 mS	ν (M–O) and/or δ (O–C=O)
900 m	910 m	–	ν_{sy} (C–O) and/or δ (O–C=O)
1320 S, 1280 sh	1300 S, 1350 m	1320 S, 1370 sh	ν_{sy} (C–O) and/or δ (O–C=O)
1470 vs, 1500 vs	1420 s, 1470 vs	1480 vs	ν_{sy} (C–O) and/or ν (C–C)
1640 Sb	1650 S, 1630 sh	1640 Sb	δ_{sy} (H–O–H)
1440–1920 b	1520–1720 b	1440–1800 b	ν_{asy} (C=O)
–	1740 mS	–	ν_{asy} (C=O)
2800–4000 Sb (split into 3080 s, 3260, 3360 s, 3480 s)	3000–3680 S (sharp)	2800–4000 Sb (peak at 3360)	ν_{sy} (O–H)+ ν_{asy} (O–H) or hydrogen bonding

s, small; vs, very small; w, weak; m, medium; S, strong; b, broad; sh, shoulder.

the region of 500–550 cm⁻¹, instead there was a sharp band at 790 cm⁻¹ due to $\nu_{\text{M-O}}$ coupled with δ (O–C=O). The strong band at 610 cm⁻¹ in AOD is assumed to be due to the coordinated water instead of the water of crystallisation as found in other compounds. However, thermal study confirmed the presence of coordinated water. The presence of lattice water also cannot be neglected [38] since there is bands at about 3000–3600 cm⁻¹ and 1650 cm⁻¹. The splitting of the broad band 2800–4000 cm⁻¹ into small peaks at 3080 s, 3260, 3360 and 3480 cm⁻¹ can be seen in COT as reported elsewhere [39]. The electronic spectrum of the solid sample of COT absorbs at 16 900, 20 000, 27 390 cm⁻¹ due to spin-allowed transitions. The bands at 39 680 and 46 500 cm⁻¹ in the UV region are due to M→L or L→M and to $\pi \rightarrow \pi^*$ transition, respectively. The bands in the UV region of AOD are due to intraligand $\pi \rightarrow \pi^*$ transition. In case of LON the f–f transition bands are observed at 20 000, 23 800, 27 390 cm⁻¹, whereas the band at 39 210 cm⁻¹ due to ligand–metal charge transfer [40]. The band observed at 46 500 cm⁻¹ is due to $\pi \rightarrow \pi$ transition.

The weight loss–temperature profile of COT in air can be seen in Fig. 1. Weight loss starts very slowly at 40°C and at around 128°C there is an inflexion corresponding to 4% weight loss, indicating the removal of the first molecule of water. This inclined weight loss completes at 190°C with 14% weight loss indicative of loss of the two and half molecule of water. The

removal of last traces of water and formation of a completely anhydrous species occurs at 310°C in TG with 16% mass loss. The theoretical mass loss for this is 16.36%. The last traces of water is removed over a long temperature range. Changes observed in DTG profile (Fig. 1) with peak temperature of 160°C as well as endotherm in DTA curve between 108°C and 190°C ($\Delta T_{\text{min}}=142^\circ\text{C}$) corresponds to the dehydration step. There is a slight exothermic process observed in the DTA curve from 190°C to 348°C but there is no change in DTG indicating that there is some phase changes or changes in crystallinity of the species. This might also be due to the transition [41] of the anhydrous compound from the amorphous state to crystalline state along with some partial decomposition of the C₂O₄²⁻ group. The very slow weight loss within the temperature range and 18% mass loss around 392°C indicates some partial decomposition of anhydrous species. In DTG a shoulder is present at 392°C along with main changes (peak temperature, 410°C) supports the partial decomposition. A small exothermic peak at 390°C in the DTA corroborated the formation of a transient intermediate as it is immediately transform to subsequent product in TG. The 18% weight loss at 392°C is consistent with the generation of Cr[Cr(C₂O₄)_{2.9}]. Similar partial decomposition of C₂O₄²⁻ has been reported [11,18,29]. The decrease in weight continues up to 426°C with a break in the weight loss at 22% and then suddenly vertical steep curve up to 436°C with 34%

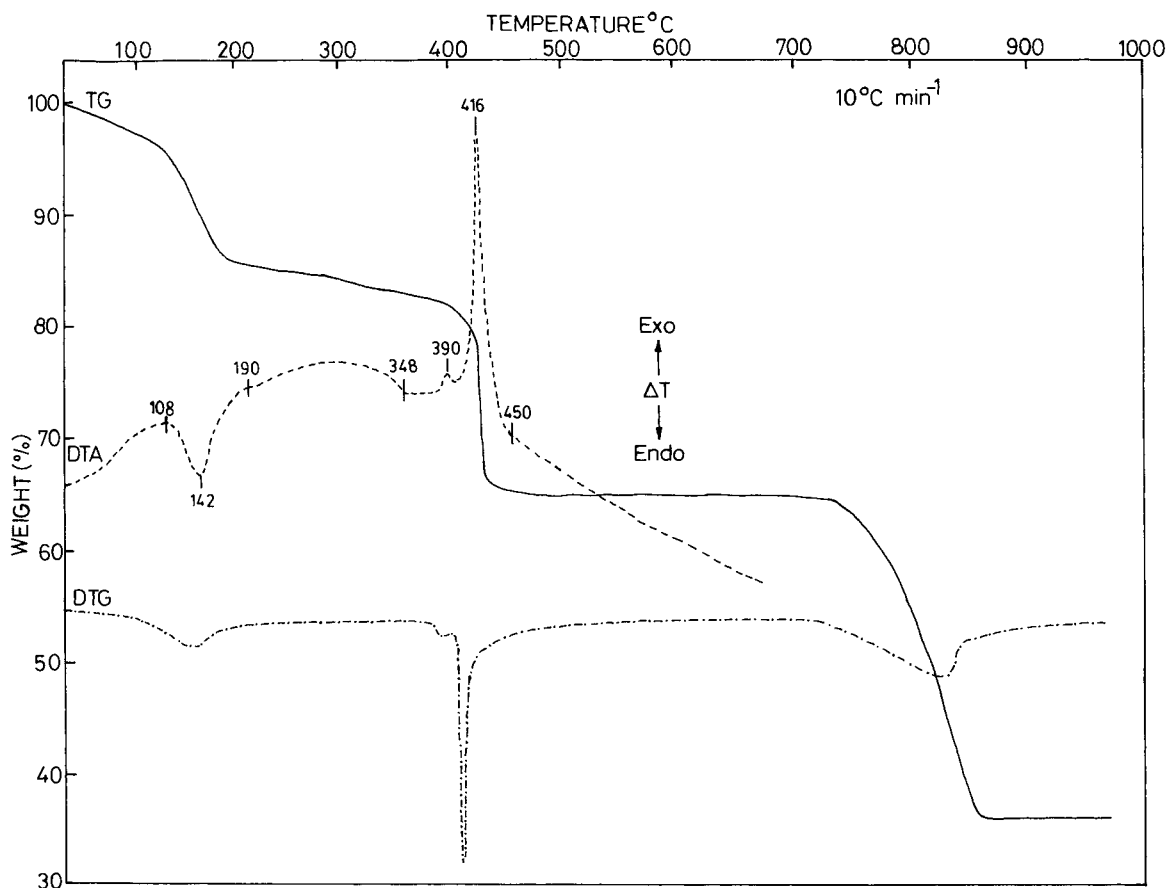


Fig. 1. TG, DTG and DTA curve of $\text{Cr}[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 4\text{H}_2\text{O}$ in air.

mass loss was observed. Subsequently, at 460°C with 35% mass loss indicative of formation of a product which is completely stable up to 679°C . A further 1% weight loss occurred very slowly up to 740°C with an overall weight loss of 36%. We tried to isolate the intermediates formed at 392°C and 426°C by temperature arrest technique but could not succeed. Instead, we isolated a yellowish compound. The weight loss was measured to be 35% which was formed in TG at 460°C . The change at 426°C , the product which was not possible to isolate is assumed to be $\text{Cr}[\text{Cr}(\text{C}_2\text{O}_4)_{2.7}]$ (theoretical weight loss, 22.42%). As with work reported [7,19], involving an intermediate binuclear complex, $[(\text{C}_2\text{O}_4)_2\text{Fe}(\text{II})-(\text{C}_2\text{O}_4)-\text{Fe}(\text{II})(\text{C}_2\text{O}_4)_2]^{6-}$, formation of the similar species in our study could not be ruled out for the intermediate at 392°C and 426°C . The reduction [22] of trivalent to divalent chromium by $\text{C}_2\text{O}_4^{2-}$ group

seems to be sufficiently competent in this context, consequently the usual process of partial decomposition through C–O bond breaking may occur. The possibility of electron transfer in some other metals was also reported by Nagase [22]. We isolated a species by pyrolysis in air at 320°C with weight loss of 17%. The elemental, analytical, IR and electronic spectral studies revealed that the species was anhydrous. The coordinated oxalato group was retained. Kinetic parameters calculated using five non-mechanistic equations [32–36] are included in Table 2. An exothermic peak in DTA ($\Delta T_{\text{max}}=416^\circ\text{C}$) as well as a sharp change in DTG up to 475°C with peak around 410°C are displayed. These are corresponding to the formation of product with 35% mass loss at 460°C in TG. The high stability of the product and the observed mass loss apparently indicate that the compound might be a mixture of Cr_2O_3 and CrC_2O_4 .

Table 2
Kinetic data evaluated by different methods

Compound	Step	Method	E^* (kJ mol ⁻¹)	log Z	ΔS^* (e.u)	Order of reaction	A (s ⁻¹)	Reaction
COT	1	a	10.42			0.4		Dehydration
		b	–					
		c	12.43			0.5		
		d	15.56				2.69 × 10 ⁵	
		e	13.59				2.20 × 10 ⁴	
	2	a	143.59			0.1		Decomposition
		b	–					
		c	153.18			0.5		
		d	79.79				1.69	
		e	87.74				1.02 × 10 ¹²	
		a	59.16			0.4		Decomposition
		b	–					
3	c	143.59			0.5			
	d	43.47				9.97 × 10 ⁴		
	e	55.61				2.87 × 10 ⁷		
	a	90.08			0.8		Decomposition	
	b	182.51	17.36	11.16				
AOD	1	c	259.49			1.0		
		d	161.25				1.87 × 10 ⁸	
		e	161.46				1.13 × 10 ²²	
		a	164.09			0.2		Decomposition
		b	–					
	2	c	136.57			2.0		
		d	16.15				1.70 × 10 ⁸	
		e	10.62				1.67 × 10 ³	
		a	13.85			0.1		Dehydration
		b	–					
LON	1	c	17.32			1.5		
		d	19.16				2.96 × 10 ³	
		e	19.62				1.09 × 10 ⁶	
		a	131.00			0.8		Decomposition
		b	127.65	8.89	-7.985			
	2	c	46.11			1.0		
		d	53.03				4.76 × 10 ²	
		e	50.67				3.11 × 10 ²	
		a	109.41			0.2		Decomposition
	3	b	–					
		c	105.31			2.0		
d		208.86				1.43 × 10 ³		
		e	201.00			1.82 × 10 ⁵		

(a) Freeman and Carroll; (b) Modified Freeman and Carroll; (c) Flynn and Wall; (d) Coats and Redfern and; (e) MacCallum–Tanner equation.

The theoretical weight loss for this is 33.69%. The assumed mixture is suggestive of the fact that the inner chromium in the complex might be reduced to CrC₂O₄ either by the evolved CO(g) or through charge transfer, and outer chromium to Cr₂O₃. Similar conclusion has been drawn earlier [19,22]. The formation of Cr(II)(C₂O₄)₂²⁻ was reported [22] from the decomposition of Cr(III)(C₂O₄)₃³⁻. Further decomposition

of the mixture started at 740°C. It can be inferred that the high stability of chromium oxalate has occurred only in the presence of oxide of the metal. Other simple metal oxalates [1,5] generally decompose at lower temperature. Our earlier study showed [18] that the stability was increased to a bit higher temperature in presence of oxide but not up to the mark of chromium oxalate. Than an inclined slope in TG up

to 858°C with 64% weight loss was observed. The residue might be Cr_2O_3 (calculated weight loss is 65.48%). The DTG profile displayed a change between 718°C and 865°C for this step. DTA was done up to 700°C only. The possibility of trace amount of CrO in the residue cannot be neglected as $\text{Cr}(\text{C}_2\text{O}_4)_2^{2-}$ decomposes [22] to CrO by C–O bond breaking. CrO immediately oxidised in air to Cr_2O_3 . Kinetic parameters calculated for this final decomposition step are shown in Table 2. The DSC profile in nitrogen up to 670°C can be seen in Figs. 2–4. The profile showed an endothermic peak between 136.8°C and 233.2°C for dehydration process. Peak between 425.6°C and 503.6°C is accounted for the first decomposition step. For the final step the change could not be recorded as scanning was done up to 670°C. The

corresponding kinetic parameters are shown in Tables 3 and 4. It is observed that the E^* calculated (Table 2) using kinetic equations for dehydration and first step decomposition are much lower than the values obtained from DSC. The weight loss of annealed sample up to 670°C was 33.65%. It suggests the formation of a mixture of Cr_2O_3 and CrC_2O_4 similar to TG study in air. It could be ascribed that the pattern of decomposition both in air and nitrogen is similar in case of chromium(III)tris(oxalato)chromate(III)tetrahydrate; generally it varies in case of other compounds. However, same end product, Cr_2O_3 was reported both in air and N_2 by Dollimore et al. [1] in their study. Kinetic parameters of the final decomposition step calculated using kinetic equations are included in Table 2.

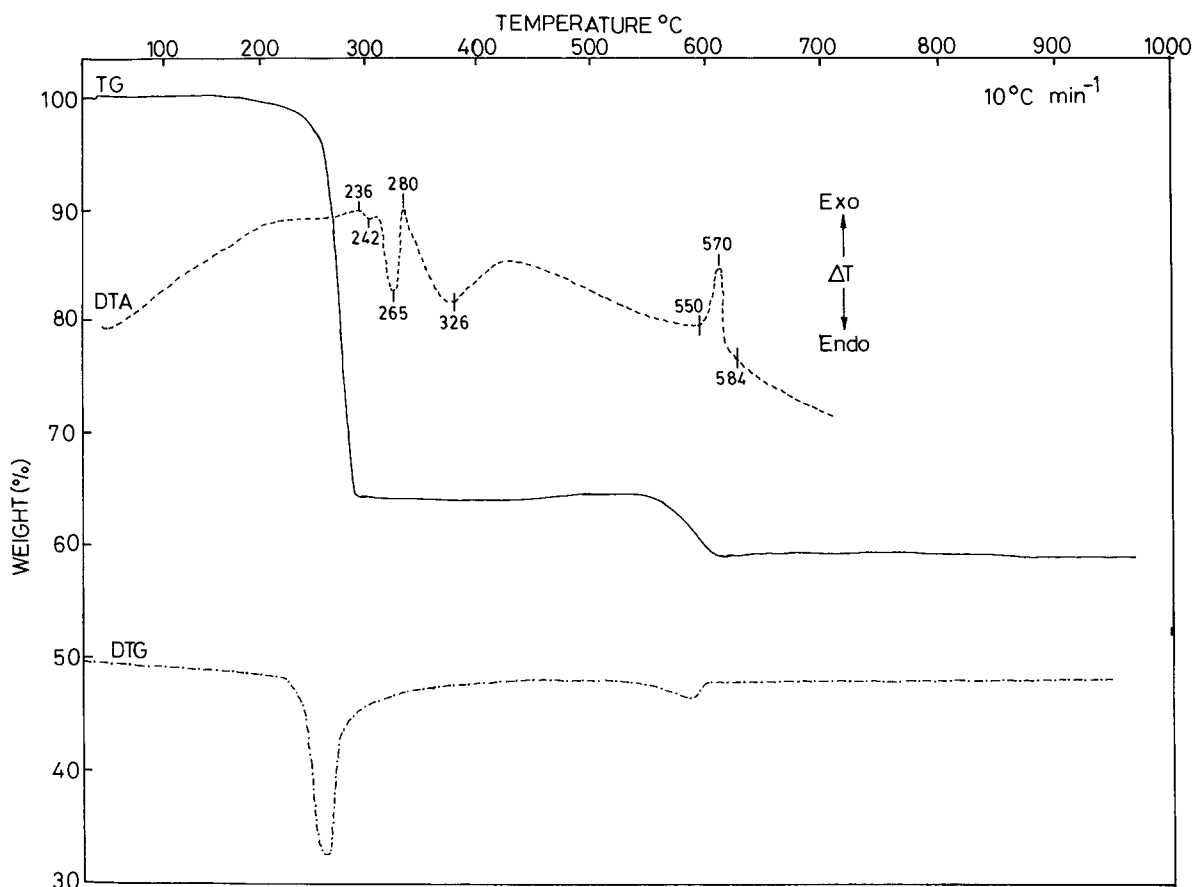


Fig. 2. TG, DTG and DTA curve of $\text{Sb}[\text{Sb}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$ in air.

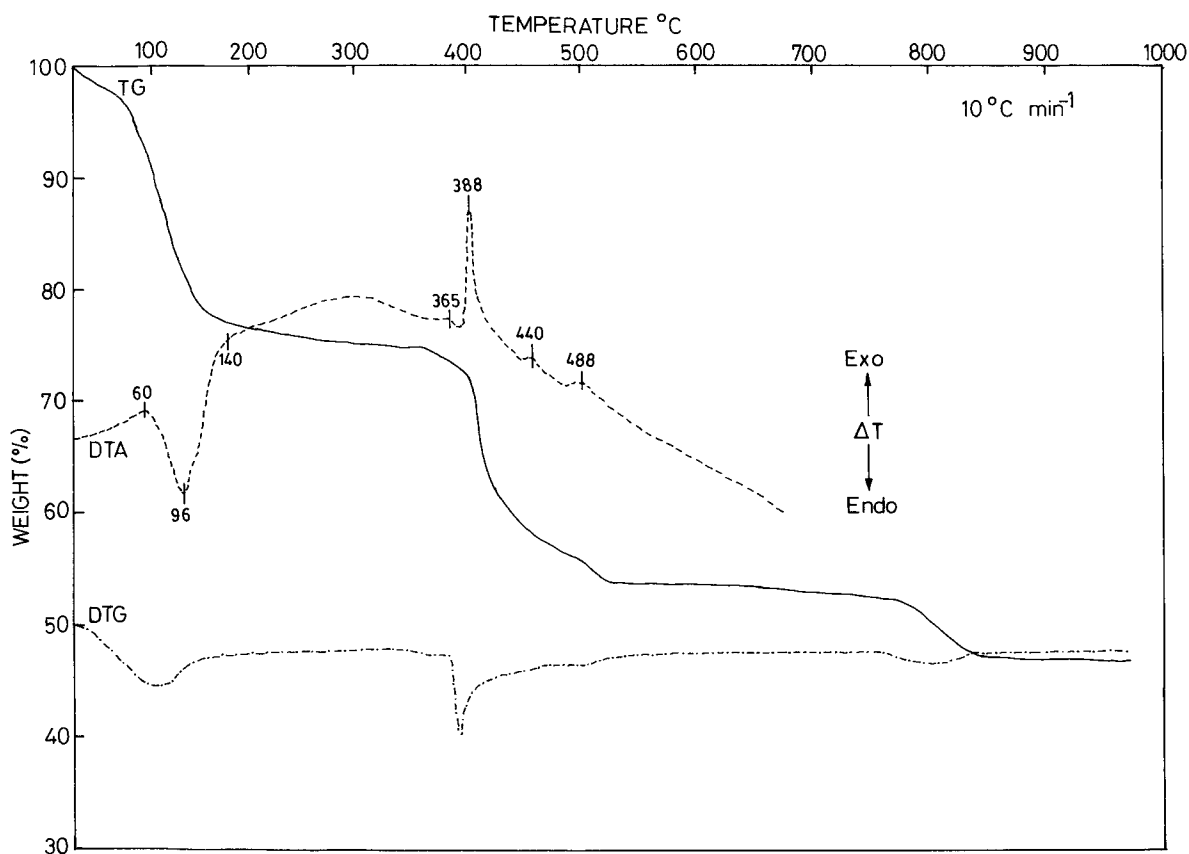
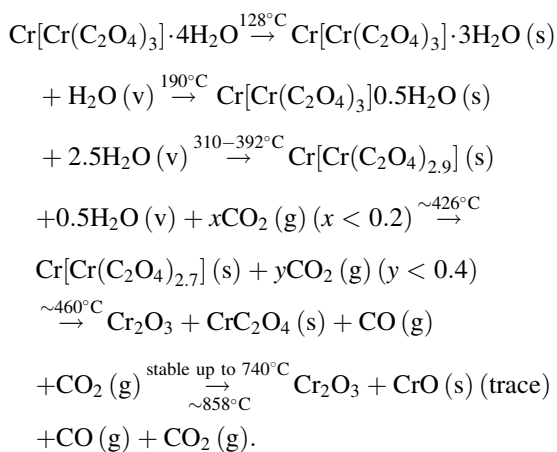


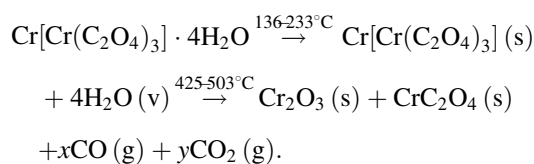
Fig. 3. TG, DTG and DTA curve of $\text{La}[\text{La}(\text{C}_2\text{O}_4)_3] \cdot 9\text{H}_2\text{O}$ in air.

Above studies suggest the following tentative mechanism for the thermal decomposition in air and nitrogen.

In air,



In nitrogen,



In thermal study of AOD in air, the weight loss starts from high temperature, 170°C in TG curve (Fig. 2). Then a steep slope up to 290°C with 36% weight loss indicates the removal of both the water molecules and some decomposition of the compound. The removal of water at high temperature indicates the coordination with Sb(III) atom as well as hydrogen bonding with coordinated oxalato group. The weight loss at 290°C apparently suggests that the compound might be $(\text{SbO})_2\text{C}_2\text{O}_4$. Corresponding to the above step, in DTG trace a sharp change between 225°C and 335°C is displayed. An endothermic peak in DTA

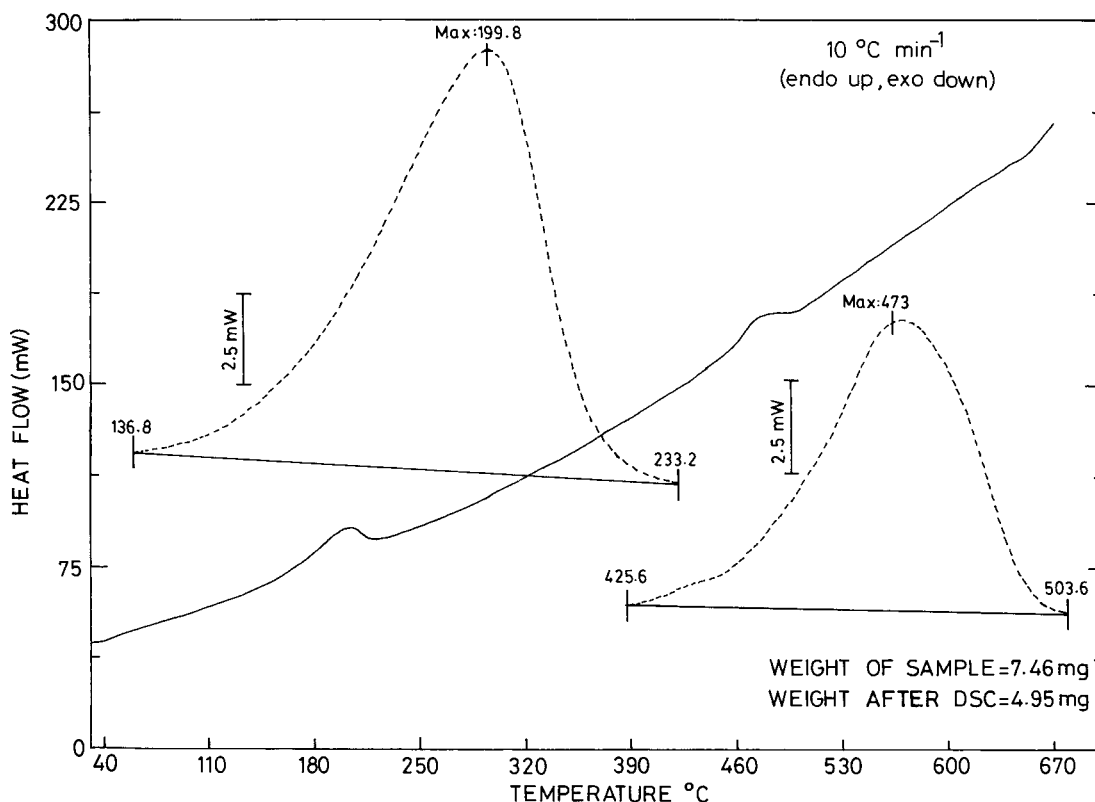


Fig. 4. DSC curve of $\text{Cr}[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 4\text{H}_2\text{O}$ in nitrogen.

(Fig. 2) between 236°C and 280°C ($\Delta T_{\text{min}}=265^\circ\text{C}$) with a small shoulder peak at 242°C corresponds to this decomposition. Kinetic parameters for the step are included in Table 2. The reaction is found to be first order. The mixture produced at 290°C is almost stable up to 550°C followed by an inclined slope up to 610°C in TG. This corresponds to the weight loss (found 41%; calculated, 40.52%) which suggests the formation of Sb_2O_5 . The residue is stable up to 970°C in TG. The estimated antimony content (found 76.6%; calculated, 75.27%) and powder XRD pattern of the residue confirmed it to be Sb_2O_5 . Corresponding to this step, the DTA curve showed an exotherm between 550°C and 584°C ($\Delta T_{\text{max}}=570^\circ\text{C}$) and in DTG a change with peak temperature of 588°C . The slight exothermic nature of the DTA curve between 326°C and 550°C might [11] be due to some phase changes or changes of crystallinity in the intermediate, $(\text{SbO})_2\text{C}_2\text{O}_4$, as well as due to some oxidation of $\text{CO}(\text{g})$ to $\text{CO}_2(\text{g})$. Kinetic parameters calculated for

the final step may be seen in Table 2. The AOD, when subjected to DSC study in N_2 (Fig. 5) up to 670°C displayed a sharp endothermic peak between 250.7°C and 309.2°C . This peak corresponds to the first step decomposition. Kinetic parameters are included in Table 3. The profile displayed another flat endothermal change between 430°C and 528.6°C which could be correlated with the second step decomposition in TG study. This flat endothermal nature manifests over a wide temperature range. However, the relevant temperature scale is much lower than the corresponding exothermal change in DTA, which in turn, indicates that the change in DSC is not a major decomposition step. The low values of kinetic parameters also suggests that the decomposition behaviour in N_2 does not comply with air. The weight loss observed at the end of scanning up to 670°C is 51.16%; indicative of the formation of a species which is not similar to the product formed at 670°C in TG. This implies that the atmosphere plays an important

Table 3
DSC data of Cr[(C₂O₄)₃]4H₂O (COT), Sb[Sb(C₂O₄)₃]·2H₂O (AOD) and La[La(C₂O₄)₃]·9H₂O (LON) in nitrogen at 10°C min⁻¹

Compound	Step	Temperature range (°C)	Peak temperature (°C)	ln <i>k</i> ₀	<i>E</i> [*] (kJ mol ⁻¹)	Δ <i>H</i> (kJ mol ⁻¹)	Δ <i>S</i> (JK ⁻¹ mol ⁻¹)	Heat of fusion (kJ mol ⁻¹)	Order of reaction	Reaction
COT	1	136.8–233.2 (endo.)	199.8	32.40 (±0.69)	143.4 (±3.09)	139.27	294.69	182.97	1.14 (±0.02)	Dehydration
	2	425.6–503.6 (endo.)	473	64.31 (±1.38)	426.8 (±9.21)	85.98	115.13	114.93	1.08 (±0.02)	Decomposition
AOD	1	250.7–309.2 (endo.)	294	71.67 (±1.54)	355.48 (±7.67)	129.09	227.68	157.73	1.02 (±0.02)	Decomposition
	2	430.0–528.6 (endo.)	487.9	35.21 (±0.76)	252.96 (±5.46)	27.02	35.51	35.97	1.02 (±0.02)	Decomposition
LON	1a.	85.7–184.9 (endo.)	138.5	26.00 (±0.56)	104.95 (±2.26)	308.39	749.25	37.19	1.23 (±0.02)	Dehydration
	1b	145.0–164.0 (endo.)	155.0	124.46 (±2.68)	453.8 (±9.8)	9.56	22.36	–	1.17 (±0.02)	Decomposition
	2	399.8–477.2 (endo.)	423.2	41.04 (±0.88)	270.15 (±5.83)	93.52	134.56	158.57	1.11 (±0.02)	Decomposition
	3	588.0–651.6 (endo.)	615.0	112.43 (±2.42)	865.32 (±18.69)	162.93	183.49	205.55	1.42 (±0.03)	Decomposition

Table 4

Prominent lines in the X-ray powder diffraction pattern of $\text{Cr}[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 4\text{H}_2\text{O}$, $\text{Sb}[\text{Sb}(\text{C}_2\text{O}_4)_3]\cdot 2\text{H}_2\text{O}$ and $\text{La}[\text{La}(\text{C}_2\text{O}_4)_3]\cdot 9\text{H}_2\text{O}$

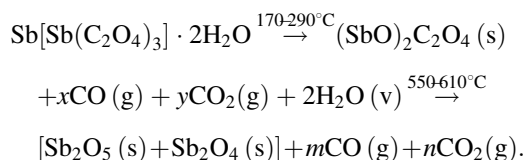
$\text{Cr}[\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 4\text{H}_2\text{O}$		$\text{Sb}[\text{Sb}(\text{C}_2\text{O}_4)_3]\cdot 2\text{H}_2\text{O}$		$\text{La}[\text{La}(\text{C}_2\text{O}_4)_3]\cdot 9\text{H}_2\text{O}$	
D (Å)	I (REL)	D (Å)	I (REL)	D (Å)	I/I ₀ (REL)
11.623	62.53	12.198	80.03	13.710	46
10.644	69.17	11.565	88.66	6.736	72
9.817	64.67	10.730	93.73	6.611	73
8.750	65.85	9.838	100.00	5.665	50
6.752	42.62	9.374	96.42	5.249	53
6.411	100.00	8.660	82.71	5.013	57
3.880	21.01	3.266	47.02	4.798	100
3.798	23.56	2.925	20.99	4.355	45
3.055	18.40	2.492	6.62	4.262	41
2.427	11.36	2.416	5.20	4.051	35
2.402	12.62			3.543	35
				3.448	31
				3.060	36
				2.868	26
				2.815	35
				2.684	23
				2.627	35
				2.506	21
				2.378	23
				2.328	35
				2.296	20
				2.255	23
				2.050	22
				2.030	24

role in decomposition. The first step in DSC might be accounted for the formation of the intermediate, Sb_2O_5 , which is converted [42] to Sb_2O_3 above 450°C . The flat change might be responsible for the step of reduction from Sb(V) to Sb(III). This might also take place with action of $\text{CO}(\text{g})$ evolved during decomposition. The calculated weight loss to get Sb_2O_3 is 46.40%, but the DSC implies the mass loss at 670°C is 51.15%. The presence of metallic antimony which gradually formed along with trace amount of antimony trioxide due to the reduction of Sb_2O_5 by evolved $\text{CO}(\text{g})$ cannot also be ignored. Two small exothermic peaks at ca. 590 and $\sim 655^\circ\text{C}$ further substantiate the reduction phenomena. Further, the possibility of the presence of carbon could be considered due to disproportionation of $\text{CO}(\text{g})$. The weight loss at the end of the scanning also supports the formation of Sb_2O (theoretical weight loss is 52.28%). Moreover, the same residue has been reported as an end product from $(\text{SbO})_2\text{C}_2\text{O}_4$ in N_2

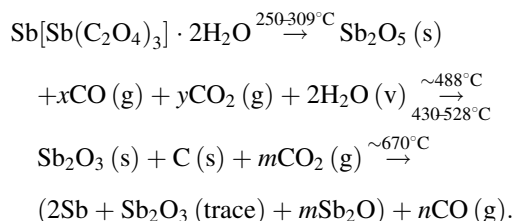
by Dollimore et al. [1] and was assumed to be a mixture of Sb and SbO .

The tentative mechanism of the thermal decomposition of AOD in air and nitrogen is suggested in the following. The formation of $\text{CO}(\text{g})$ at the end in the proposed scheme in nitrogen is suggested due to reducing action of carbon on Sb_2O_3 at high temperature; the remaining trace amount of Sb_2O_3 might be in polymeric structure [42].

In air,



In nitrogen,



The compound, LON, starts to lose weight from beginning and an inclined slope up to 175°C in TG (Fig. 3) with a weight loss of 23% (calculated, 23.03%) indicates the formation of a complete anhydrous species. An endothermic peak at 60 – 140°C ($\Delta T_{\text{min}} = 96^\circ\text{C}$) in DTA (Fig. 3) and a change between 42°C and 160°C in DTG curve are for the dehydration step. Kinetic parameters of this step are included in Table 2. The anhydrous species starts to lose weight gradually over a long temperature range in TG and about 25.3% weight loss at 360°C apparently indicates the partial breaking of $\text{C}_2\text{O}_4^{2-}$ group. At 404°C , a break in the TG curve with 28% weight loss produced a transient intermediate, $\text{La}[\text{La}(\text{C}_2\text{O}_4)_x]$ (where $2.5 < x < 3$) with partial decomposition, which could be assumed as $\text{La}[\text{La}(\text{C}_2\text{O}_4)_{2.5}]$ (found 28%; calculated, 29.28%). Usha et al. [29] reported the removal of all the nine water molecules between 50°C and 250°C in $\text{LaCo}(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ along with some partial decomposition of oxalato group. The exothermic nature of DTA profile in the range 140 – 365°C supports this partial decomposition. The intermediate immediately produced a stable product at 526°C in TG (46%

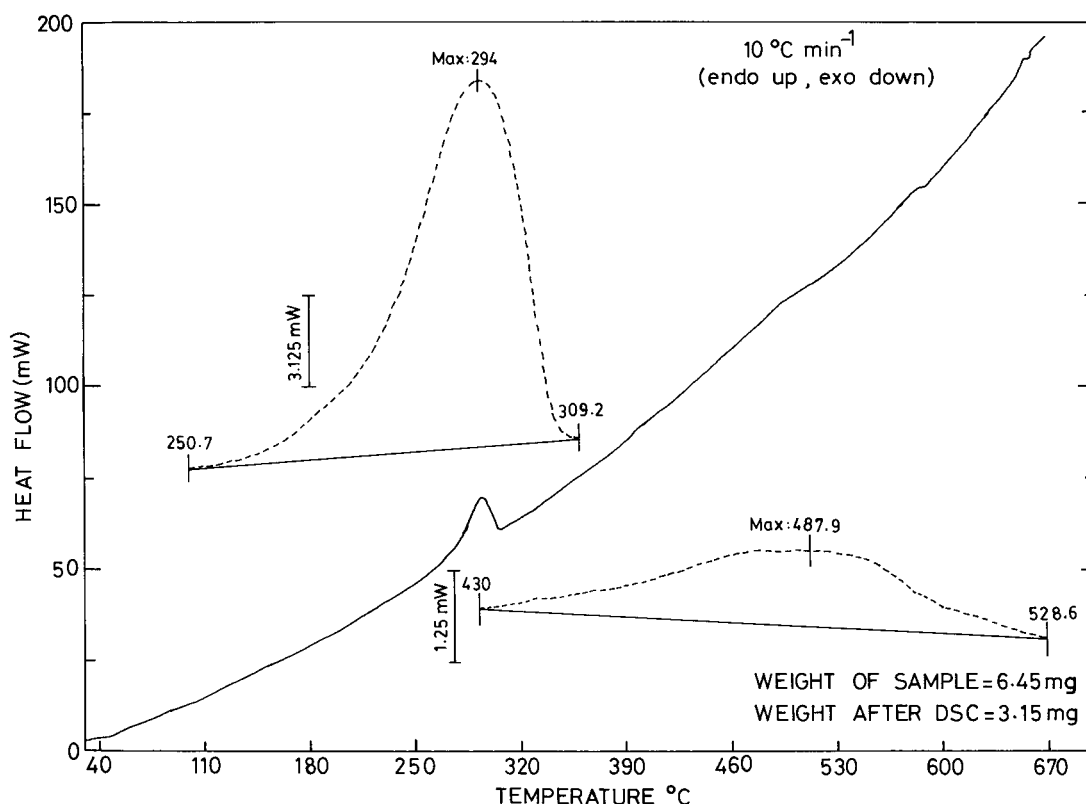


Fig. 5. DSC curve of $\text{Sb}[\text{Sb}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$ in nitrogen.

weight loss) through a break at $\sim 494^\circ\text{C}$ (44% weight loss). This break suggests the formation of a transient intermediate oxycarbonate, $\text{La}_2\text{O}(\text{CO}_3)_2$ (theoretical weight loss is 42.93%) which is immediately decomposed to dioxycarbonate, $\text{La}_2\text{O}_2\text{CO}_3$ at 526°C (theoretical weight loss is 47.47%). The slight difference of weight loss observed with theoretical value might be due to the presence of trace of oxycarbonate with $\text{La}_2\text{O}_2\text{CO}_3$. However, the product is not totally stable in long temperature range; a further gradual weight loss of $\sim 2\%$ occurs up to 776°C with a weight loss of 48% indicative of the formation of complete $\text{La}_2\text{O}_2\text{CO}_3$. Similar compound was reported by Dharwadkar et al. [27]. However, they only reported $\text{La}_2\text{O}_2\text{CO}_3$. The possibility of the formation of $\text{La}_2\text{O}(\text{CO}_3)_2$ was not indicated in their study in air, but in CO_2 both compounds were reported. In the present study, it can be assumed that the possibility of formation of $\text{La}_2\text{O}(\text{CO}_3)_2$ as an intermediate in air which, in turn, is contaminated with CO_2 , obtained from decomposition of the precursor and dispropor-

tionation of $\text{CO}(\text{g})$; as the study was done in static air. Corresponding to above changes, in DTG curve a broad change between 340°C and 532°C with some breaks is displayed. The DTA profile shows a sharp exotherm with ΔT_{max} of 388°C followed by two very small exothermal changes at ~ 440 and $\sim 488^\circ\text{C}$. These could be accounted for the decomposition and also suggest [11] the solid–solid interaction or some phase changes or changes of crystallinity i.e. hexagonal to tetragonal [27] in the product before generating a quite stable residue. Finally, from 776°C to 838°C a sharp inclined slope in TG indicates the formation of a stable product, La_2O_3 (mass loss found 53%; calculated, 53.72%). The DTG change from 760 – 845°C is accounted for the final change. The oxide is stable up to 1000°C . The pyrolysed product at 900°C in furnace was isolated. The colour is greyish white and the observed weight loss was 47%. The powder XRD pattern of the species are given in Table 5. The difference between the observed (pyrolysed product) and calculated weight losses (calcu-

Table 5

Prominent lines with d-spacing and intensity of the calcined products of $\text{Sb}[\text{Sb}(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$ (AOD) at 630°C and of $\text{La}[\text{La}(\text{C}_2\text{O}_4)_3] \cdot 9\text{H}_2\text{O}$ (LON) at 650°C and 900°C

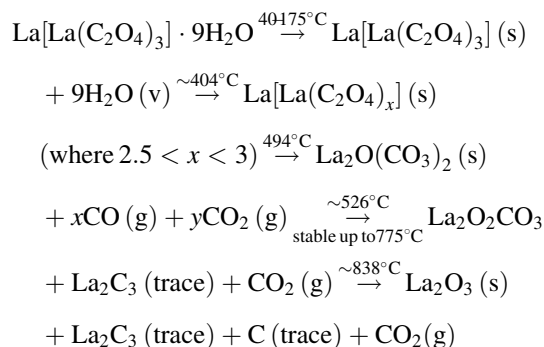
Product of AOD at 630°C		Product of LON at 650°C		Product of LON at 900°C	
D (Å)	I/I ₀ (REL)	D (Å)	I/I ₀ (REL)	D (Å)	I/I ₀ (REL)
5.951	25	6.839	37	6.839	34
3.442	35	6.133	35	6.397	36
3.107	20	5.424	33	5.683	45
2.982	96	3.936	28	5.158	32
2.941	45	3.034	39	3.280	33
2.925	21	2.914	21	3.205	30
2.650	24	2.873	19	2.833	16
2.567	32	2.351	13	2.288	19
2.416	6	2.260	14	2.147	12
1.862	25	2.197	14	1.878	19
1.799	24	2.068	12	1.709	8
1.722	20	2.043	14	1.663	9
1.553	30	1.954	11	1.623	9
1.487	13	1.774	12	1.597	8
1.478	10	1.748	11		
1.442	8	1.683	11		
1.287	4				
1.150	8				
1.052	6				

lated 53.72% for La_2O_3) may be due to the presence of residual free unoxidised carbon along with La_2O_3 [43]. It might also be due to the formation of trace amount of LaC_2 /or La_2C_3 at high temperature. The data in Table 5 suggest the presence of La_2C_3 along with the main product La_2O_3 in calcined residue. Interestingly, prior to the final decomposition product, the isolated calcined product at 650°C in furnace (48.62% weight loss) confirmed the presence of trace amount of carbon, which, in turn, got converted to carbides along with $\text{La}_2\text{O}_2\text{CO}_3$. Powder XRD data (Table 5) provide the evidence for the above conclusion. The calculated kinetic parameters for the first and second decomposition steps are included in Table 2. In the thermal profile of DSC (Figs. 5 and 6) in nitrogen clearly shows the different decomposition behaviour from air. Large endotherm between 85.7°C and 184.9°C with a shoulder change, around 155°C is for dehydration. We enlarged the endotherm for kinetic analysis by changing the heat flow axis, the overlapping shoulder splits into ca. 151°C and 156°C, which indicated the removal of water in stepwise fashion in N_2 . The demarcated area between 145

and 164°C including two shoulder changes was subjected to kinetic analysis, and data are included in Table 3. The low value of ΔH and ΔS for the shoulder peak during the removal of water might be considered as a suggestive of the transition of the compound from amorphous to crystalline state. The E^* seems to be quite high in comparison to both the whole dehydration, and the first decomposition step, indicative of the slow process of transition. The ΔH value of only 1.4 kcal mol⁻¹ has been reported [41] for this type of transition. Kinetic parameters for the whole dehydration process are given in Table 3. The study suggests that the anhydrous species is formed both in nitrogen and air approximately at similar temperatures. The further DSC profile shows (Fig. 6) three different sharp changes (endotherm) within range of 399.8–651.6°C. The first endotherm between 399.8°C and 477.2°C indicates some changes or formation of an intermediate followed by last endotherm at 588–651.6°C, which suggests further decompositions. The weight loss at the end of the scanning up to 670°C is 34.38%. This indicates that the compound might be $\text{La}_2(\text{CO}_3)_3$ (Theoretical weight loss is 34.97%). The anhydrous species with some partial decomposition might be formed corresponding to the step at 399.8–477.2°C with some physical changes supported by two very small endotherms around 535°C and 563°C in the range of 514–587°C. Kinetic parameters of both the decomposition steps are recorded in Table 3. The values of E^* and $\ln k_0$ increase from dehydration to decomposition whereas ΔH seems to be dependent on the area of the endotherm of the respective changes.

The above results suggest the following tentative scheme for the thermal decomposition of LON in air from TG and in nitrogen from DSC studies.

In air,



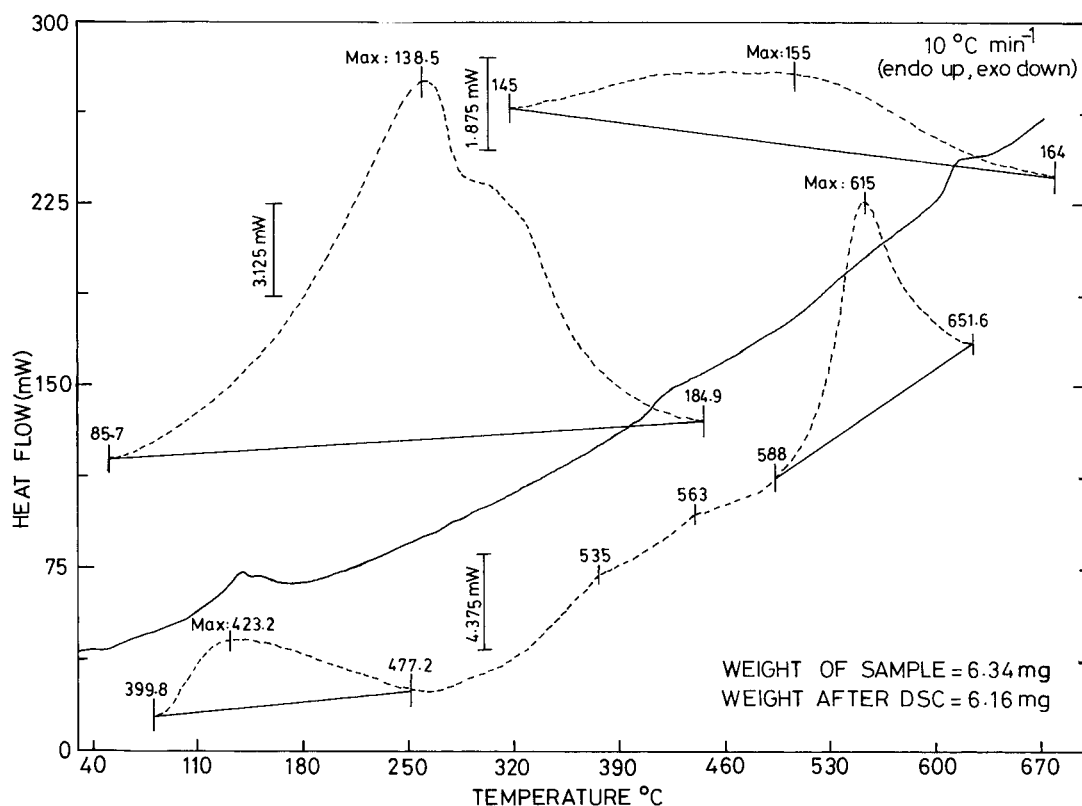
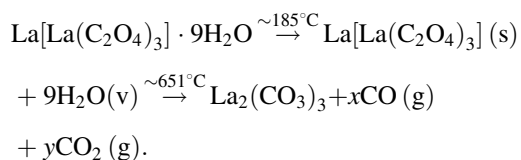


Fig. 6. DSC curve of $\text{La}[\text{La}(\text{C}_2\text{O}_4)_3] \cdot 9\text{H}_2\text{O}$ in nitrogen.

In nitrogen,



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