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Synthesis, characterization and the thermal decomposition of potassium tris(oxalato)lanthanum(III)nonahydrate

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Abstract

Potassium tris(oxalato)lanthanum(III)nonahydrate, $K_3[La(III)(C_2O_4)_3]\cdot 9H_2O$, has been synthesized and characterized by elemental analysis and IR spectral studies. Thermal studies (TG, DTG and DTA) in air showed that the anhydrous compound formed at ca. 192°C. The final end product at 1000°C was shown to be a mixture of La_2O_3, K_2CO_3, K_2O, $KLaO_2$ and La_2C_3, through the formation of an intermediate mixture of $K_2C_2O_4$ and $K[La(C_2O_4)_x]$ (where $1.5 < x < 2$) at ca. 293°C, and $K_2C_2O_4$ and $La_2O_2CO_3$ at ca. 528°C. DSC study in nitrogen upto 650°C showed that the end product was a mixture of $K_2C_2O_4$ and $La_2O_2CO_3$. The kinetic parameters, mainly E^* of the dehydration and decomposition steps in TG, were calculated using four non-mechanistic equations. The kinetic parameters, E^*, ΔH, ΔS obtained from DSC study are discussed. Some of the decomposition products were identified by IR and X-ray powder diffraction studies. A tentative mechanism for the decomposition in air is proposed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal decomposition; TG–DTA; DSC; Activation energy; X-ray diffraction

1. Introduction

A comprehensive review of oxalato complexes of transition and non-transition metals of various types and their applicability may be found elsewhere [1]. Wendlandt and George [2] studied $K_3[M(OX)_3]\cdot xH_2O$ (where M = Cr, Fe, Co and Rh) by thermogravimetry. Due to photosensitive nature these compounds, $K_3[M(OX)_3]$ (where M = Mn, Co) have also been studied by Wendlandt and Simmons [3,4], where the bivalent metal complexes of the type, $K_2[M(OX)_2]$ were formed as intermediates. The thermal decomposition of $K_3Fe(OX)_3$ in nitrogen beyond 460°C led [5] to a mixture of K_2CO_3 and free iron. Bancroft et al. [6] have also examined the thermal decomposition of $K_3[Fe(OX)_3]$ and suggested the presence of $K_6[(C_2O_4)_2Fe(OX)Fe(C_2O_4)_2]$ (OX = quadridentate oxalato group) as intermediate. The final residue of thermal decomposition of $K_3[Al(OX)_3]$ has been reported [7] as a mixture of Al_2O_3, K_2CO_3 and K_2O. The thermal decomposition reactions of a number of metal oxalato complexes of potassium of the type, $K_3[M(OX)_3]\cdot xH_2O$ (where M = Al, V, Cr, Mn, Fe, Co, Rh) and $K_2[M(OX)_2]\cdot xH_2O$ (where M = Cu, Zn, Pd, Pt) were studied [8] in helium atmosphere. The decomposition pattern of all the complexes were compared. The thermolysis of alkali tris(oxalato/malonato)ferrates(III) have been studied [9,10], where the decomposition mode in both the precursors,

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$M_3[Fe(C_2O_4)_3]\cdot xH_2O$ and $M_3[Fe(CH_2C_2O_4)_3]\cdot xH_2O$ (where M = Li, Na, K) are similar. Due to complexing ability and oxidation state sensitivity, the iron carboxylates of alkali metal are used as inorganic precursors for the preparation of ferrites. Although, the potassium bis/tris(oxalato)metallates of various types have been studied, the complexes with lanthanum are still scarce. Therefore, in continuation of our work on oxalato complexes [11–16] as well as the recent work [17] on the type $M_3[La(C_2O_4)_3]\cdot xH_2O$ (where $x = 9$ for M = Li and $x = 8$ for M = Na), the thermal decomposition of hitherto unknown potassium tris-(oxalato)lanthanum(III)nonahydrate has been undertaken. Keeping in view the possibility of formation of metal oxide or mixed metal oxide and their possible catalytic applicability, the study reveals the importance of the thermal decomposition mode of precursor to obtain the desired end product. This communication reports the synthesis, characterization and the thermal decomposition of potassium tris(oxalato)-lanthanum(III)nonahydrate, $K_3[La(C_2O_4)_3]\cdot 9H_2O$, in air and nitrogen. The kinetic parameters of each step of the decomposition are calculated and a tentative scheme of the decomposition is also proposed.

2. Experimental

The chemicals used were of A.R. grade purity. The preparative method is an extension of the methods adopted [11–16] for bimetallic oxalato complexes. Lanthanum hydroxide, prepared from lanthanum chloride, was made free from chloride. It was dissolved in glacial acetic acid and heated on a steam bath. Then stoichiometric quantities of a solution of potassium chloride was added. A white compound was precipitated by dropwise addition of hot saturated solution of oxalic acid. The compound was filtered off and purified by standard procedures [18]. The water contents were determined gravimetrically [18] and thermogravimetrically. The metal contents were estimated by a literature method [16]. Carbon and hydrogen contents were estimated on a Carlo–Erba 1108 elemental analyser.

IR spectra, thermal data (DTA, TG, DTG and DSC) and X-ray powder diffraction patterns were recorded as described earlier [16].

3. Results and discussion

3.1. Characterization of complex

The complex, $K_3[La(III)(C_2O_4)_3]\cdot 9H_2O$, is obtained as a white powder. It is insoluble in water or in common organic solvents, but decomposes in strong acid or alkali. The water analysis revealed that the compound contains nine molecules of water. The microanalytical data and estimated metal contents show good agreement for the proposed formula of the complex. The IR peaks are assigned (Table 1) like earlier studies [11–18,33], which shows the presence of a chelated $C_2O_4^{2-}$ group.

3.2. Decomposition of complex

The thermal profiles (TG, DTG and DTA) of $K_3[La(III)(C_2O_4)_3]\cdot 9H_2O$, are shown in Fig. 1. In the TG curve, the first water molecule is removed at 90°C and a plateau at 167°C indicates the elimination of the remaining seven molecules of water (mass loss, found, 20.5%; calcd., 21.12%). The compound become anhydrous at ca. 192°C (found, 24%; calcd., 23.76%). Nature of DTG change between 35°C and 215°C shows the stepwise deaquation. An endothermic peak in DTA between 90°C and 180°C ($\Delta T_{\min} = 137$°C) corresponds to dehydration. The E^* (activation energy) (Table 2) of the dehydration step calculated from TG slope using non-mechanistic equations, Freeman and Carroll [19], Flynn and Wall [20], Coats and Redfern [21] and MacCallum–Tanner

Table 1
Selected bands in the IR spectrum of $K_3[La(III)(C_2O_4)_3]$ $9H_2O$

IR bands (cm^{-1})	Assignments
2880–3760b	ν_{sy} (O–H) + ν_{asy}(O–H) or hydrogen bonding
1630S	δ_{sy}(H–O–H)
1500–1800b	ν_{asy}(C=O)
1365s	ν_{sy}(C–O) and/or ν(C–C)
1320mS	ν_{sy}(C–O) and/or δ(O–C=O)
800mS	ν(La–O) and/or δ(O–C=O) or coordinated water
600s	Water of crystallization
524s	ν_{sy}(C–C) and/or ring deformation
445m, 400s	ν(La–O) and/or ring deformation
345s	δ(O–C=O)
310vs	Out-of-plane bending

b, broad; S, strong; s, small; vs; very small; m, medium.

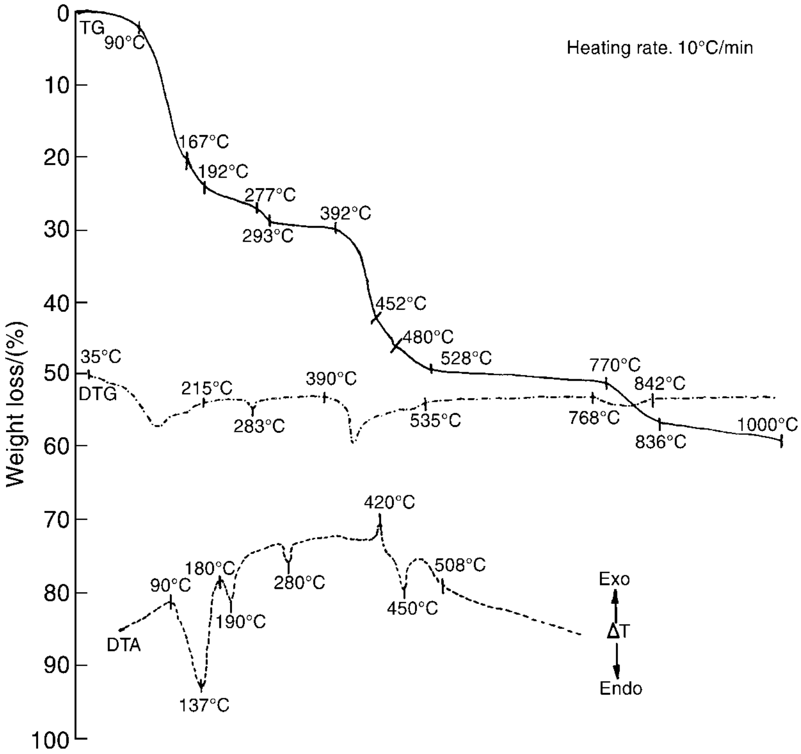

Fig. 1. TG, DTG and DTA curves of $K_3[La(III)(C_2O_4)_3]\cdot 9H_2O$ in air.

equation [22] are found to be in good agreement with each other. Further, a small endothermic peak in DTA at 190°C is due to removal of the last remaining water molecule and may be due to rearrangement of an anhydrous species which separates as $K_2C_2O_4$ and $K[La(C_2O_4)_2]$. Further, corresponding to a change at ca. 283°C in DTG and a small endotherm at 280°C in DTA, in TG a small but distinct step (277–293°C) is observed. The mass loss of 29% at 293°C apparently suggests [4] the intermediate is a mixture of

Table 2
Kinetic data evaluated by the methods, (a) Freeman and Carroll, (b) Flynn and Wall, (c) Coats and Redfern and (d) MacCallum–Tanner equation

Compound	Step	Method	E^* (kJ mol^{-1})	Order of reaction	A (s^{-1})	Reaction
$K_3[La(C_2O_4)_3]$ $9H_2O$	1	a	34.00			
		b	35.40	1.0		
		c	35.12		4.60×10^8	Dehydration
		d	34.70		3.85×10^8	
	2	a	40.16			
		b	41.00	1.0		
		c	40.00		5.17×10^6	Decomposition
		d	39.96		3.73×10^6	
	3	a	152.00			
		b	150.50	1.0		
		c	152.70		7.5×10^7	Decomposition
		d	153.60		9.6×10^8	

Table 3
X-ray powder diffraction pattern of the pyrolysed products of $K_3[La(III)(C_2O_4)_3]9H_2O$ at 340°C, 550°C and 970°C

Pyrolysed product		
d (Å) (at 340°C)	d (Å) (at 550°C)	d (Å) (at 970°C)
2.2055	2.1021	2.1238
2.1428	2.0147	2.0763
2.0016	1.9581	2.0000
1.9541	1.8822	2.0019
1.8649	1.8224	1.9468
1.7789	1.7765	1.8895
1.7083	1.7548	1.8853
1.6795	1.7001	1.8638
1.6501	1.6465	1.7837
1.6175	1.6174	1.7811
1.5727	1.5947	1.7494
1.5339	1.5731	1.6895
1.5123	1.5530	1.6486
1.4782	1.5353	1.6125
1.4572	1.4993	1.5842
1.4231	1.4838	1.5582
1.3964	1.4479	1.5131
1.3775	1.4140	1.4993
1.3621	1.3639	1.4520
1.3441	1.3577	1.4305
1.3105	1.3488	1.3996
1.2824	1.3200	1.3821
1.2742	1.3058	1.3675
1.2639	1.2632	1.3439
1.2400	1.2346	1.3161
1.2200	1.1947	1.2922
1.2004	1.1752	1.2858
1.1886	1.1655	1.2679
1.1709	1.1477	1.2538
1.1519	1.1185	1.2365
1.1359	1.1072	1.2048
1.1272	1.1002	1.1905
1.1033	1.0553	1.1735
1.0778	1.0379	1.1637
1.0661	1.0272	1.1548
1.0528	1.0014	1.1507
1.0204	0.9884	1.1338
1.0136	0.9881	1.1222
0.9962	0.9745	1.1116
0.9805	0.9657	1.0791
0.9748	0.9528	1.0727
0.9680	0.9311	1.0528
0.9612	0.9239	1.0457
0.9464	0.9147	1.0395
0.9423	0.9072	1.0337
0.9350	0.8980	1.0175
0.9233	0.8946	1.0108
0.9100	0.8894	1.0055
0.9042	0.8841	1.0021
0.8992	0.8785	0.9930
0.8962	0.8719	0.9885
0.8870	0.8690	0.9818
0.8840	0.8656	0.9766
0.8702	0.8688	0.9638
0.8624	0.8554	0.9544
0.8556	0.8513	0.9509
0.8486	0.8466	0.9420
0.8458	0.8456	0.9377
0.8417	0.8415	0.9295
0.8390	0.8378	0.9270
0.8337	0.8326	0.9213
0.8268	0.8296	0.9161
0.8229	0.8276	0.9093
	0.8245	0.9031
		0.8948
		0.8884
		0.8780
		0.8742
		0.8698
		0.8648
		0.8568
		0.8525
		0.8457
		0.8411
		0.8352
		0.8313
		0.8277

$1/2K_2C_2O_4$ and $K_2[La(C_2O_4)_2]$ (calcd. mass loss, 30.21%). Moreover, $K_2Fe(C_2O_4)_2$ is reported [23,24] as intermediate in the decomposition of $K_3[Fe(C_2O_4)_3]$. Although, the formation of intermediates with reduction of iron species, like $K_6Fe_2^{II}(OX)_5$ are reported [10,25–27]; the existence of La^{II} is not found in this study. As the product formed at 293°C is stable upto 392°C in TG, the pyrolysed product at 340°C is subjected to X-ray powder diffraction (XRD) and IR study. The XRD data (Table 3) confirmed [28] the presence of $K_2C_2O_4$. The other mismatched d-values may be due to $K[La(III)(C_2O_4)_x]$. The IR spectrum shows the presence of a $C_2O_4^{2-}$ group. It is concluded that the product at 293°C in TG is likely [17] to be a mixture of $K_2C_2O_4$ and $K[La(III)(C_2O_4)_x]$ (where $1.5 < x < 2$). Similar partial fragmentation of an oxalate group can be found elsewhere [15,29]. The inclined slope in TG upto 528°C, with a mass loss of 49.3%, indicates further decomposition to lanthanum dioxycarbonate, $La_2O_2CO_3$. Prior to the formation of mixture of $K_2C_2O_4$ and $1/2La_2O_2CO_3$ (calcd. mass loss, 48.55%), in TG two clear breaks at 452°C and

480°C are displayed. The break at 480°C with 46% mass loss, apparently suggests the intermediate is transient which may be a mixture of $K_2C_2O_4$ and lanthanum oxycarbonate, $1/2La_2O(CO_3)_2$ (calcd. mass loss, 45.32%). The type of DTG changes between 390°C and 535°C corresponds to the above changes. Moreover, the respective exothermic (i.e. oxidative decomposition of $K[La(C_2O_4)_x]$) and endothermic peaks (i.e. due to changes of $La_2O(CO_3)_2$ to $La_2O_2CO_3$) at 420°C and 450°C followed by exothermal nature upto 508°C in the DTA profile supports the TG changes. The E^* values (Table 2) calculated from TG curve (392–528°C portion) using four non-mechanistic equations [19–22] are found to be in excellent agreement. The product formed at 528°C in TG is stable over a long temperature range; the pyrolysed product at 550°C shows the IR bands at ca. 1650 and 1615 cm^{-1}, which indicates the presence [1] of $K_2C_2O_4$. The XRD data (Table 3) further confirmed the presence of $K_2C_2O_4$ along with a trace of K_2CO_3. The remaining mismatched *d*-values may be due to $La_2O_2CO_3$. Further IR bands due to CO_3^{2-} group at 1360–1550, 1030, 670 (also due to K_2CO_3) and ca. 845 cm^{-1} gives credence [29,30] to the presence of a dioxycarbonate of lanthanum. In TG, 2% mass loss up to 770°C (obs. 51.3%) from 528°C, may be due to decomposition of potassium oxalate to K_2CO_3. However, $K_2C_2O_4$ decomposes [10] to K_2CO_3 at 700°C. The trace of K_2CO_3 identified from XRD data indicates that the decomposition of $K_2C_2O_4$ starts before 550°C where $La_2O_2CO_3$ acts as a catalyst. The IR band at ca. 670 cm^{-1} and another at ca. 710 cm^{-1} are due [31] to K_2CO_3. Moreover, the presence of a trace of KCO and LaCO cannot be ruled out as detected [28] from XRD data (Table 3), which is due to reaction of CO(g) evolved during decomposition. The mixture of K_2CO_3 and $1/2La_2O_2CO_3$ at 770°C (calcd.mass loss, 52.64%) further decomposes as shown by a slope in TG upto 836°C. The mass loss of 57% at 836°C indicates the product is a mixture of K_2CO_3 and $1/2La_2O_3$ (calcd. loss 55.87%). DTG change in the range 768–842°C is for the above changes. The mass loss in TG continues due to melting of K_2CO_3 to K_2O. The K_2CO_3 melts [32] at 910°C. The solid–solid reaction of K_2CO_3 and K_2O (molten state) with La_2O_3 at high temperature yields potassium lanthanite, $KLaO_2$. The mass loss of 59.5% at 1000°C in TG supports the presence of $1/2K_2O$, $1/2K_2CO_3$ and $1/2La_2O_3$ (calcd. 59.10%) in the final residue. The IR bands at 710, 670, 640 and 415 cm^{-1} of the gray white calcined product at 970°C for 30 min suggests [31] the presence of K_2CO_3 and La_2O_3. The XRD data (Table 3) confirmed [28] the presence of La_2O_3, K_2CO_3 (trace), K_2O and $KLaO_2$. A trace of La_2C_3 is also detected from XRD data as carbon formed due to disproportionation of CO(g) to CO_2(g) reacts with a portion of La_2O_3 at high temperature. The E^* values calculated for the final TG step (770–836°C portion) are shown in Table 3. The values are found to be similar for all the methods [19–22]. The DSC profile (Fig. 2) in nitrogen shows several endothermic peaks. The peaks are integrated and the kinetic parameters are included in Table 4. A large endotherm between 31.38–179.61°C (Fig. 2a) including a shoulder peak in the range 91.52–109.71°C (Fig. 2b) are for the stepwise release of water. Immediately after the dehydration step, a small endothermic peak between 185.02–195°C (Fig. 2c) with large E^* value suggests some rearrangement of anhydrous form which may take place very slowly and is quite stable. Further endothermic decomposition of the species takes place and corresponds to another medium endotherm in the

Table 4
DSC data of $K_3[La(III)(C_2O_4)_3]\cdot 9H_2O$ in nitrogen

Step	Temperature range (°C)	Peak Temperature (°C)	ln k_0	E^* (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (JK^{-1} mol^{-1})	Order of reaction
a	81.38–179.61	138.25	26.87 ± 0.58	106.32 ± 2.29	287.55	699.20	1.14 ± 0.02
b	91.51–109.71 (shoulder peak)	101.59	214.97 ± 4.64	676.86 ± 14.62	4.50	12.02	1.97 ± 0.04
c	185.02–195.00	190.00	290.93 ± 6.28	1129.38 ± 24.39	2.59	5.60	1.33 ± 0.02
d	270.77–295.28	284.60	195.01 ± 4.21	918.06 ± 19.83	16.11	28.89	1.39 ± 0.03
e	299.68–302.93	301.16	1539.39 ± 33.25	7355.00 ± 158.89	0.14	0.25	2.02 ± 0.04
f	312.57–320.69	316.73	303.47 ± 6.55	1501.83 ± 32.45	0.42	0.72	0.81 ± 0.01
g	423.75–500.53	453.66	58.80 ± 1.27	387.02 ± 8.36	50.20	69.08	1.29 ± 0.02

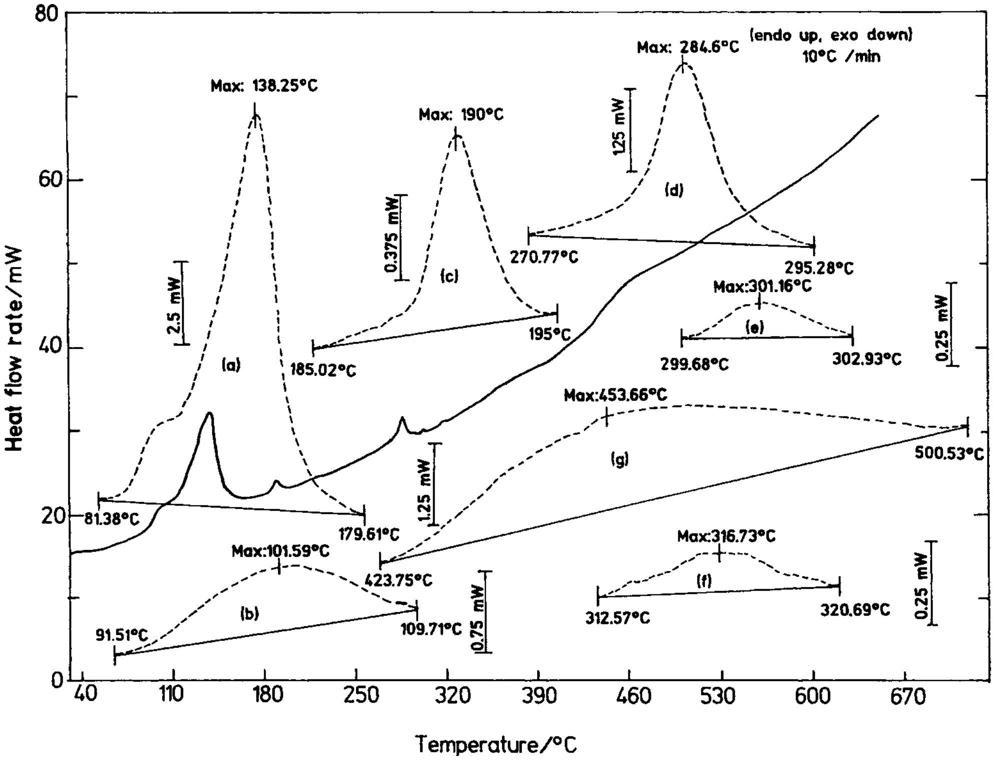

Fig. 2. DSC curves of $K_3[La(III)(C_2O_4)_3]{\cdot}9H_2O$ in nitrogen.

range 270.77–295.28°C (Fig. 2d). The product at this stage may be similar to the product assumed at 293°C from TG study in air. The E^* value (Table 4) of this step is also very high. Immediately after this step, two very small endotherms are observed (Fig. 2e and f). Further, the flat endothermic nature of the DSC curve between 423.75–500.53°C (Fig. 2g) is for final decomposition in this study in nitrogen. The mass loss of 48.22% of the annealed sample upto 650°C indicates the formation of $K_2C_2O_4$ and $1/2La_2O_2CO_3$ (calcd. loss 48.55%).

The water vapour, carbon monoxide and carbon dioxide evolved during decomposition were identified by IR spectroscopy [33].

Above study suggests the following tentative mechanism for the thermal decomposition in air.

$$K_3[La(C_2O_4)_3]\cdot 9H_2O \xrightarrow{90^\circ C} K_3[La(C_2O_4)_3]\cdot 8H_2O(s) + H_2O(v) \xrightarrow{167^\circ C} K_3[La(C_2O_4)_3]\cdot H_2O(s) + 7H_2O(v)$$

$$\xrightarrow{\text{ca. }190^\circ C} K_2C_2O_4(s) + K[La(C_2O_4)_2](s) + H_2O(v) \xrightarrow{\text{ca. }293^\circ C} K_2C_2O_4(s) + K[La(C_2O_4)_x](s)$$

$$(\text{where}1.5 < x < 2) + l\text{CO}(g) \xrightarrow{480^\circ C} K_2C_2O_4(s) + 1/2La_2O(CO_3)_2(s){+}m\text{CO}(g){+}n\text{CO}_2(g) \xrightarrow{528^\circ C}$$

$$K_2C_2O_4(s) + 1/2La_2O_2CO_3(s) + p\text{CO}_2(g) \xrightarrow[\text{pyrolysed product at }550^\circ C]{528-770^\circ C} K_2C_2O_4(s)(\text{trace}) + K_2CO_3(s)$$

$$+1/2La_2O_2CO_3(s) + x\text{CO}(g) \xrightarrow{770-836^\circ C} K_2CO_3(s) + 1/2La_2O_3(s){+}y\text{CO}(g){+}z\text{CO}_2(g) + C(s)$$

$$\xrightarrow[\text{pyrolysed product at }970^\circ C]{1000^\circ C} 1/2La_2O_3(s) + 1/2K_2CO_3(s) + 1/2K_2O(s) + KLaO_2(s) + La_2C_3(s)$$

4. Conclusions

The thermal studies (TG, DTG and DTA) in air shows that the potassium oxalate separates from $K[La(C_2O_4)_x]$ (where $1.5 < x < 2$) at a much lower temperature than the lithium and sodium analogues [17]. Subsequently slow decomposition of potassium oxalate to K_2CO_3 takes place as with lithium and sodium oxalate [17], but La_2O_3 was produced at 836°C through the formation of both oxycarbonate and dioxycarbonate at 480°C and 528°C respectively. Whereas in case of lithium analogue the formation of oxycarbonate was not observed, sodium analogue produced only $La_2O(CO_3)_2$ at 538°C. Like $M_3[La(C_2O_4)_3]\cdot xH_2O$ (where $M = Li$ and Na) [17], the compound $K_3[La(C_2O_4)_3]\cdot 9H_2O$, also produced $KLaO_2$ along with K_2O and La_2C_3 through the solid–solid reaction of K_2CO_3 and La_2O_3 at high temperature (ca 1000°C). A mixture of potassium oxalate and lanthanum dioxycarbonate was assumed to be the end product at 650°C in nitrogen from the DSC study. The E^* values calculated by four non-mechanistic equations were in excellent agreement for dehydration and two decomposition steps.

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