Thermal Decomposition of Lanthanum O-Hydroxybenzoate and O-Bromobenzoate

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Abstract

The conditions of thermal analysis of Lanthanum -O-Hydroxybenzoate and Lanthanum -O-Bromobenzoate were studied .

The Hydrated complexes lose water of crystallization in two steps . Lanthanum -O-Hydroxybenzoate starts to lose water of crystallization between (60-230)^{o}C , but Lanthanum -O-Bromobenzoate loses water of crystallization between (100-320)^{o}C .

The intermediate products $La_2O_3(OHC_6H_4COO)_5$ and $La_2(BrC_6H_4COO)_6$ were obtained by heating the two complexes at(320-350)^{o}C and (320-380)^{o}C respectively . In the fourth step , anhydrous structures of the complexes decomposed in one step and then were transformed to La_2O_3 . These results are using TG,DTG,DTA,IR and (X – ray) diffraction techniques . DTA curves revealed exothermic peaks for the decomposition steps , but endothermic peaks were obtained from the dehydration of complexes .

الخلاصة

درست في هذا البحث ظروف التحلل الحراري لكل من المعقدين اورثوهيدروكسي بنزوات اللنثنم المائية واورثوبروموبنزوات اللنثنم المائية . وتبين ان المعقدين يفقدان ماء التبلور في خطوتين منفصلتين ، وان المعقد اورثوهيدروكسي بنزوات اللنثنم يفقد ماء التبلور عند التسخين ما بين (60-230)^{o}م ولكن المعقد اورثوبروموبنزوات اللنثنم فقد ماء التبلور عند التسخين ما بين (100-320)^{o}م ، وتم الحصول على نواتج وسطية

هي $La_2(BrC_6H_4COO)_6$, $La_2O_3(OHC_6H_4COO)_5$ كخطوة ثالثة عند تسخين المعقدين منزوعي الماء ما بين (320-350)°م و (320-380)°م على التوالي .

اما الخطوة الاخيرة فتضمنت تحلل التراكيب في الخطوة السابقة بخطوة واحدة انتهت بتكوين اوكسيد اللنثنم La_2O_3 . تم الحصول على هذه النتائج باستخدام تقنيات كل من IR,DTA,DTG,TG وحيود الاشعة السينية (X-RAY) ، واظهرت منحنيات التحليل الحراري التفاضلي DTA قمماً باعثة للحرارة في خطوات التحلل في حين اظهرت قمماً ماصة للحرارة في خطوتي نزع ماء التبلور من المعقدين .

Introduction

Lanthanum-O- Hydroxybenzoate ($La(OHC_6H_4COO)_3.3H_2O$) was known by Soge et. al [1,2] and lost water of crystallization at 220°C Sove et.al[3,4] have obtained anhydrous complexes of Lanthanum -O-Hydroxy-benzoate at 320 °C . Prozorovskaya et al.[5,6] studied the thermal decomposition of Lanthanum-O-Bromobenzoate by TG and IR spectra and determined its density and solubility in water and dilute acids. Matyukhin et al [7-9] studied water of crystallization in Lanthanum –O-Hydroxybenzoate and Lanthanum –O- Bromobenzoate by TG , DTG , DTA , X-ray , and IR spectra. The aim of this work is to anextension the study of thermal decomposition of these complexes in air atmosphere .

Experimental

Lanthanum -O-Hydroxybenzoate precipitate[3] was prepared in decomposition reaction by adding equivalent amounts of 0.2 M solutions of O-Hydroxybenzoate at pH 4.3 to a hot solution of $La(NO_3)_3$ at pH 3.8 .

The precipitate formed was heated in water solution for two hours , filtered off , washed with water and dried at 50 °C .

Lanthanum -O- Bromobenzoate precipitate[3] was prepared by adding equivalent amounts of 0.2 M solution of O-Bromobenzoate at pH 4.2 to a hot solution of $La(NO_3)_3$ at pH 3.8 . The precipitate was heated in water solution for two hours , filtered off , washed and dried at 60°C .

The stability of the prepared complexes was studied by thermal decomposition in air atmosphere by TG , DTG , and DTA .

The TG , DTG and DTA curves were recorded . The measurements were made

on a derivatograph at a heating rate of 10 deg. Min^{-1} . The samples were heated in air atmosphere in platinum crucibles .

The results are compiled in table (1) and the typical thermograms are illustrated in fig(1) . The water content was determined from the TG and DTG curves and the elemental analysis data are given in table (2) .

The carbon and hydrogen content of the prepared complex were determined by elemental analysis using V_2O_5 as an oxidizing agent[6] .

The bromine content was determined by the schoniger method[4] . The Lanthanum content was determined from the TG and DTA curves by converting the complexes into La_2O_3 at 550^oC .

The thermal decomposition of the compounds were studied by Derivatograph (Q- 1500 D) Hungarian Optial works MOM Budapest , in platinum crucible , at temperatures 20-1000 ^oC and heating rate of 10 deg / min , FTIR Spectroscopy using (Perkin – Elmer 684 infrared Spectro-photometer , and X-ray diffraction using (Philips Corporation type PW 1051 / 30) on the data in cluded in the ASTM cards .

Result and discussion

Thermal studies of Lanthanum -O- Hydroxybenzoate ($La(OHC_6H_4COO)_3.\ 3H_2O$) were obtained by heating in air atmosphere and the decomposition occurred in four steps .

In the first step it begins to lose water of crystallization at low temperature (60-170 ^oC) which lost two molecules .

$$La(OHC_6H_4COO)_3.\ 3H_2O \xrightarrow{60\text{-}170\ ^oC} La(OHC_6H_4COO)_3.\ H_2O + 2\ H_2O$$

The third water molecule is lost at 210-230 ^oC and the anhydrous salt is formed . Therefore , the water molecules are bound in different forms .

$$La(OHC_6H_4COO)_3.\ H_2O \xrightarrow{210\text{-}230\ ^oC} La(O\ HC_6H_4COO)_3 + H_2O$$

The water molecules of crystallization lost between 60-170 ^oC may be outer sphere , but the third water molecule is coordinated in the inner sphere .

The two steps of dehydration are endothermically steps , as shown in DTA curve (fig 1) .

The anhydrous Lanthanum -O- Hydroxybenzoate that was heated at the third step between 320-350^oC is

16.5 O_2

transformed exothermally to **$La_2O_3(OHC_6H_4COO)_5$** in the presence of air , as follows :

$$4La(OHC_6H_4COO)_3 \longrightarrow 2La_2O_3(OHC_6H_4COO)_5 + 14CO_2 + 5H_2O$$

These results suggest that Lanthanum -O- Hydroxybenzoate exists as a dimer in this temperature range . Which was confired by the X-ray diffraction .

Table (1) Elemental analysis of $La_2O_3(OHC_6H_4COO)_5$ complex .

Elemental analysis	La %	C %	O %	H %
Found	26.52	42.71	28.39	2.39
Calculated	27.497	41.543	28.486	2.472

The DTA curve in this study recorded exothermic peak between 210 ^oC due to polymorphic transformation[6].

The fourth step , the anhydrous Lanthanum Hydroxybenzoate decomposes exothermically to La_2O_3 between 400-550 ^oC , Which were obtained in TG and DTA curves , (Fig 1) were observed by X-ray diffraction and ASTM cards .

Lanthanum -O-Bromobenzoate $[La_2(BrC_6H_4COO)_3.2H_2O]$ was studied on heating in air at mosphere in five steps .

In the first two steps , the molecules are dehydrated endothermically in the temperature range 100-180 ^oC which lost one and half molecules of water .

$$La(BrC_6H_4COO)_3.2H_2O \xrightarrow{100\text{-}180\ ^oC} La(BrC_6H_4COO)_3.0.5H_2O + 1.5\ H_2O$$

The third step involves the loss of the remaining half water molecules between 220-320 ^oC and the anhydrous salt is formed .

$$La(BrC_6H_4COO)_3.0.5H_2O \xrightarrow{220\text{-}320\ ^oC} La(BrC_6H_4COO)_3 + 0.5H_2O$$

Propably the water of crystallization at the first step is outer sphere water , but some molecules of

complex have one water molecule coordinated in the inner sphere .

The three steps of dehydration are endothermically . The results are given by DTA curves (fig 2) .

The anhydrous $La(BrC_6H_4COO)_3$ compound between 320-380 ^oC DTA curve were observed exothermic peak , but endothermic peak were observed at the same range by DTG curve Brzyska[10] concluded that in this temperature range poly morphic transformation takes place .

$$2La(BrC_6H_4COO)_3 \xrightarrow{320\text{-}380\ ^oC} La_2(BrC_6H_4COO)_6$$

The fifth step of anhydrous $La_2(BrC_6H_4COO)_6$ decomposes exothermically to produce La_2O_3 between 450 – 600 ^oC , these results were obtained in TG and DTA curves[11] .

$$La_2(BrC_6H_4COO)_6 + 7O_2 \longrightarrow La_2O_3 + 6HBr + 7CO_2 + 9H_2O$$

DTG curve gives endothermic peak at 540 ^oC .

Table (2) : Thermal decomposition results of $La(OHC_6H_5COO)_3.3H_2O$ in air atmosphere

TG Loss of weight	Types of decomposition	Loss of weight %		Temperature Range ^oC	DTG Peak ^oC	Exo or Endo reaction	Loss of H_2O molecules
		Found	Calculated				
First step H_2O	Dehydration of outer sphere water molecules	6.01	5.96	60-170	150	Endothermic reaction	2
Second step H_2O	Dehydration of inner sphere water molecules	2.88	2.98	210-230	220	Endothermic reaction	1
Third step	Oxidation and decomposition	11.25	11.34	320-350	327	Exothermic reaction	---
Fourth step	decomposition	55.01	54.718	400-550	516	Exothermic reaction	---

Table (3) : Thermal decomposition results of $La(BrC_6H_5COO)_3.2H_2O$ in air atmosphere

TG Loss of weight	Types of decomposition	Loss of weight %		Temperature Range ^oC	DTG Peak ^oC	Exo or Endo reaction	Loss of H_2O molecules
		Found	Calculated				
First step H_2O	Dehydration of outer sphere water molecules	2.21	2.15	100-180	157	Endothermic reaction	1.5
Second step H_2O	Dehydration of inner sphere water molecules	0.91	0.717	220-320	302	Endothermic reaction	0.5
Third step Polymorphic transformation	Dimer formed	----	----	320-380	362	Exothermic reaction	---
Fourth step O-Bromobenzoate	Decomposition of complex to metal oxide	82.92	84.14	450-600	574	Exothermic reaction	9

Table (4) : Elemental Analysis of $La_2(BrC_6H_5COO)_6$ complex .

	La %	Br %	O %	C %	H %
Found	18.1	33.01	12.68	34.3	1.59
Calculated	18.8	32.47	12.99	34.1	1.62

The FTIR spectra recorded for prepared complexes over the range 7000-200 cm^{-1} confirmed the elemental analysis results . The IR spectrum of the first complex heated at 350^oC , the position of absorption bands of asymmetrical and you should mention these vibration, C=O ester and C–O do not change compared with the spectrum of Lanthanum -O- Hydroxybenzoate .

The bands for OH^- in complexes (3550 cm^{-1}) and from hydrated at (3450 and 1630 cm^{-1}) disappear , but the bands of La-O- La bond appears at 620 cm^{-1} [4] .

It is preperred to give the spectra of at least the original complexes before thermal treatment in order to compare the absorption of the products .

Conclusion

The high temperatures of dehydration of Lanthanum -O-hydroxybenzoate (60-230) ^{o}C , O-bromobenzoate (100-320) ^{o}C suggest that some of water molecules crystallization is inner sphere .

Lanthanum O- hydroxybenzoate at low temperature range of (60-170) ^{o}C it loses two molecules the remaining water molecules are lost at (210-230) ^{o}C these results indicat that water molecules are bound in different ways . Probably the water of crystallization lost at low temperature is outer sphere . These results suggest that Lanthanum -O-hydroxybenzoate exists as a dimer at the third step between (320-350) ^{o}C which was confirmed the results by the X-ray diffraction .

The anhydrous Lanthanum dimer decomposes exothermically to La_2O_3 between (400-550)^{o}C which were obtained in TG and DTA curves (Fig 1).Lanthanum -O- bromobenzoate at low temperature range (100-180) ^{o}C it loses one and half molecules of water which is outer sphere . The third step in volves the loss of the remaining half water molecules at (220 – 320) ^{o}C .

Polymorphic transformatiom takes place[10] at the fourth step between (320-380)^{o}C . Anhydrous Lanthnum -O-bromobenzoate decompose oxothermically to La_2O_3 between (450 – 600) ^{o}C .

Note : all the stractures were observed in study was confirmed by X-ray diffraction analysis .

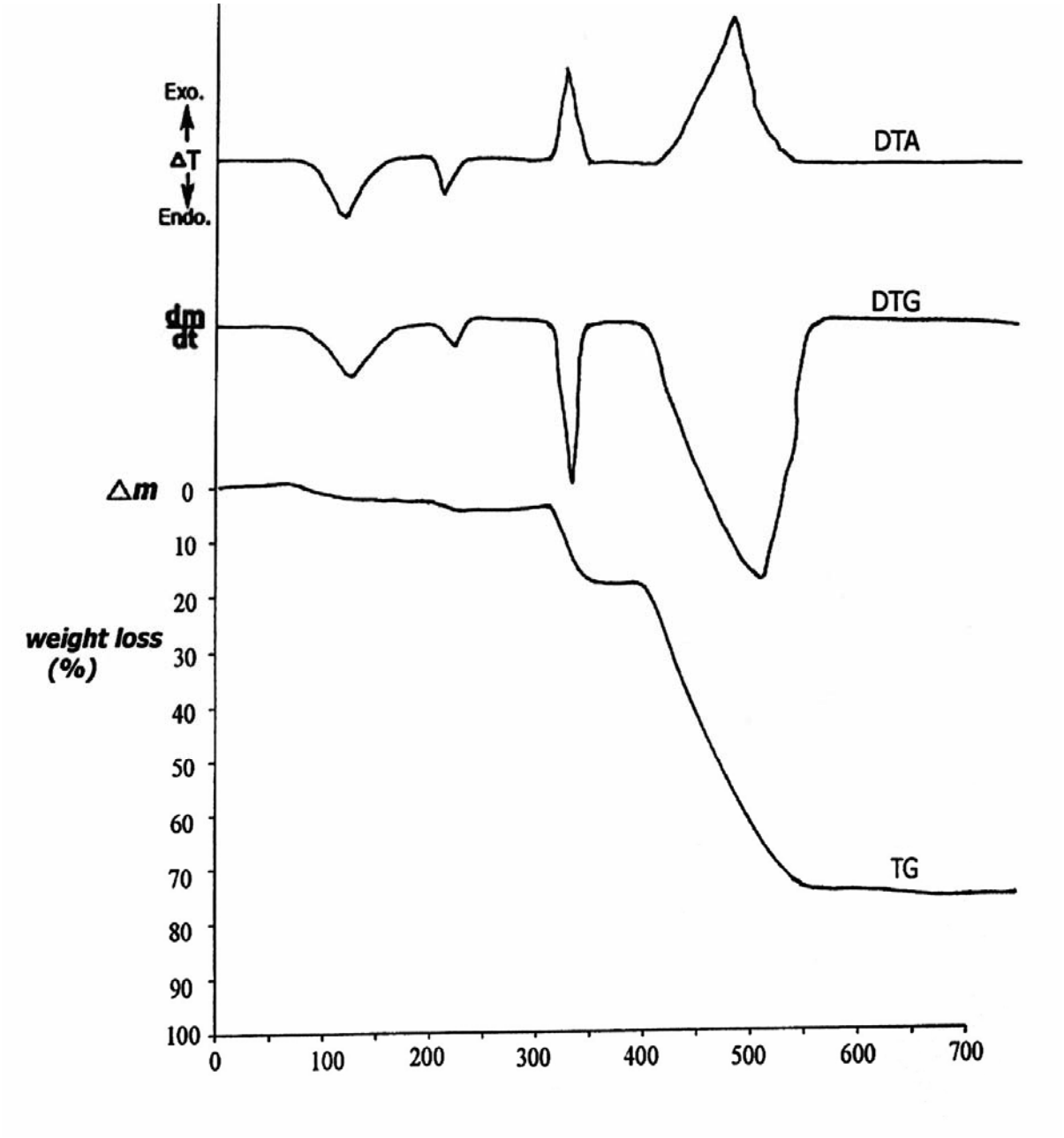

Fig (1) TG , DTG and DTA curves of Lanthanum -O- Hydroxybenzoate thermal decomposition ($La(OHC_6H_4COO)_3.3H_2O$) .

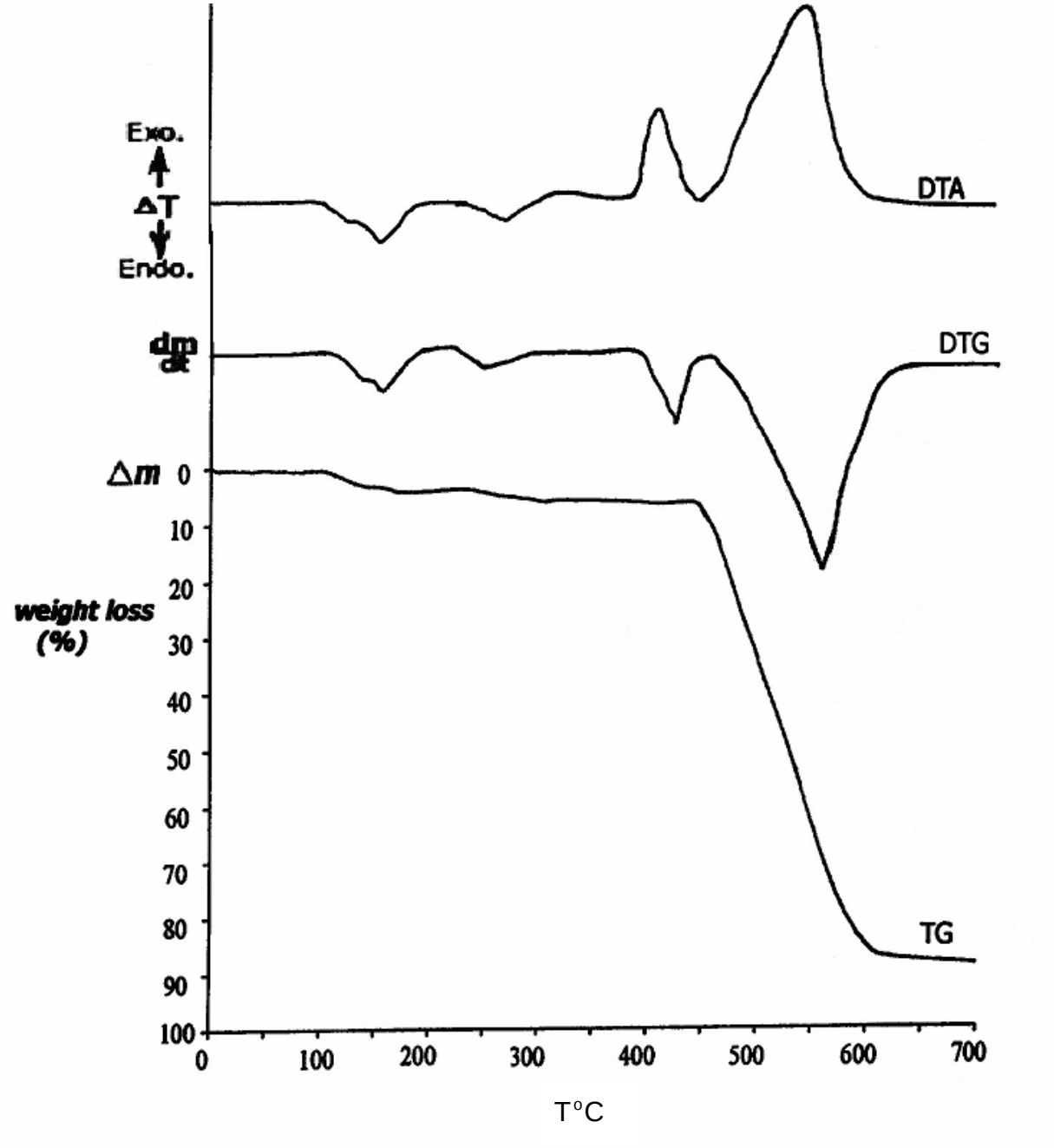

Fig (2) TG , DTG and DTA curves of Lanthanum -O- Bromobenzoate thermal decomposition (La $(BrC_6H_4COO)_3.2H_2O$) .

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