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Mechanistic aspects of thermal decomposition of thorium oxalate hexahydrate: A review

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ABSTRACT

Current studies on thorium oxalate hexahydrate and its decomposition intermediates are being presented using a combination of thermal, X-ray diffraction and IR spectral methods. It has been shown here that thorium oxalate dihydrate formed by the thermal dehydration of thorium oxalate hexahydrate undergoes partial thermal decomposition to form a polynuclear complex at 165 °C, which further decomposes at higher temperatures to a hydroxyoxalate, a carbonate and finally to thorium oxide. Formation of thorium oxalate monohydrate and/or anhydrous thorium oxalate could not be seen here.

1. Introduction

The large abundance of thorium in the earth's crest, about three times that of uranium, and its long-term availability make the thorium fuel cycle very attractive. Thorium, primarily in the form of ThO_2, is an important component of the fuel for the breeder reactors [1–3]. Sinterability of the oxide powder is an important consideration in the development of the flow sheet for thoria fabrication and is dependent largely on the physical and chemical nature as well as the thermal history of the precursor powder [4,5]. The thermal decomposition of thorium oxalate hexahydrate has been studied by a number of research groups in the context of the search for a precursor of sinterable thoria. However, there are conflicting results on the nature of intermediates formed at elevated temperatures [6–10]. According to Padmanabhan et al. [9] anhydrous thorium oxalate decomposes directly to form thoria while D' Eye and Sellman [10] had reported the formation of thorium carbonate from anhydrous thorium oxalate which subsequently decomposes to give thoria. EGA is an important tool in interpreting the various intermediate reaction steps but its application seems to be low in past as we could find only a single report [11] using EGA-MS measurements. Current studies are based on simultaneous TG-DTA-EGA-MS approach to understand the mechanistic aspects involved in the thermal decomposition of thorium oxalate hexahydrate. Further, to substantiate the observed thermal data, high temperature XRD as well as IR studies have been carried out on the starting compound and also on the intermediates formed at elevated temperatures. Details of these studies along with the results obtained are being discussed here.

2. Experimental details

Thorium oxalate hexahydrate was prepared from nuclear grade thorium oxide obtained from Indian Rare Earths Ltd., Mumbai. The oxide was dissolved in minimum amount of nitric acid. The clear solution was treated with 1 M oxalic acid to precipitate thorium oxalate. The precipitate was filtered and washed several times with water and dried in air. Identification of the dried precipitate was carried out using X-ray diffraction measurements on a X-ray

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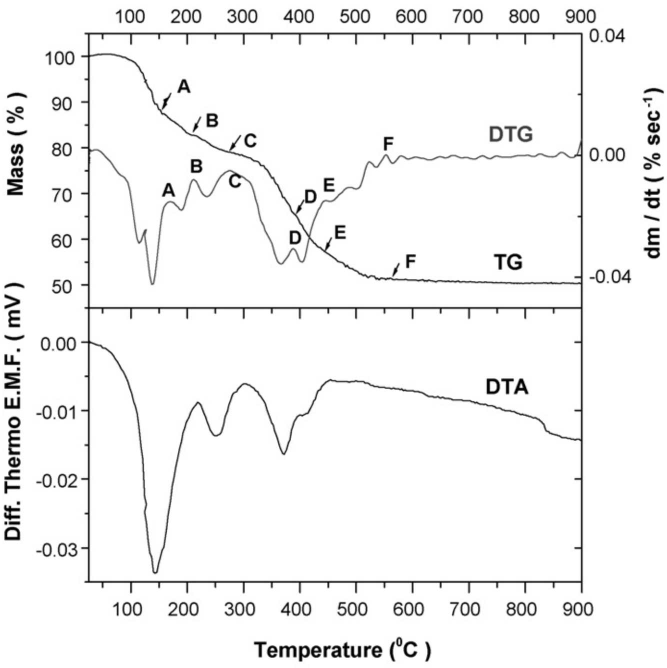
Diffractometer (Model PW1710, Philips, The Netherlands) using nickel filtered Cu-Kα radiation.

High temperature X-ray diffraction (HTXRD) patterns of the starting composition as well as of the intermediates formed at elevated temperatures were also recorded with Philips X'pert diffractometer with an Anton Parr high temperature attachment. Platinum heater with platinum rhodium thermocouple spot welded at the bottom, is used to measure the temperature. The sample was placed on platinum heater and heated to the desired temperature at a rate of 10 °C min^{-1} and held for 10 min and then the diffraction pattern was recorded in the 2θ range of 10–80°.

The TG-DTA-EGA-MS data were recorded using a Netzsch Thermal Analyser, Model STA 409, coupled to a Balzers Quadrupole Mass Spectrometer, Model QMG 311, via a heated capillary. Accurately weighed sample (about 100 mg) was used in all the measurements that were carried out at a heating rate of 10 K min^{-1} in high purity argon flow (80 mL min^{-1}). Recrystallised alumina sample holders were used. In this work Pt vs. Pt-10% Rh thermocouples were used as temperature and differential temperature sensors.

Samples were mixed with KBr in a suitable ratio and pellets were made for Infrared measurements in the range of 400–4000 cm^{-1} using FTIR spectrometer (Model MB 102, Bomem, Canada) using CsI window. The whole FTIR compartment was continuously purged by high purity nitrogen and additionally molecular sieves/silica gel were used to minimize the water and carbon dioxide background in the recorded spectra.



Step A : 70 – 165 °C, Step B : 165 – 215 °C , Step C : 215 – 280 °C,
Step D : 280 – 400 °C , Step E : 400 – 450 °C , Step F : 450 – 520 °C.

Fig. 1. TG-DTG-DTA curves for thorium oxalate hexahydrate.

3. Results and discussion

Thorium oxalate hexahydrate was prepared as reported elsewhere [8] and its stoichiometric composition was confirmed by XRD analysis. The recorded XRD pattern for the compound matches well with the reported XRD pattern of thorium oxalate hexahydrate with JCPDS card no. 22-1485. The compound was used as precursor for all measurements reported here.

Simultaneous TG-DTA curves along with DTG curve for thorium oxalate hexahydrate are shown in Fig. 1. The EGA-MS curves recorded simultaneously with TG-DTA curves are shown in Fig. 2. The recorded HTXRD patterns are given in Fig. 3 and the recorded IR spectra of thorium oxalate hexahydrate and the intermediates formed at elevated temperatures have been shown in Fig. 4. Observed weight losses in various temperature ranges are given in Table 1. IR characteristic group frequencies have been given in Table 2.

Fig. 1 and Table 1 show that total mass loss [49.2%] obtained during steps A–F, by heating the sample to 800 °C is in good agreement with that for the formation of thorium oxide from thorium oxalate hexahydrate [48.8%]. It is clear from Table 1 that thorium oxalate hexahydrate dehydrates during step A in the temperature range of 70–165 °C to form thorium oxalate dihydrate. Formation of thorium oxalate dihydrate was also confirmed by the recorded HTXRD pattern as shown in Fig. 3 which matches well with the reported JCPDS card no. 18-1385 of thorium oxalate dihydrate. This compound has an orthorhombic structure with four molecular formula units per unit cell [12].

The EGA-MS curve given in Fig. 2 shows that thorium oxalate dihydrate loses carbon monoxide ($m/z = 28$), carbon dioxide ($m/z = 44$) and water vapour ($m/z = 18$) above 160 °C. The DTA curve shows the process to be endothermic and the corresponding mass loss in the temperature range of 165–215 °C (step B) is only 3.9%. Similar gas evolution pattern was observed in the temperature region of 200 °C by Dash et al. [11]. They have reported the simultaneous release of water, carbon monoxide and carbon dioxide and, according to them this reaction process leads to the formation of a substoichiometric anhydrous $Th(C_2O_4)_{2-x}$. As the proper decomposition mechanism has not been proposed, the quantity [x] remains unexplained and needs exploration through measurements. The observation of low temperature release of water vapor, carbon mono oxide and carbon dioxide can be explained by invoking polymerisation of the thorium oxalate dihydrate through oxalate bridging to form a hydrated complex involving four thorium atoms

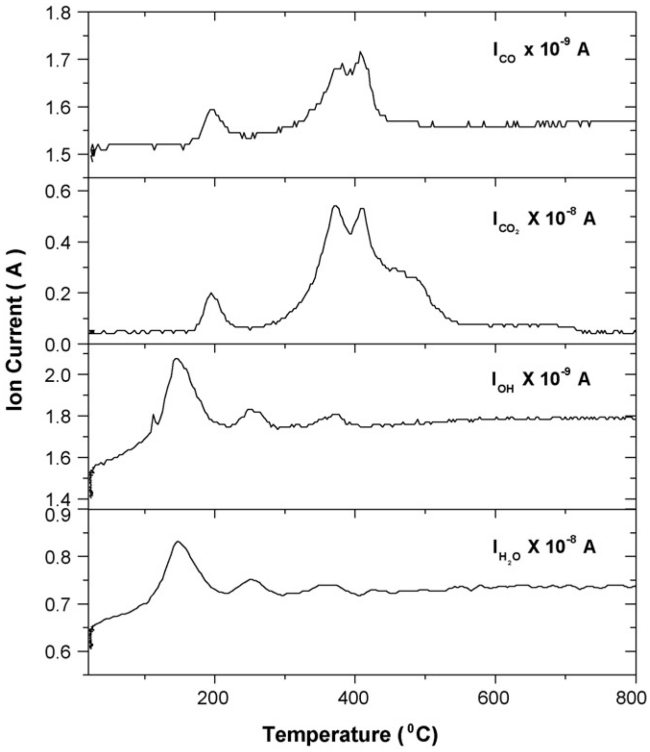


Fig. 2. EGA-MS curves recorded simultaneously with TG-DTA.

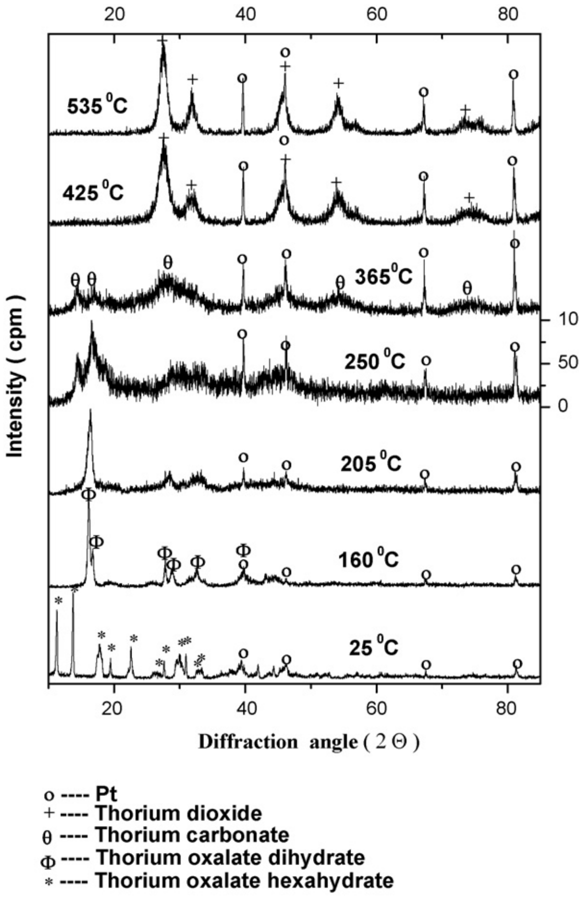


Fig. 3. High temperature X-ray diffraction patterns of thorium oxalate hexahydrate, intermediates and thorium dioxide.

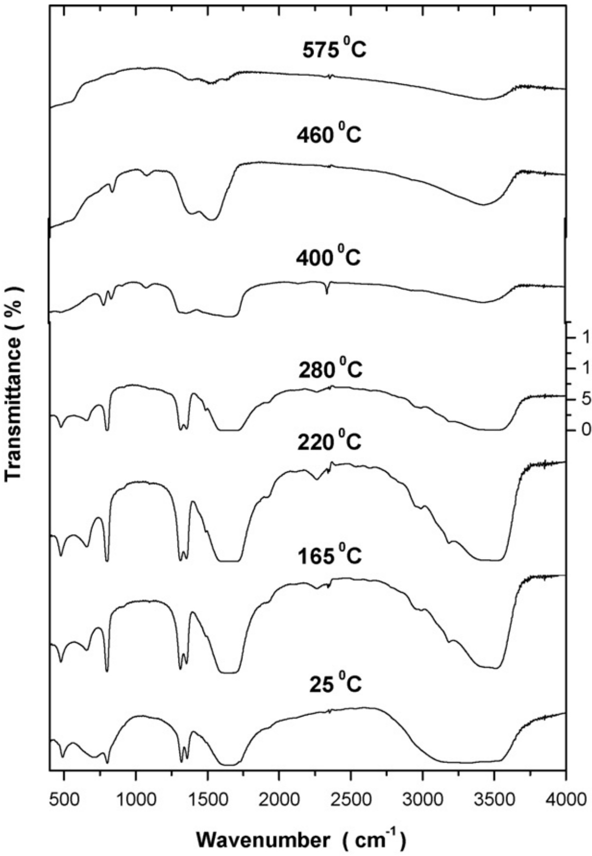


Fig. 4. IR spectra for thorium oxalate hexahydrate and intermediates.

in the molecule. It has already been reported that Th(IV) metal centers in Th $(C_2O_4)_2(H_2O)_2{\cdot}2H_2O$ are polymerised through oxalate $(C_2O_4{}^{2-})$ linkages [13]. The crystal structure of this compound, based on single crystal analysis, consists of a central thorium (IV) metal ion bound to four distinct oxalate anions. Each oxalate is coordinated to the metal center in a bidentate manner. As the reported data are on a compound similar to thorium oxalate dihydrate which clearly indicates the possibility of polymerisation existing in these type of thorium oxalate complexes.

Infrared studies have been carried out to substantiate the suggested polymerisation mechanism for the observed EGA-MS patterns during step B in the temperature region of 165–215 °C. IR spectra shown in Fig. 4 (165 °C) and Fig. 4 (220 °C) shows the wave number shift from 710 to 660 cm^{-1} and also from 487 to 470 cm^{-1}. It can be seen from Table 2 that these wave numbers represent the libration modes of coordinated/lattice water. The shift in wave number may be due to the interaction between the four molecular formula units present in one unit cell of thorium oxalate dihydrate. The lattice water movement/interaction in form of intermolecular hydrogen bonding may be responsible for this observed wave number shift towards lower end. Further this implies that thorium oxalate dihydrate exists in polymerised form through intermolecular hydrogen bonding. It has already been reported that the crystalline architecture may sustain on hydrogen bonding and can be substantiated from the architecture of many other oxalate ligand bearing compounds [14,15]. As the effect of hydrogen bonding cannot be seen in powder XRD patterns, the recorded HTXRD pattern for thorium oxalate dihydrate matches well with the reported pattern [12].

XRD patterns shown in Fig. 3 indicate that the crystalline nature of the compounds is being lost above 200 °C and the intermediates formed in the temperature region of 205–365 °C are amorphous. It can be seen from Fig. 3 that there is not much difference in the diffraction patterns recorded at 205 and 250 °C with respect to the most intense peak except for peak broadening and amorphization of the compounds. Polymerisation and dehydration process in the temperature region of 160–280 °C may be responsible for the observed amorphization of the compounds. Further it can be seen from IR patterns in the temperature region of 160–280 °C (Fig. 4) that there is no noticeable shift in peaks except the change

Table 1
Thermogravimetric analysis and proposed reaction mechanism for thorium oxalate hexahydrate decomposition.

Reaction step	Temperature range (°C)	Observed mass loss (%)	Theoretical mass loss (%)	Proposed Decomposition Mechanism
A	70–165	12.9	13.95	$4Th(C_2O_4)_2.6H_2O \rightarrow 4Th(C_2O_4)_2.2H_2O + 16H_2O$
B	165–215	3.9	4.3	$4Th(C_2O_4)_2{\cdot}2H_2O \rightarrow Th_4(C_2O_4)_6(HC_2O_4)_1(OH)_3{\cdot}5H_2O + H_2O + CO + CO_2$
C	215–280	3.9	4.3	$Th_4(C_2O_4)_6(HC_2O_4)(OH)_3{\cdot}5H_2O \rightarrow 5H_2O + Th_4(C_2O_4)_6(HC_2O_4)(OH)_3$
D	280–400	14.2	12.9	$Th_4(C_2O_4)_6(HC_2O_4)(OH)_3 \rightarrow Th(OH)_2C_2O_4 + 6CO + 2CO_2 + 2Th(CO_3)_2 + ThO_2 + H_2O$
E	400–450	7.7	4.3	$Th(OH)_2C_2O_4 \rightarrow ThO_2 + H_2O + CO_2 + CO$
F	450–720	6.6	8.5	$2Th(CO_3)_2 \rightarrow 2ThO_2 + 4CO_2$

Table 2
Infrared characteristic wave numbers.

Ref. No.	Functional group	Region (cm^{-1})	Intensity	Comment
[17]	CO_3^{--}, carbonate	1530–1320	vs	b
		1100–1020	w	
		890–800	m	
[17]	Carbonate ion	1380–1250	s	
	complexes	1090–1020	w	
	(including bridging)	900–720	s	
	M–O stretch	<500		
[17]	$C_2O_4^{--}$, oxalate	1730–1680	s	C=O str.
		1490–1400		C–O and C–C band
[22]	Oxalato complexes	1300–1260	w	C–O and O–C=O band
		500–415		Ring and O–C=O dif. vib.
		−365		O–C=O dif. vib.
		590–290		M–O str. and O–C=O
[17]	Lattice water	3600–3200	m	H–O–H str.
	Coordinated/	1630–1600	m	H–O–H def. vib.
[20]	adsorbed water	600–300	m–w	Due to lib. mode vib.
[21]	Aquo/coordinated water	3550–3200	m	H–O–H str., due to hydrogen bonding these bands may be observed at even lower freq., may be broad band
	Aquo complex	760 -590	m	H–O–H def. vib.
		1200–600	m	No. of bands
		600–300	m–w	No. of bands, M–O bands also observed for true aquo complex and also due to lib. mode vib.
[16,17]	M–OH, hydroxo complex	3760–3000	m	O–H str.
		1200–700		M–O–H dif. vib.
		900–300		M–O str.
[16]	Hydroxo/oxalato complex	830–770	m	O–C=O and H–O–H bands

in the intensity of the peaks. It indicates that the basic structure of the compound bearing oxalate ligand is remaining unchanged till 280 °C and complete breakdown of the oxalate structure has not started yet. The decrease in peak intensity can be attributed to the evolution of water vapor, carbon dioxide and carbon mono oxide at 165 °C during the polymerisation process of dihydrate and dehydration of the polymerised complex at 280 °C. The evolved gas pattern at 165 °C cannot be attributed to possible contamination of thorium oxalate hexahydrate with oxalic acid during preparation of the compound or to various experimental factors involved because the similar pattern has been observed by other researchers [11]. And also, pure oxalic acid was decomposed under identical conditions and found that oxalic acid decomposes at much lower temperature [120 °C] than the observed temperature region of interest [160 °C].

The peaks at 710 and 487 cm^{-1} in Fig. 4 (165–280 °C) represent the librational modes of vibration of lattice/coordinated water. The peaks observed in the region 3600–3200 cm^{-1} may be due to the H–O–H stretching vibrations of lattice/coordinated water while the peaks in the region 1730–1600 cm^{-1} show the presence of H–O–H deformation modes of the lattice/coordinated water. Presence of peaks in this region also suggest the involvement of oxalate group through the vibrations listed in Table 2. The peak at 800 cm^{-1} in Fig. 4 (165–280 °C) may be due to the bending modes of vibrations of coordinated water. There is no shift in this peak till 220 °C, suggesting that the loss of coordinated water °Ccurs only above 220 °C and also there is no change in the coordination sphere of metal ion. Also, the TG step C, in the temperature range of 215–280 °C with 3.9% mass loss of the initial mass of thorium oxalate hexahydrate (Fig. 1), is accompanied by release of water vapour only (Fig. 2). It can be seen from the EGA-MS patterns given in Fig. 2 that the ion current for $m/z = 28$ and 44 are almost negligible in the temperature region of 215–280 °C (step C) while the observed signal for $m/z = 17$ and 18 is well above the baseline. These observations suggest that the polynuclear complex dehydrates completely by the temperature of 280 °C as given in Table 1. This reaction step could be explained by the release of five molecules of water from the hydrated polynuclear complex formed in the earlier reaction step B [165–215 °C] rather than any cleavage of the compound. Based on the TG/DTG results alone, the observed mass loss of 3.9% in each of the two consecutive steps, match well with that of successive removal of single water molecule from thorium oxalate dihydrate and so it would be interpreted as the formation of thorium oxalate monohydrate and anhydrous thorium oxalate, respectively as has been reported [6,8,11] earlier. In the present context, as the difference between the electronegativities of thorium and oxygen is more, the corresponding Th–O bond may have ionic character and so coordinated water may behave as lattice water, giving IR peaks corresponding to the libration modes of vibration. Due to this ionic character of M–O bond, it becomes difficult to draw a clear cut line between the lattice water and coordinated water present in the molecule while representing the structure of the molecule. However, the present set of experiments involving EGA-MS measurements, clearly show the release of water vapor, carbon dioxide and carbon monoxide above 160 °C and in the temperature region of 215–280 °C (step C) only water vapor is evolved. Also, XRD pattern at 205 °C as shown in Fig. 3 does not match with either of the reported patterns of thorium monohydrate [JCPDS card no. 28-1367] or anhydrous thorium oxalate [JCPDS card no. 22-1478]. In view of the current investigations, thermal decomposition mechanism of thorium oxalate hexahydrate should be reviewed. Current set of experiments propose the polymerisation of thorium oxalate dihydrate in accordance with Ziegelgruber et al. [13] and not the formation of mono/anhydrous thorium oxalate [6,8,11].

It can be seen from Table 2 that the oxalate functional characteristic wave numbers are in the region of 1730–1680, 1490–1400, 1300–1260 cm^{-1}. The region 1200–700 cm^{-1} represent M–O–H dif. vib. in M–OH/hydroxo complexes while 900–300 cm^{-1} represent M–O stretching in the complex. Also 830–770 cm^{-1} suggest the presence of O–C=O in oxalato complexes. Fujita et al. [16] has assigned the peak at about 800 cm^{-1} to O–C=O bending in oxalato complexes. A shift of this wave number to 770 cm^{-1} in the residue formed at 400 °C may be due to the change in nature of bonding between thorium and oxalate group. Also the small absorption peak at 935 cm^{-1}, completely absent in the carbonate residue obtained at 460 °C, may be assigned to hydroxy group [17] present in hydroxy oxalates. According to IR characteristic wave numbers [16] shown in Table 2, the appearance of characteristic peaks for carbonate (1050 and 830 cm^{-1}) can be seen (Fig. 4) only for the IR patterns recorded for the residues formed at the temperatures of 400 and

460 °C. Hence these peaks should be attributed to the presence of thorium carbonate.

Further if we compare the IR spectrum in Fig. 4 (400 °C) with the spectra in Fig. 4 (165–280 °C), the peaks corresponding to lattice/coordinated water (660 and 470 cm^{-1}) are missing from Fig. 4 (400 °C), suggesting the complete removal of lattice/coordinated water by this temperature. In the absence of lattice/coordinated water, the presence of peak at 770 cm^{-1} suggest the presence of M–O–H bonding and the involvement of hydroxo complex. The observance of this peak can be explained on the basis of M–O–H deformation vibrations in hydroxo complexes as given in Table 2. And so the formation of thorium hydroxo complex involving oxalato group at this temperature is being suggested here along with the formation of thorium carbonate.

This metal hydroxo complex is not involving carbonate group because if we see the recorded IR pattern at 460 °C in Fig. 4, the peak at 770 cm^{-1}, corresponding to M–O–H deformation vibration is completely missing and the spectrum is having only the peaks corresponding to carbonate functional group. Hence these IR results indicate the presence of hydroxyoxalate group at 400 °C due to the formation of thorium hydroxyoxalate.

These observations suggest the presence of hydroxyoxalate and carbonate groups, and so, indicate the possible formation of thorium hydroxy oxalate and thorium carbonate at the temperature of 400 °C. TG curve (Fig. 1) shows a mass loss of 14.2% and the EGA-MS curve (Fig. 2) shows release of water, carbon monoxide and carbon dioxide in the temperature range of 280–400 °C (step D). The observed mass loss and evolution of gases may be due to the decomposition of dehydrated polynuclear complex above 280 °C to form thorium carbonate, thoria and thorium hydroxyoxalate as indicated by the observed IR and XRD data. Formation of thorium carbonate and thoria as intermediates by the temperature of 400 °C have already been reported [18].

Formation of thorium dioxide could be seen from the XRD pattern recorded at 425 °C, given in Fig. 3 matches well with the reported XRD pattern for thorium dioxide [18]. IR measurements given in Fig. 4 indicate the presence of hydroxyl group at 400 °C. Also evolution of water upto 450 °C can be seen on EGA-MS patterns given in Fig. 2 along with release of carbon dioxide and carbon monoxide. All these informations, if put together, can be concluded as; thorium hydroxy oxalate decomposes to form thorium dioxide by evolving water vapour, carbon dioxide and carbon monoxide during step E in the temperature range of 400–450 °C. The mass loss steps in the temperature region of 400–720 °C (steps E and F) are not well resolved on the TG curve due to possibility of overlapping reaction processes as being suggested by DTG and EGA-MS patterns. This explains the difference between the observed and theoretical values of mass loss percentage for the individual steps above 400 °C in Table 1. Evolution of CO_2 along with carbon monoxide and water vapors was observed (Fig. 2) in the temperature region of 400–450 °C (step E). It may be due to the decomposition of Th $(OH)_2C_2O_4$ to thoria as has been proposed in the decomposition mechanism given in Table 1. Thoria formation at 400 °C was also observed and reported by Aybers [19].

The recorded XRD patterns, shown in Fig. 3 (365 °C) and Fig. 3 (535 °C) match well with the reported XRD patterns [11] and [18] of thorium carbonate and thorium dioxide respectively. Presence of typical amorphous doublet peaks in HTXRD patterns as shown in Fig. 3 (365 °C) is the characteristic feature of carbonates due to the various conformations of $CO_3{}^{-}$ group [11]. Though broad peaks and amorphized product formation can be seen from the temperature of 205 °C as shown in Fig. 3 but thorium carbonate formation takes place above 250 °C only. Also, it can be seen from Fig. 2 that CO_2 is the only volatile observed above the temperature of 450 °C. All these observations suggest that the thorium carbonate formed in the temperature region of 280–400 °C (step D) decomposes above 450 °C by evolving CO_2 to form thorium dioxide as has been proposed in Table 1. D' Eye and Sellman [10] have shown that thorium carbonate decomposes directly to thoria without forming the intermediate thorium oxycarbonate. It has also been reported [11,19] that thorium carbonate is formed as an intermediate, decomposing to thorium oxycarbonate which subsequently decomposes to thoria. However, it should be mentioned here that formation of thorium oxycarbonate is being predicted by stoichiometric balance only. Dash et al. have recorded the XRD pattern of the residue, proposed it to be thorium oxycarbonate on the basis of stoichiometric balance, and found that the recorded pattern is almost similar to thorium carbonate. It was found to be amorphous in nature with broad peaks like thorium carbonate [11]. It is difficult to get certified thorium oxycarbonate and also not possible to draw any meaningful conclusion based on stoichiometric balance alone especially if the reaction steps are not well resolved on TG curve. In the present case, some reaction steps are not well resolved on TG curve and so DTG and EGA-MS patterns have also been taken into account to define the temperature region of individual reaction step and to calculate mass loss on TG curve in the respective temperature region. Observed and reported IR, XRD and EGA-MS patterns/data along with TG-DTG-DTA data have been used to propose the formation of thorium carbonate and its decomposition to thoria as given in Table 1. The observed mass loss above 550 °C on TG curve given in Fig. 1 is found to be less than 0.5% and no exothermicity could be seen on DTA curve in the temperature range. These observations suggest that the chances CO_2 formation due to disproportion reaction [$2CO \rightarrow C + CO_2$] are negligible. Moreover it indicates that the thoria formed will be almost free from carbon contamination as has been reported as major drawback of non-aqueous route of thoria formation [19].

4. Conclusion

The thermal analysis data involving TG, DTG, DTA and EGA measurements along with XRD and IR analysis show that thorium oxalate monohydrate and anhydrous thorium oxalate are not formed during the thermal decomposition of thorium oxalate hexahydrate as have been mentioned in some reports. Instead, present studies confirm that formation of thoria from the thermal decomposition of thorium oxalate hexahydrate is a multistep decomposition reaction process. Thorium oxalate hexahydrate dehydrates to give thorium oxalate dihydrate as an intermediate which polymerises to form a hydrated polynuclear thorium oxalate complex. This polymerised intermediate compound dehydrates and decomposes to thorium oxide through the formation of a hydroxyoxalate and carbonate of thorium as intermediates.

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