

**Note****THERMAL STUDIES ON COMPLEXES OF THORIUM(IV) WITH 2,6-LUTIDINE *N*-OXIDE AND TETRAMETHYLENE SULPHOXIDE**

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In recent years, a number of complexes of thorium(IV) with oxo-ligands containing X=O groupings, where X = C, N, P, S, and As, have been isolated and characterized. But the thermal investigations of these complexes have been carried out to a limited extent. Patel and co-workers [1,2] have reported the results on thorium(IV) perchlorato complexes with pyridine *N*-oxide and quinoline *N*-oxide by differential thermal studies. They extended their studies to thorium(IV) complexes with dimethyl sulphoxide [3] and diphenyl sulphoxide [4]. Bagnall et al. [5] have also reported some thermal results on dimethyl sulphoxide and hexamethyl phosphoramide. From this laboratory, we have recently reported the thermal studies on thorium(IV) complexes of pyrazolones [6] and with various aromatic amine *N*-oxides [7,8]. In the present study, we report the thermal decomposition characteristics, i.e., cleavage of the metal–ligand bond and the accompanying enthalpy change as determined by thermogravimetry (TG), differential thermal gravimetry (DTG), and differential thermal analysis (DTA) of thorium(IV) complexes of 2,6-lutidine *N*-oxide (LNO) and tetramethylene sulphoxide (TMSO) and their intermediates.

**EXPERIMENTAL**

All complexes under investigation were synthesized as reported earlier [9] while  $\text{ThCl}_4 \cdot 2 \text{LNO}$  was prepared using the method of Karayannis et al. [10]. Differential thermal analyses and thermogravimetry units employed were similar to those described earlier [9]. All experiments were carried out in static air. Heating rates employed were  $10^\circ\text{C min}^{-1}$  for DTA and  $5^\circ\text{C min}^{-1}$  in the case of TG.

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TABLE I  
Thermal data on Th(IV) complexes of LNO and TMSO

Complex	Decomn. Temp. (°C)		Decomn. product	TGA wt. loss %		DTG peak
	Initial	Final		Found	Calcd.	
$\text{Th}(\text{ClO}_4)_4 \cdot 6 \text{ LNO}$	160	328	$\text{ThO}_2$	80.19	80.70	Exo
$\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ LNO}$	137	203	$\text{Th}(\text{NO}_3)_4 \cdot 3 \text{ LNO}$	11.20	12.65	Exo
	205	421	$\text{Th}(\text{NO}_3)_4$	54.28	50.61	Endo
	500	675	$\text{ThO}_2$	70.20	72.83	Exo
$\text{ThCl}_4 \cdot 2 \text{ LNO}$	170	295	$\text{ThCl}_4$	40.10	39.67	Endo
	410	500	$\text{ThOCl}_2$	49.92	48.54	
	510	660	$\text{ThO}_2$	55.93	57.41	Exo
$\text{ThBr}_4 \cdot 2 \text{ LNO}$	165	275	$\text{ThBr}_4$	29.67	30.82	Endo
	415	510	$\text{ThOBr}_3$	47.11	46.36	
	590	670	$\text{ThO}_2$	67.31	66.91	Endo

Th(NCS) <sub>4</sub> ·2 LNO	160	270	Th(NCS) <sub>4</sub>	35.91	34.64	Exo
	490	590	ThO(NCS) <sub>2</sub>	49.31	48.73	
	620	690	ThO <sub>2</sub>	60.92	62.81	Endo
Th(ClO <sub>4</sub> ) <sub>4</sub> ·10 TMSO	195	240	Th(ClO <sub>4</sub> ) <sub>4</sub> ·6 TMSO	23.67	24.91	Exo with shoulder
	280	450	ThO <sub>2</sub>	85.32	84.19	Exo
Th(NO <sub>3</sub> ) <sub>4</sub> ·6 TMSO	190	210	Th(NO <sub>3</sub> ) <sub>4</sub> ·3 TMSO	29.32	28.26	Exo
	210	300	Th(NO <sub>3</sub> ) <sub>4</sub>	57.91	56.52	
	310	480	ThO <sub>2</sub>	77.01	76.08	Exo
ThCl <sub>4</sub> ·4 TMSO	180	210	ThCl <sub>4</sub> ·2 TMSO	26.82	26.32	Endo
	230	300	ThCl <sub>4</sub>	53.01	52.65	
	350	530	ThOCl <sub>2</sub> <sup>a</sup>	57.79	59.62	Exo
	160	210	ThBr <sub>4</sub> ·2 TMSO	21.98	21.48	Endo
ThBr <sub>4</sub> ·4 TMSO	240	300	ThBr <sub>4</sub>	43.32	42.97	
	340	525	ThOBr <sub>2</sub> <sup>a</sup>	53.18	55.78	Exo
	130	265	Th(NCS) <sub>4</sub>	31.32	30.95	Exo
Th(NCS) <sub>4</sub> ·2 TMSO	300	410	ThO(NCS) <sub>2</sub>	46.19	45.83	Endo
	490	618	ThO <sub>2</sub>	58.96	60.71	Exo

<sup>a</sup> Mixed with some ThO<sub>2</sub>.

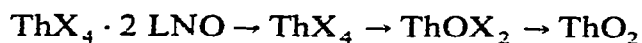
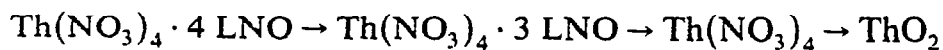
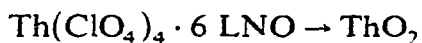
## RESULTS AND DISCUSSION

The results of thermal analyses of Th(IV) complexes are presented in Table 1.

*Th(IV)-LNO complexes*

The TG and DT curves of Th(IV) complexes of LNO do not show the presence of water and the decomposition takes place in different ways. The DTG curve of  $\text{Th}(\text{ClO}_4)_4 \cdot 6 \text{ LNO}$  reveals only one sharp exothermic peak at ca.  $165^\circ\text{C}$ , at which temperature the complex explodes with great smoke due to the oxygen content of the perchlorate [6,7]. The complex behaves similarly during its pyrolysis. The TG curve shows that the complex starts to decompose at  $160^\circ\text{C}$  and continues up to  $328^\circ\text{C}$ , after which it corresponds to  $\text{ThO}_2$ . From the pyrolysis curve it is also found that no stable intermediate perchlorate-LNO complexes have been formed as in the case of the thorium(IV) perchlorate complex of 4-amino antipyrine [6]. TG analysis of  $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ LNO}$  shows that the complex is stable up to  $137^\circ\text{C}$ , beyond which decomposition starts and continues up to  $204^\circ\text{C}$  (exo peak at  $200^\circ\text{C}$ ). Analysis of the thermogram shows that one molecule of LNO is lost at this stage. The composition of the compound at this stage corresponds to  $\text{Th}(\text{NO}_3)_4 \cdot 3 \text{ LNO}$ . It is assumed that in the  $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ LNO}$  complex, one of the LNO molecules is loosely bonded to the Th(IV) metal. Rickard and Woollard [11] recently synthesized the tris complex, which is more stable than the tetrakis complex.  $\text{Th}(\text{NO}_3)_4 \cdot 3 \text{ LNO}$  decomposes in the  $205\text{--}421^\circ\text{C}$  temperature region, losing all the remaining LNO molecules. Finally,  $\text{ThO}_2$  is obtained as residual mass at  $675^\circ\text{C}$ . Decomposition of the chloro and bromo complexes is completed in three steps similar to  $\text{Th}(\text{NCS})_4 \cdot 2 \text{ LNO}$  [8]. In both the cases all the ligand molecules attached to the Th(IV) metal are lost below  $300^\circ\text{C}$ , as shown by the break in the TG curve and the endo peak in the DTG curve. The final product is  $\text{ThO}_2$  preceded by the formation of the oxo-halide [5]. TG or DT studies of  $\text{ThI}_4 \cdot 4 \text{ LNO}$  could not be done as this complex decomposes slowly at room temperature with evolution of iodine vapour.

The analyses of the thermograms indicate the following decomposition schemes



(X = Cl, Br or NCS).

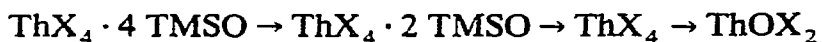
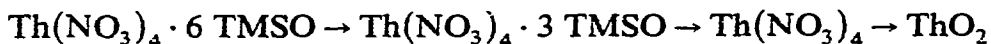
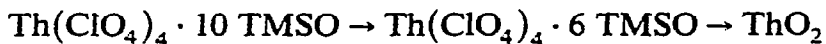
### *Th(IV)-TMSO complexes*

The DTG profiles of the TMSO complexes of Th(IV) show two major changes, one endothermic and the other exothermic, the endo peaks being quite small. An exothermic peak at ca. 205°C and a shoulder at ca. 270°C in the DTG curve of  $\text{Th}(\text{ClO}_4)_4 \cdot 10 \text{ TMSO}$  indicate the start of the decomposition. From TG analyses, it is found that four molecules of TMSO are removed at this stage and a stable complex  $\text{Th}(\text{ClO}_4)_4 \cdot 6 \text{ TMSO}$  is formed. Infrared studies of both the complexes, i.e.,  $\text{Th}(\text{ClO}_4)_4 \cdot 10 \text{ TMSO}$  and  $\text{Th}(\text{ClO}_4)_4 \cdot 6 \text{ TMSO}$ , indicate that TMSO is bonded to the Th(IV) metal via its oxygen atom. This behaviour is different from that of  $\text{Th}(\text{ClO}_4)_4 \cdot 12 \text{ DMSO}$ . Krishnan and Patel [3] found that in this complex six molecules of DMSO are lost at 180°C, and IR studies indicate that in  $\text{Th}(\text{ClO}_4)_4 \cdot 6 \text{ DMSO}$  a rearrangement in bonding between DMSO and metal occurs by donation of a lone pair of electrons from the sulphur to the metal and not oxygen to metal. Further heating of  $\text{Th}(\text{ClO}_4)_4 \cdot 6 \text{ TMSO}$  caused the loss of all the TMSO molecules and  $\text{ThO}_2$  was obtained as an end product. Previous workers studied the DTA of ruthenium [12] and lanthanide [13] complexes of TMSO and found that the ligand loss starts at 200°C (near the b.pt. of TMSO) and continues up to 340°C. The TG curve of  $\text{Th}(\text{NO}_3)_4 \cdot 6 \text{ TMSO}$  indicates that three molecules of TMSO are lost up to 210°C and a more stable compound,  $\text{Th}(\text{NO}_3)_4 \cdot 3 \text{ TMSO}$ , is obtained. A comparison of the IR studies of  $\text{Th}(\text{NO}_3)_4 \cdot 6 \text{ TMSO}$  and  $\text{Th}(\text{NO}_3)_4 \cdot 3 \text{ TMSO}$  indicates that in the hexakis complex [9] the nitrate absorption bands appear at 1370  $\text{cm}^{-1}$  and 820  $\text{cm}^{-1}$  due to ionic nitrate, while the existence of the bicovalently bonded nitrate group is evident by the presence of bands at 1488  $\text{cm}^{-1}$  ( $\nu_4$ ), 1290  $\text{cm}^{-1}$  ( $\nu_1$ ), 1020  $\text{cm}^{-1}$  ( $\nu_2$ ), 805  $\text{cm}^{-1}$  ( $\nu_6$ ), 735  $\text{cm}^{-1}$  ( $\nu_3$ ) and 700  $\text{cm}^{-1}$  ( $\nu_5$ ). In the tris complex no ionic nitrate band was observed around 830  $\text{cm}^{-1}$  and the ionic nitrate presumably becomes covalent as in the case of the  $\text{Th}(\text{NO}_3)_4$ -DMSO complex [14]. In both hexakis and tris complexes TMSO is bonded to the metal via its oxygen atom [14]. Since we have not studied the X-ray powder diffraction of the complexes, we are unable to say with certainty whether the complex  $\text{Th}(\text{NO}_3)_4 \cdot 3 \text{ TMSO}$  also exists in all the three  $\alpha$ ,  $\beta$  and  $\gamma$  modifications similar to  $\text{Th}(\text{NO}_3)_4 \cdot 3 \text{ DMSO}$  [14]. Between 210 and 300°C remaining TMSO molecules are lost, and finally a broad circular exotherm at ca. 450°C is obtained due to complete oxidation of the complex.

Decomposition of the chloro and bromo complexes is completed in three steps. In the first step, the complexes lose two molecules of the ligand as shown by the break in the TG curve and the peak in the DTG curve. The final product is a mixture of oxo-halide and oxide [6]. In  $\text{Th}(\text{NCS})_4 \cdot 2 \text{ TMSO}$ , the deligation process is completed between 130 and 265°C. An exo peak at 618°C is due to oxidation of the metal to  $\text{ThO}_2$  preceded by the oxo-species.

In the case of TMSO complexes the thermograms indicate the following

decomposition schemes:



(X = Cl or Br)



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