Thermochimica Acta, 56 (1982) 247–252
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

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

A.K. SRIVASTAVA * and R.K. AGARWAL **
*Meerut College, Meerut-250001 (India)*

(Received 5 January 1981)

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 $ThCl_4 \cdot 2$ 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°C min$^{-1}$ for DTA and 5°C min$^{-1}$ in the case of TG.

---

* To whom correspondence should be addressed.

** L.R. Post-graduate College, Sahibabad, Ghaziabad, India.

0040-6031/82/0000–0000/$02.75

TABLE I

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

| Complex | Decompn. Temp. (°C) | | Decompn. product | TGA wt. loss % | | DTG peak |
|---|---|---|---|---|---|---|
| | Initial | Final | | Found | Calcd. | |
| $Th(ClO_4)_4 \cdot 6$ LNO | 160 | 328 | $ThO_2$ | 80.19 | 80.70 | Exo |
| $Th(NO_3)_4 \cdot 4$ LNO | 137 | 203 | $Th(NO_3)_4 \cdot 3$ LNO | 11.20 | 12.65 | Exo |
| | 205 | 421 | $Th(NO_3)_4$ | 54.28 | 50.61 | Endo |
| | 500 | 675 | $ThO_2$ | 70.20 | 72.83 | Exo |
| $ThCl_4 \cdot 2$ LNO | 170 | 295 | $ThCl_4$ | 40.10 | 39.67 | Endo |
| | 410 | 500 | $ThOCl_2$ | 49.92 | 48.54 | |
| | 510 | 660 | $ThO_2$ | 55.93 | 57.41 | Exo |
| $ThBr_4 \cdot 2$ LNO | 165 | 275 | $ThBr_4$ | 29.67 | 30.82 | Endo |
| | 415 | 510 | $ThOBr_3$ | 47.11 | 46.36 | |
| | 590 | 670 | $ThO_2$ | 67.31 | 66.91 | Endo |

| | | | | | | |
|---|---|---|---|---|---|---|
| $Th(NCS)_4 \cdot 2$ LNO | 160 | 270 | $Th(NCS)_4$ | 35.91 | 34.64 | Exo |
| | 490 | 590 | $ThO(NCS)_2$ | 49.31 | 48.73 | |
| | 620 | 690 | $ThO_2$ | 60.92 | 62.81 | Endo |
| $Th(ClO_4)_4 \cdot 10$ TMSO | 195 | 240 | $Th(ClO_4)_4 \cdot 6$ TMSO | 23.67 | 24.91 | Exo with shoulder |
| | 280 | 450 | $ThO_2$ | 85.32 | 84.19 | Exo |
| $Th(NO_3)_4 \cdot 6$ TMSO | 190 | 210 | $Th(NO_3)_4 \cdot 3$ TMSO | 29.32 | 28.26 | Exo |
| | 210 | 300 | $Th(NO_3)_4$ | 57.91 | 56.52 | |
| | 310 | 480 | $ThO_2$ | 77.01 | 76.08 | Exo |
| $ThCl_4 \cdot 4$ TMSO | 180 | 210 | $ThCl_4 \cdot 2$ TMSO | 26.82 | 26.32 | Endo |
| | 230 | 300 | $ThCl_4$ | 53.01 | 52.65 | |
| | 350 | 530 | $ThOCl_2$ [a] | 57.79 | 59.62 | Exo |
| $ThBr_4 \cdot 4$ TMSO | 160 | 210 | $ThBr_4 \cdot 2$ TMSO | 21.98 | 21.48 | Endo |
| | 240 | 300 | $ThBr_4$ | 43.32 | 42.97 | |
| | 340 | 525 | $ThOBr_2$ [a] | 53.18 | 55.78 | Exo |
| $Th(NCS)_4 \cdot 2$ TMSO | 130 | 265 | $Th(NCS)_4$ | 31.32 | 30.95 | Exo |
| | 300 | 410 | $ThO(NCS)_2$ | 46.19 | 45.83 | Endo |
| | 490 | 618 | $ThO_2$ | 58.96 | 60.71 | Exo |

---

[a] Mixed with some $ThO_2$.

## 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 $Th(ClO_4)_4 \cdot 6$ LNO reveals only one sharp exothermic peak at ca. 165°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°C and continues up to 328°C, after which it corresponds to $ThO_2$. 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 $Th(NO_3)_4 \cdot 4$ LNO shows that the complex is stable up to 137°C, beyond which decomposition starts and continues up to 204°C (exo peak at 200°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 $Th(NO_3)_4 \cdot 3$ LNO. It is assumed that in the $Th(NO_3)_4 \cdot 4$ 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. $Th(NO_3)_4 \cdot 3$ LNO decomposes in the 205–421°C temperature region, losing all the remaining LNO molecules. Finally, $ThO_2$ is obtained as residual mass at 675°C. Decomposition of the chloro and bromo complexes is completed in three steps similar to $Th(NCS)_4 \cdot 2$ LNO [8]. In both the cases all the ligand molecules attached to the Th(IV) metal are lost below 300°C, as shown by the break in the TG curve and the endo peak in the DTG curve. The final product is $ThO_2$ preceded by the formation of the oxo-halide [5]. TG or DT studies of $ThI_4 \cdot 4$ 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

$Th(ClO_4)_4 \cdot 6\,LNO \rightarrow ThO_2$

$Th(NO_3)_4 \cdot 4\,LNO \rightarrow Th(NO_3)_4 \cdot 3\,LNO \rightarrow Th(NO_3)_4 \rightarrow ThO_2$

$ThX_4 \cdot 2\,LNO \rightarrow ThX_4 \rightarrow ThOX_2 \rightarrow ThO_2$

($X =$ 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 $Th(ClO_4)_4 \cdot 10$ 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 $Th(ClO_4)_4 \cdot 6$ TMSO is formed. Infrared studies of both the complexes, i.e., $Th(ClO_4)_4 \cdot 10$ TMSO and $Th(ClO_4)_4 \cdot 6$ TMSO, indicate that TMSO is bonded to the Th(IV) metal via its oxygen atom. This behaviour is different from that of $Th(ClO_4)_4 \cdot 12$ 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 $Th(ClO_4)_4 \cdot 6$ 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 $Th(ClO_4)_4 \cdot 6$ TMSO caused the loss of all the TMSO molecules and $ThO_2$ 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 $Th(NO_3)_4 \cdot 6$ TMSO indicates that three molecules of TMSO are lost up to 210°C and a more stable compound, $Th(NO_3)_4 \cdot 3$ TMSO, is obtained. A comparison of the IR studies of $Th(NO_3)_4 \cdot 6$ TMSO and $Th(NO_3)_4 \cdot 3$ TMSO indicates that in the hexakis complex [9] the nitrate absorption bands appear at 1370 $cm^{-1}$ and 820 $cm^{-1}$ due to ionic nitrate, while the existence of the bicovalently bonded nitrate group is evident by the presence of bands at 1488 $cm^{-1}$ ($\nu_4$), 1290 $cm^{-1}$ ($\nu_1$), 1020 $cm^{-1}$ ($\nu_2$), 805 $cm^{-1}$ ($\nu_6$), 735 $cm^{-1}$ ($\nu_3$) and 700 $cm^{-1}$ ($\nu_5$). In the tris complex no ionic nitrate band was observed around 830 $cm^{-1}$ and the ionic nitrate presumably becomes covalent as in the case of the $Th(NO_3)_4$-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 $Th(NO_3)_4 \cdot 3$ TMSO also exists in all the three $\alpha$, $\beta$ and $\gamma$ modifications similar to $Th(NO_3)_4 \cdot 3$ 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 $Th(NCS)_4 \cdot 2$ 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 $ThO_2$ preceded by the oxo-species.

In the case of TMSO complexes the thermograms indicate the following decomposition schemes:

$Th(ClO_4)_4 \cdot 10\ TMSO \rightarrow Th(ClO_4)_4 \cdot 6\ TMSO \rightarrow ThO_2$

$Th(NO_3)_4 \cdot 6\ TMSO \rightarrow Th(NO_3)_4 \cdot 3\ TMSO \rightarrow Th(NO_3)_4 \rightarrow ThO_2$

$ThX_4 \cdot 4\ TMSO \rightarrow ThX_4 \cdot 2\ TMSO \rightarrow ThX_4 \rightarrow ThOX_2$

$(X = Cl$ or $Br)$

$Th(NCS)_4 \cdot 2\ TMSO \rightarrow Th(NCS)_4 \rightarrow ThO(NCS)_2 \rightarrow ThO_2$

## REFERENCES

1 P. Rama Murthy and C.C. Patel, Can. J. Chem., 42 (1964) 856.
2 V. Krishnan and C.C. Patel, Can. J. Chem., 44 (1966) 972.
3 V. Krishnan and C.C. Patel, J. Inorg. Nucl. Chem., 26 (1964) 2201.
4 V.V. Savant and C.C. Patel, J. Less-Common Met., 24 (1971) 459.
5 K.W. Bagnall, D. Brown, P.J. Jones and J.G.H. Du Preez, J. Chem. Soc., (1966) 737.
6 A.K. Srivastava, Mahesh Srivastava and R.K. Agarwal, Ind. Eng. Chem., Prod. Res. Dev., in press.
7 R.K. Agarwal, P.C. Jain, V. Kapur, S. Sharma and A.K. Srivastava, Transition Met. Chem., 5 (1980) 237.
8 R.K. Agarwal, Mahesh Srivastava and A.K. Srivastava, J. Inorg. Nucl. Chem., 43 (1981) 203.
9 R.K. Agarwal, A.K. Srivastava and T.N. Srivastava, Transition Met. Chem., 5 (1980) 95.
10 N.M. Karayannis, A.N. Speca, L.L. Pytlewski and M.M. Labes, J. Less-Common Met., 22 (1970) 117.
11 C.E.F. Rickard and D.C. Woollard, Inorg. Nucl. Chem. Lett., 14 (1978) 207.
12 T. Bora and M.M. Singh, Transition Met. Chem., 3 (1978) 27.
13 K. Nagase, H. Yokobayashi, A. Iwase and K. Sone, Thermochim Acta, 17 (1976) 335.
14 P.J. Alvey, K.W. Bagnall and D. Brown, J. Chem. Soc., (1973) 2326.