Short Communications

THERMOGRAVIMETRIC STUDIES OF DIPYRIDINIUM COMPLEXES OF CERIUM(IV), THORIUM(IV) AND ZIRCONIUM(IV)

M. L. KAUL, B. L. KALSOTRA and R. N. KAPOOR

Department of Chemistry, University of Jammu, Jammu-180001, India

(Received January 10, 1976; in revised form August 3, 1976)

The TG curves of dipyridinium complexes of Ce(IV), Th(IV) and Zr(IV) have been reported. The mode of decomposition of the cerium and thorium complexes is broadly comparable but the decomposition of Zr complex shows some variation.

Although the preparation of complexes of cerium [1], thorium [2] and zirconium [3] with pyridinium cations has already been reported, there is no reference in literature regarding thermogravimetric studies. This communication deals with the thermogravimetric study of the dipyridinium metal complexes, $(C_5H_6N)_2MCl_6$ (where M stands for Ce, Th and Zr).

Experimental

The compounds were prepared by the methods already reported [1 – 3]. The prepared samples were analyzed for carbon and hydrogen (micro-analytic method) metal (as dioxide MO_2) and halogen (as AgCl) to ensure the purity of the compounds. The analytical data are given in Table 1. The thermogravimetric data were collected using a Stanton thermobalance model TR – 1.

Weighed samples of the dried metal complexes were stored in freshly tared crucibles (after heating to 1000°) placed in a desiccator. For TG studies, the samples were subjected to a heating rate of 4 ± 0.2° per minute in an atmosphere of air and the data were collected up to a temperature of 1000°, the period of maximum rise in temperature being about 4 hours. The sensitivity of the balance per small chart division was 1 mg, the chart range being 100 mg. The TG curves shown were obtained by plotting points from the original graph on X and Y axes. The type of volatile products lost during the course of heating was computed from weight losses.

Results

The TG curves obtained are shown in Fig. 1.

Dipyridinium cerium hexachloride $(C_5H_6N)_2CeCl_6$. The compound yielded (curve *a*, Fig. 1) a horizontal line extending up to 200° showing the stability of

the compound up to this temperature. The decomposition starts at 200° and continues up to 290° when another horizontal portion of the curve is obtained. The weight remaining at this stage corresponded to $CeCl_4$. This indicates the loss of pyridine together with two HCl molecules without the formation of any intermediate stable product. At 330° there started a gradual loss in weight up to 420°. At 420° another horizontal line was obtained. The weight at this stage corresponded to dioxide form CeO_2 which remained stable during subsequent heating.

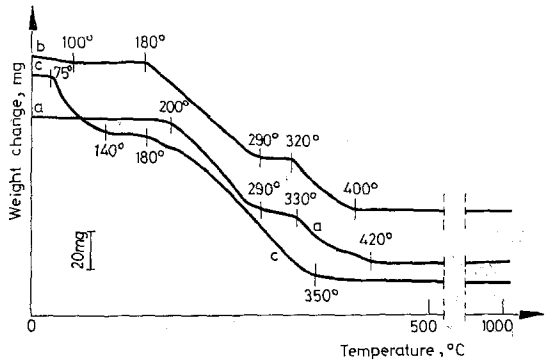

Fig. 1. TG curves of *a* $(C_5H_6N)_2CeCl_6$; *b* $(C_5H_6N)_2ThCl_6$; *c* $(C_5H_6N)_2ZrCl_6$.

Dipyridinium thorium hexachloride $(C_5H_6N)_2ThCl_6$. A very small initial loss of adherent moisture was recorded up to 100° as shown in TG curve *b*, Fig. 1. Between 100° and 180° there was no further loss in weight and a horizontal line was obtained giving the range of thermal stability of the complex compound. Beyond 180° a regular loss of weight was recorded up to 290°. Between 290° and 320° was obtained another horizontal line. The weight remaining at this stage corresponded to the chloride form $ThCl_4$. A further loss in weight was recorded from 320°. At 400° another horizontal line was obtained which corresponded to ThO_2. During the subsequent increase in temperature there was no further loss in weight and ThO_2 remained stable up to 1000°.

Table 1

Compound	Carbon %		Hydrogen %		Metal %		Chlorine %	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$(C_5H_6N)_2CeCl_6$	23.30	23.41	2.40	2.35	27.20	27.31	41.40	41.46
$(C_5H_6N)_2ThCl_6$	19.93	19.86	2.00	1.99	38.46	38.36	35.25	35.16
$(C_5H_6N)_2ZrCl_6$	25.80	25.87	2.65	2.60	19.60	19.65	45.70	45.82

Dipyridinium zirconium hexachloride $(C_5H_6N)_2ZrCl_6$. A horizontal line was obtained up to 75° as shown in curve *c*, Fig. 1. The compound is not stable beyond 75° as a sharp loss in weight was recorded at this temperature. At 140° another horizontal line was recorded. The weight remaining at this stage corresponded to $C_5H_6NZrCl_5$ showing the loss of one pyridine and one HCl molecule simultaneously. At 180° further loss in weight was recorded up to 350°. At 350° another horizontal line corresponding to the formation of the dioxide ZrO_2 was obtained. No further loss was recorded during subsequent heating.

The TG curves of cerium and thorium compounds are broadly comparable; the mode of decomposition is rather different in the case of the zirconium complex.

References

1. D. C. BRADELY, A. K. CHATTERJEE and W. WARDLAW, J. Chem. Soc., (1956) 2260.
2. D. C. BRADELY, SAAD and W. WARDLAW, J. Chem. Soc., (1954) 1091.
3. D. C. BRADELY, F. M. ABDUL HALIM, E. A. SADAK and W. WARDLAW, J. Chem. Soc., (1952) 2032.