Thermochimica Acta, 60 (1983) 115–117
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

THERMAL BEHAVIOUR OF THIOUREA COMPLEXES OF METAL SULPHATES

M.R. UDUPA

Department of Chemistry, Indian Institute of Technology, Madras-600 036 (India)

(Received 27 May 1982)

The thermal behaviour of transition metal complexes is largely dependent on the nature of the ligand, the stereochemistry of the metal ion and the associated anions, apart from the experimental conditions. Wendlandt and Smith [1] reviewed extensively the thermal properties of metal amine complexes. The coordination compounds, on heating, undergo thermal dissociation followed by the oxidation or reduction of the metal ion due to the electron transfer mechanism and the oxidation of the ligand. Depending on the prevailing atmosphere and the furnace temperature, the intermediate products may undergo chemical reaction. We are interested in the thermal decomposition studies of S-ligated metal complexes under diverse experimental conditions, including the change in sample containers. Reported in this note are the results of the thermal behaviour of thiourea complexes of Co(II), Ni(II), Cu(I), Zn(II) and Cd(II) sulphates following thermogravimetry employing mullite and platinum crucible containers.

EXPERIMENTAL

Thiourea (tu) complexes have been prepared by following the reported methods [2–4]. $Cu(tu)_3SO_4$ and $Ni(tu)_4SO_4 \cdot CH_3OH$ were obtained by the interaction of thiourea with the respective metal sulphates in ethanolic and methanolic media, respectively. $Cu(tu)_4SO_4$ was prepared from aqueous solutions of tu and copper(II) sulphate. Similarly, $Zn(tu)_3SO_4$ and $Cd(tu)_3SO_4$ have been obtained by interacting the metal sulphates with thiourea in 1:3 mole ratio in water.

About 200 mg samples of the complexes were taken in mullite and platinum crucibles and heated from room temperature continuously at the rate of 6°C min^{-1} in air on a Stanton recording thermobalance.

0040-6031/83/0000–0000/$03.00

RESULTS AND DISCUSSION

The TG curves of the metal complexes obtained under similar conditions using mullite and platinum crucibles are given in Fig. 1. For a particular complex, the initial temperature of decomposition and the total weight loss at the end of the reaction are the same in both crucibles. However, there is a marked difference in the thermal curves in the intermediate temperature range 400–600°C in the two sample containers.

$Co(tu)_3SO_4$ starts decomposing at 180°C and about 60% weight loss occurred by 450°C. The final product obtained at 880°C is found to be Co_3O_4. Increase in weight is noticed around 500°C which remarkable in platinum crucible. $Ni(tu)_4SO_4 \cdot CH_3OH$ loses 10% of its weight between 90 and 140°C due to the removal of methanol. The complex decomposes to give NiO as the end product at 800°C. As in the cobalt complex, an increase in weight in the TG curve is noticed around 480°C.

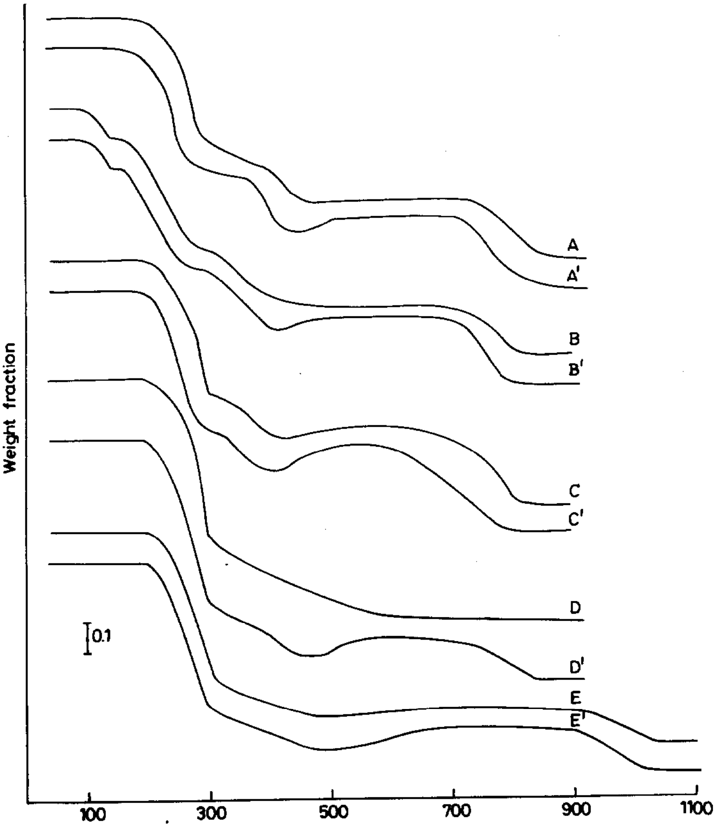

Fig. 1. TG curves of $Co(tu)_3SO_4$ (A,A′), $Ni(tu)_4SO_4CH_3OH$ (B,B′), $Cu_2(tu)_4SO_4$ (C,C′), $Zn(tu)_3SO_4$ (D,D′) and $Cd(tu)_3SO_4$ (E,E′). A, B, C, D, E, in mullite crucibles; A′, B′, C′, D′, E′, in platinum crucibles.

$Cu_2(tu)_4SO_4$ decomposes at 200°C and the final product of decomposition at 800°C is found to be CuO. However, there is an increase in weight in both the crucibles in the temperature range 400–550°C, which is extensive in platinum. $Zn(tu)_3SO_4$ starts decomposing at 200°C and, after an initial fast reaction, ZnO is obtained as the final product at 620°C in the mullite crucible. It is interesting to note that an increase in weight occurs between 500 and 600°C in the platinum crucible and ZnO, as the end product, is obtained at 850°C. $Cd(tu)_3SO_4$ decomposes at 210°C and the end residue is found to be CdO at 1080°C in the two crucibles. The increase in weight is observed between 500 and 700°C.

In separate experiments, the complexes were heated to around 500°C and the intermediate products obtained found to be a mixture of metal sulphide, metal oxide and metal sulphate. The metal sulphide so formed may be oxidized as according to

$$MS + \tfrac{3}{2}\,O_2 \rightarrow MO + SO_2 \qquad (1)$$

$$SO_2 + \tfrac{1}{2}\,O_2 \rightleftharpoons SO_3 \qquad (2)$$

$$MO + SO_3 \rightarrow MSO_4 \qquad (3)$$

$$MS + 3\,MSO_4 \rightarrow 4\,MO + 4\,SO_2 \qquad (4)$$

The increase in weight is thus attributed to sulphate formation as in eqn. (3). It has been reported that a platinum surface acts as a catalyst in the decomposition of certain ammonium compounds [5] and in the oxidation of metal sulphides in air [6]. Thus, the enhanced increase in weight in the platinum crucibles is attributed to the catalytic influence of platinum in favouring reaction (2) to proceed. The formation of ZnO in the mullite crucible is below the normal temperature range of zinc sulphate decomposition [7]. This may probably be due to reaction (4) taking place more favourably at this temperature. The product SO_2 may be oxidized in platinum but not in mullite crucibles, which facilitates the formation of the $ZnSO_4$ indicating the weight increase. The $ZnSO_4$ thus formed decomposes between 720 and 850°C, which is the normal temperature of its decomposition.

REFERENCES

1 W.W. Wendlandt and J.P. Smith, The Thermal Properties of Transition-Metal Ammine Complexes, Elsevier, Amsterdam, 1967.
2 W.G. Palmer, Experimental Inorganic Chemistry, Cambridge University Press, Cambridge, 1959.
3 F.A. Cotton, O.D. Faut and J.T. Mague, Inorg. Chem., 3 (1964) 17.
4 M.R. Udupa, J. Chem. Educ., 57 (1980) 825.
5 G. Liptay, M. Berenyi and E. Sarkany, Hung, Sci. Instrum., 15 (1968) 31.
6 M.R. Udupa and G. Aravamudan, Curr. Sci., 39 (1970) 206.
7 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963.