Thermochimica Acta, 53 (1982) 225–227
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

THERMAL DECOMPOSITION OF URANYL GLYCOLATE

M.R. UDUPA

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

(Received 30 July 1981)

The thermal decomposition studies of uranium oxalates [1,2], formate [3] and acetate [4] revealed that the carboxylates decompose to give oxides of uranium around 400°C. The final residue in air is invariably found to be U_3O_8. Our interest was to produce UO_2 at moderate temperatures from simple uranium compounds as it is a technologically important oxide used in the fabrication of nuclear fuel pellets. Reported in this communication are the preparation, characterization and thermal behaviour of dioxobisglycolatouranium(VI), UG, following thermogravimetry, differential thermal analysis and mass spectral studies.

EXPERIMENTAL

An aqueous solution of uranyl acetate dihydrate (4.2 g in 20 ml water) was refluxed with 10 ml of 50% glycolic acid for an hour. The resultant solution was concentrated on a water bath and diluted with acetone. The precipitated UG was collected on a filter, washed with acetone and dried. Analytical results were: found, C 11.6, H 1.52, U 57.2%; calcd. for $C_4H_6O_8U$, C 11.44, H 1.44, U 56.67%.

The infrared spectrum of the compound was taken on a Perkin Elmer 257 spectrometer using the KBr pellet technique. The X-ray powder diffraction patterns were recorded using Cu K_α radiation. The thermal decomposition studies were made using a Stanton thermobalance in air and a Mettler TG–DTA simultaneous thermal analyzer in an argon atmosphere at a continuous heating rate of 4–6°C min^{-1}. The mass spectra studies were carried out using a Varian mass spectrometer with the ion source filament operating at 70 eV.

RESULTS AND DISCUSSION

UG is a yellow crystalline compound and with d_{hkl} values (in Å) of 6.38s, 5.18s, 4.42 m, 3.59 m, 3.49 s, 3.43 s, 3.30 m, 2.64 w, 2.56 w, 2.49 w, 2.43 m, 2.37 w, 2.30 m, 2.11. The infrared spectrum of the compound compared with those of transition metal glycolates [5,6] indicates that the frequencies noticed at 3320 (ν_{OH}) and 1085 ($\nu_{C\text{-}OH}$) are indicative of the bonding of the –OH group of glycolate to U. The

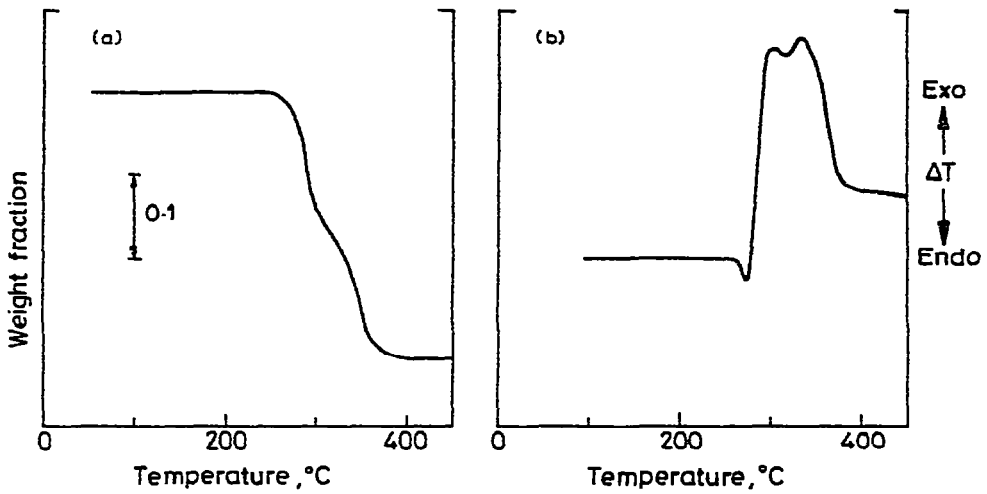

Fig. 1. (a) TG plot of uranyl glycolate. (b) DTA plot of uranyl glycolate.

characteristic symmetric and asymmetric carboxyl stretching frequencies observed at 1590 and 1410 cm^{-1} clearly suggest the carboxyl bonding to the metal resulting in a 5-membered chelate ring. A medium intensity band at 862 cm^{-1} is the characteristic of asymmetric stretching frequency (ν_3) of the O–U–O group [7]. Thus, uranium in UG is 6-coordinated with the two oxygen atoms and the two glycolate groups in positions *trans* to each other.

The TG and DTA curves in argon are illustrated in Fig. 1. The TG curve suggests that UG is stable up to 250°C and decomposes in the temperature range 250–400°C. The weight loss observed at 400°C is found to be 33.4%, which agrees with the calculated weight loss of 33.2% for the formation of U_3O_8. The X-ray powder patterns of the residue showed characteristic d_{hkl} values corresponding [8] to U_3O_8 (4.22s, 3.31w, 2.72s, 2.66m, 2.07m, 1.95w). In order to discover whether any other intermediate uranium oxide was formed during the decomposition, the X-ray

TABLE 1

Mass spectral data of uranyl glycolate

m/e	Intensity (%)	Assignment
16	22	O
17	66	OH
18	91	OH_2
28	89	CO
29	56	COH
30	48	HCOH
44	100	CO_2
45	16	COOH
46	7	HCOOH

patterns of the residue obtained by heating UG to 350°C were examined. The diffractogram showed a high background with a few very broad reflections which corresponded to the intense lines of UO_3, suggesting the formation of UO_3 as an intermediate phase.

The DTA curve showed a small endotherm at 275°C followed immediately by an exotherm at 300°C, which are attributed to the fission of UO_2–glycolate bonds. The other exothermic effect at 330°C is tentatively assigned to the reduction of UO_3 to U_3O_8 as found in the decomposition of ammonium uranate [9]. The thermal behaviour in air is found to be similar to that in argon, suggesting that air apparently does not influence the decomposition of UG.

The mass spectral data obtained at 270°C are tabulated in Table 1. The fragmentation products observed at 240, 250, 260 and 270°C are similar but differ only in their relative intensities. The major fragments are CO_2 and H_2O though, as expected, there exists also a small amount of formic acid as the degradation product.

ACKNOWLEDGEMENT

The author wishes to thank Professor Dr. Krebs, Münster, F.R.G., for his interest in the work and for providing mass spectral and TG–DTA results.

REFERENCES

1 W.W. Wendlandt, T.D. George and G.R. Horton, J. Inorg. Nucl. Chem., 17 (1961) 273.
2 V.M. Padmanabhan, S.C. Saraiya and A.K. Sundaram, J. Inorg. Nucl. Chem., 12 (1960) 356.
3 G.D. Buttress and M.A. Hughes, J. Chem. Soc. A, (1968) 1272.
4 P.S. Clough, D. Dollimore and P. Grundy, J. Inorg. Nucl. Chem., 31 (1969) 36.
5 A. Fishinger, A. Sarapu and A. Companion, Can. J. Chem., 47 (1969) 2629.
6 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1978.
7 ASTM X-ray data file 2.276.
8 J.L. Woolefrey, J. Inorg. Nucl. Chem., 38 (1976) 347.
9 G.H. Price, J. Inorg. Nucl. Chem., 33 (1971) 4085.