Thermochimica Acta, 31 (1979) 121–125
© Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

Ternary uranium oxides from thermal decomposition of uranyl butyrates with divalent cations

R. M. ROJAS, V. GONZALEZ, J. BERMÚDEZ AND M. L. DE PAZ
Instituto de Química Inorgánica "Elhúyar" del C.S.I.C., Facultad de Ciencias Químicas, Universidad Complutense, Madrid 3 (Spain)

(Received 22 May 1978)

The formation of ternary oxides of uranium with cobalt, nickel and with monovalent or divalent cations, in which the existence of uranium(V) was indicated, have been described[1–3].

Bacmann[4, 5] on studying the thermal decomposition of cobalt monouranate observed the formation of a new cobalt uranium compound, $Co_3U_2O_8$, in which the uranium also has an oxidation number of five.

Bobo[6] described the formation of a non-stoichiometric cobalt uranate, which retains the structure of the stoichiometric compound. He indicated also the existence of $CoUO_3$ and of a cubic solid solution of the fluorite type, formed by the reaction between UO_2 and CoO heated above 1000 °C.

As a consequence of solid state reactions in the residues of the thermal decomposition of cobalt uranyl butyrate, some of the substances indicated above are formed, and the progressive reduction of uranium(VI) is observed.

EXPERIMENTAL

Synthesis

Both cobalt and nickel uranyl butyrates, were isolated as well formed crystals by mixing aqueous solutions of uranyl and metallic butyrates. The air-dried products were analyzed and the results are given below:

Calculated for $Co[UO_2(C_3H_7COO)_3]_2 7H_2O$ (%): C, 23.10; H, 4.49; U, 38.17; Co, 4.73. Found (%): C, 22.87; H, 4.46; U, 39.12; Co, 4.83.

Calculated for $Ni[UO_2(C_3H_7COO)_3]_2 7H_2O$ (%): C, 23.10; H, 4.49; U, 38.18; Ni, 4.71. Found (%): C, 22.87; H, 4.46; U, 39.08; Ni, 4.80.

The IR spectra of both complexes are analogous to those observed for similar compounds[7].

Apparatus

DTA was carried out with a Dupont model 990 apparatus, with the high temperature cell, Pt thermocups and Pt/Pt–13%Rh thermocouples. A heating rate of 10°C min^{-1}, static air atmosphere and precalcined alumina as reference material were used. Thermogravimetric analyses were made on the initial compounds using the Dupont 990 thermobalance.

DTA and thermogravimetric analyses have been made on samples previously heated to 700°C using a Mettler model TA 1 apparatus. A dynamic dry air atmosphere and 6°C min^{-1} heating rate were selected.

Carbon and hydrogen were determined quantitatively by the microcombustion method, with a Coleman model 33 microanalyzer. The uranium and divalent metal were analyzed by X-ray fluorescence spectroscopy, using a Philips model 1540 spectrometer.

The X-ray diffraction diagrams were obtained using both Debye–Scherrer and Guinier cameras, and diffractometric techniques (Ni filtered, CuKα radiation).

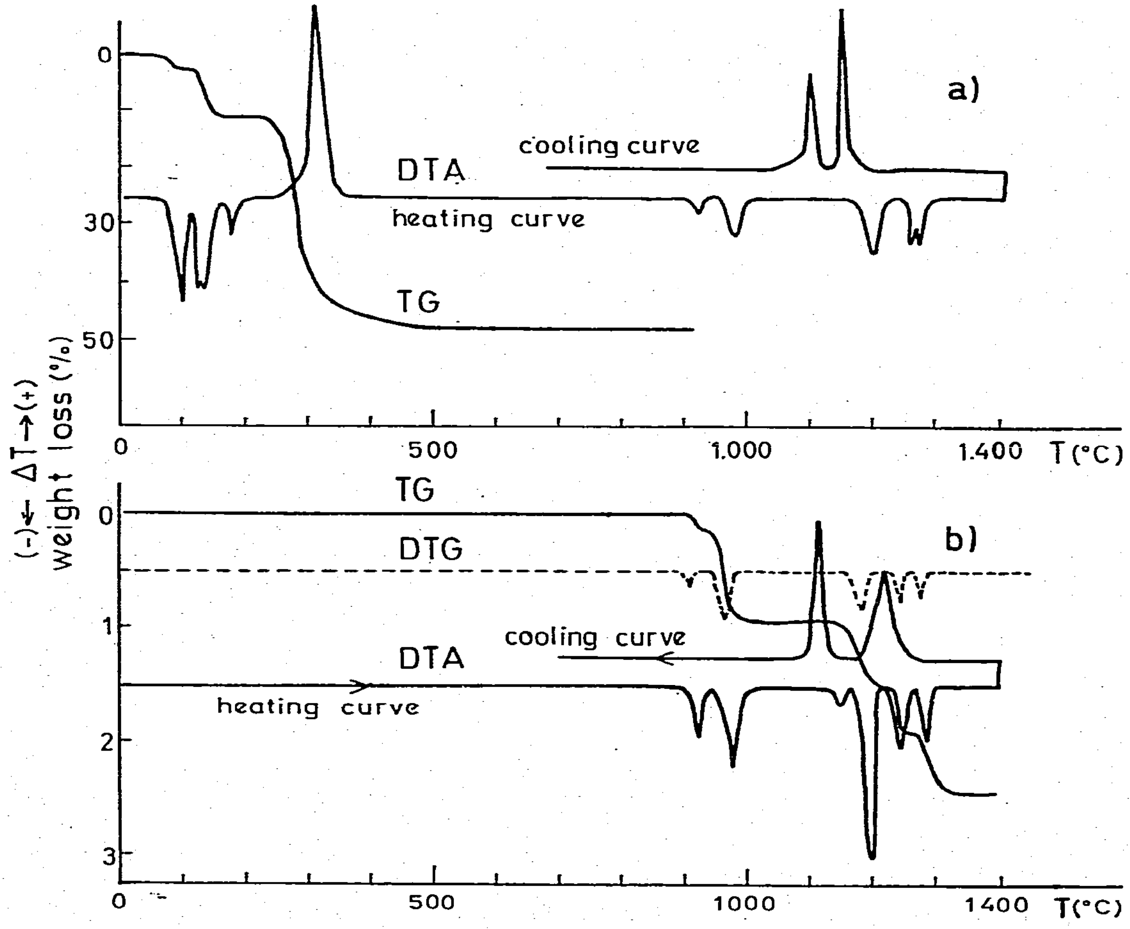

Fig. 1. DTA and TG curves of $Co[UO_2(C_3H_7COO)_3]_2 7H_2O$. (a) Initial compound, (b) ignited to 700°C.

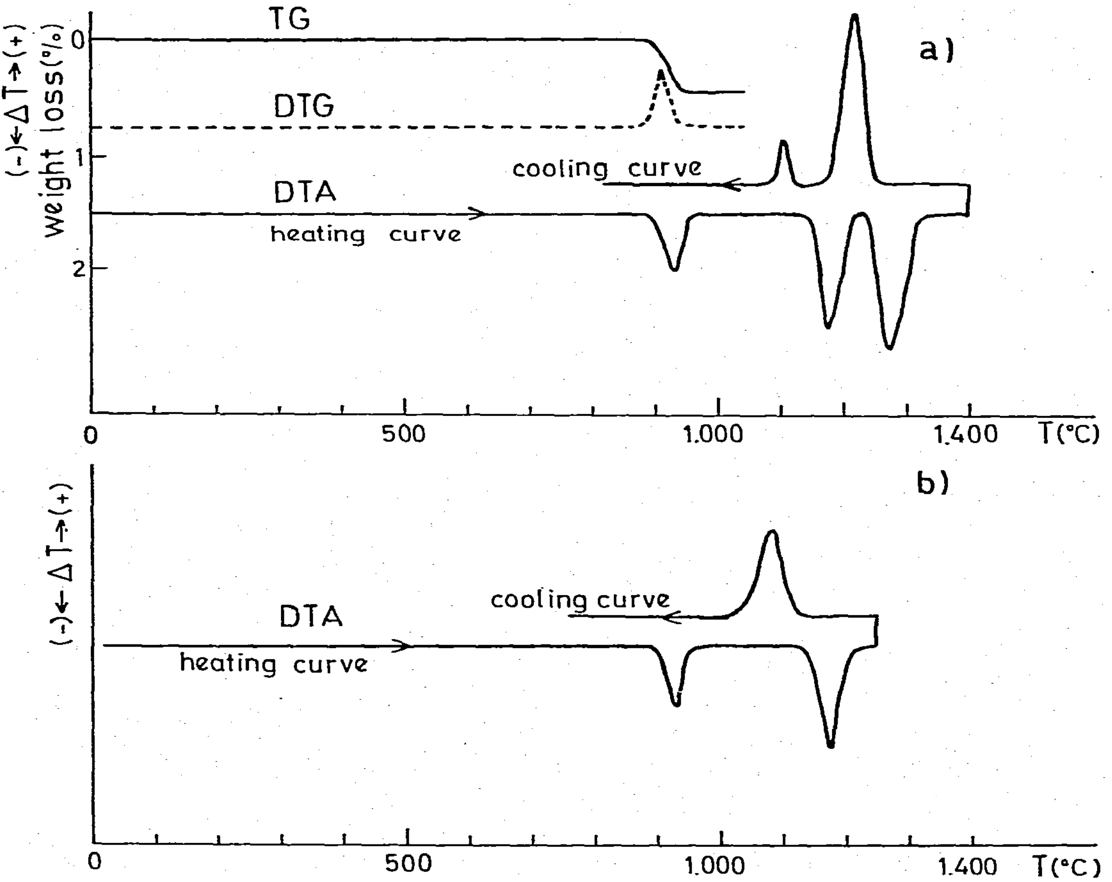

Fig. 2. (a) DTA and TG curves of $CoUO_4$, (b) DTA curve of the mixture $UO_2(NO_3)_2 6H_2O/CoO$ 2:3 ignited to 700°C.

RESULTS AND DISCUSSION

Thermal and X-ray studies

The complexes dehydrate between 100 and 150°C; anhydrous cobalt uranyl butyrate melts at 180°C and both compounds decompose exothermally between 250–350°C giving, as residues, a mixture of cobalt and nickel (α-form) tri- and monouranates[8, 9]. A small endothermic effect is observed in the DTA curve of cobalt uranyl butyrate between 900–930°C, accompanied by a weight loss of 0.12% (Fig. 1b). Bearing in mind the possibility of the reaction $CoUO_4 \rightarrow CoUO_{4-x}$[6], differential and thermogravimetric curves were obtained for pure cobalt uranate, and the same transformation was observed (Fig. 2a). It can be concluded that non-stoichiometric $CoUO_{3.9}$ is formed as a well defined compound, between 900–930°C, without any modification to the X-ray diffraction pattern. This fact has been tested by comparing the Guinier diagrams of cobalt monouranate heated at 850 and 980°C.

Cobalt triuranate decomposes to the monouranate and U_3O_8, this being the mixture identified at 1000°C, while for the nickel compound the residue consists of NiO and U_3O_8 which do not react in the temperature range studied (up to 1400°C).

TABLE 1

SEQUENCE OF REACTIONS OBSERVED IN THE THERMAL DECOMPOSITION OF COBALT AND NICKEL URANYL BUTYRATES

Compounds	*Thermal effect (T°C)*	*Wt. loss (%)*	
		Calc.	*Found*
$2\ Co[UO_2(C_3H_7COO)_3]_2 7H_2O$			
↓	70– 110	2.88	2.85
$2\ Co[UO_2(C_3H_7COO)_3]_2 5H_2O$			
↓	110– 160	7.22	7.30
$2\ Co[UO_2(C_3H_7COO)_3]_2$	170– 186		
↓	250– 350	38.01	37.77
$CoUO_4 + CoU_3O_{10}$			
↓	900– 936	0.12	0.12
$CoUO_{3.9} + CoU_3O_{10}$			
↓	936–1000	0.828	0.825
$CoUO_{3.9} + CoUO_4 + 2/3\ U_3O_8$			
↓	1140–1209	0.550	0.554
$CoUO_{3.9} + 1/3\ Co_3U_2O_8 + 7/9\ U_3O_8$			
↓	1227–1259	0.425	0.417
$1/3\ Co_3U_2O_8 + 1/3\ CoU_2O_6 + 2/3\ CoO + 8/9\ U_3O_8$			
↓	1260–1300	0.550	0.561
$2\ CoU_2O_6$			
$2\ Ni[UO_2(C_3H_7COO)_3]_2 7H_2O$			
↓	60– 110	4.40	4.33
$2\ Ni[UO_2(C_3H_7COO)_3]_2 4H_2O$			
↓	110– 150	5.70	5.77
$2\ Ni[UO_2(C_3H_7COO)_3]_2$			
↓	250– 380	37.86	37.86
$NiUO_4 + NiU_3O_{10}$			
↓	940–1000		
$4/3\ U_3O_8 + 2\ NiO$			

Between 1140 and 1210°C, cobalt monouranate reacts with some U_3O_8 and the formation of $Co_3U_2O_8$ takes place. On increasing the temperature, the hexagonal ordered form of CoU_2O_6 is formed[2]; at this stage, a mixture of hexagonal CoU_2O_6, $Co_3U_2O_8$, U_3O_8 and a small quantity of cobalt oxide can be identified in the X-ray powder diagram of the residue heated at 1270°C and quenched in liquid nitrogen. Finally, at 1300°C, the cubic disordered form of CoU_2O_6, with $a = 5.25_7$ Å, is obtained.

The thermal behaviour of both cobalt and nickel uranyl butyrates is resumed in Table 1.

During the experimental work, $Co_3U_2O_8$ was synthesized by mixing uranyl nitrate and cobalt oxide CoO, and the X-ray patterns of the mixture heated at 800°C were observed to correspond to $CoUO_4$, this temperature being considerably lower than that necessary to obtain this type of uranate[8]. Thermal studies were made on the mixture UO (NO) 6H O/CoO in 2:3 molar ratio heated at 700°C; the thermo gram obtained is reproduced in Fig. 2(b). As can be seen, the formation of $Co_3U_2O_8$ occurs between 1150–1200 °C with an endothermic and reversible reaction.

According to the results indicated above, it can be concluded that the non-stoichiometric cobalt uranate, $CoUO_{3.9}$ exists as a well defined compound, and that some oxygen is eliminated at atmospheric pressure, since all the thermal studies were carried out under these conditions. The possible existence of ordered defects is not shown by the X-ray diffraction patterns technique, but studies by electron diffraction microscopy are under way.

REFERENCES

1 S. Kemmler-Sack and W. Rüdorf, *Z. Anorg. Allg. Chem.*, 354 (1967) 255.
2 S. Kemmler-Sack, *Z. Anorg. Allg. Chem.*, 358 (1968) 226.
3 S. Kemmler-Sack, E. Stumpp, W. Rüdorf and H. Erfurth, *Z. Anorg. Allg. Chem.*, 352 (1967) 287.
4 M. Bacmann, *Bull. Soc. Fr. Mineral. Cristallogr.*, 94 (1971) 442.
5 M. Bacmann, *Acta Crystallogr., Sect. B*, 29 (1973) 1570.
6 J. C. Bobo, *C.R. Acad. Sci., Ser. C.*, 262 (1966) 553.
7 J. F. Arenas, R. M. Rojas and J. Bermúdez, *An. Quim.*, 69 (1973) 869.
8 H. R. Hoekstra and R. H. Marshall, *Advan. Chem. Ser.*, 71 (1967) 211.
9 W. L. Marshall and J. S. Gill, *J. Inorg. Nucl. Chem.*, 26 (1964) 277.