Thermochimica Acta, 71 (1983) 247–255
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF CESIUM HEXANITRATOURANIUM(IV)

SMT. S.R. BHARADWAJ and M.S. CHANDRASEKHARAIAH *

Reactor Chemistry Section, Chemical Group, Bhabha Atomic Research Centre, Bombay 400 085 (India)

M.S. GILL AND S.C. JAIN

Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085 (India)

(Received 15 June 1983)

ABSTRACT

As cesium hexanitratouranium(IV), $Cs_2U(NO_3)_6$, has the same Cs:U stoichiometry as that of Cs_2UO_4, thermal decomposition of this nitrato complex in air and nitrogen was studied in detail as a possible alternate method of preparing pure Cs_2UO_4. The volatility of cesium nitrate, which is one of the intermediate products, changed this Cs:U ratio during thermal decomposition. Hence, only $Cs_2U_2O_7$ was obtained on heating the sample to 775 K or higher. A scheme for the thermal decomposition of $Cs_2U(NO_3)_6$ is given by combining the observed TG, XRD and IR data.

INTRODUCTION

Accurate thermal and thermodynamic data of Cs_2UO_4 are essential for the analysis of cesium transport from oxide fuel pellets to the clad of the fuel pins [1–6]. A number of reports containing such data have been published. However, the difficulties of preparing pure Cs_2UO_4 in gram quantities [7,8] have hindered considerably the researchers from obtaining data of sufficient accuracy.

The usual method of heating a mixture of cesium carbonate and uranium oxide [7,8] suffers from difficulty in maintaining the correct Cs:U stoichiometry through accurate weighing of hygroscopic cesium carbonate. Other alternate methods reported are either cumbersome [9] or may not always give the desired product. Therefore, an attempt was made to obtain this compound by thermal decomposition of cesium–uranium oxycomplexes such as mixed oxalates, mixed carbonates or mixed nitrates.

---

* To whom all correspondence should be addressed.

Among these mixed salts, $Cs_2U(NO_3)_6$ has the same Cs:U ratio as Cs_2UO_4 and it can be prepared as a pure, anhydrous powder. Hence, a detailed study of the thermal decomposition of this mixed nitrate was carried out and the results are presented in this paper.

EXPERIMENTAL

An anhydrous sample of cesium hexanitratouranium(IV) was prepared by reacting uranium(IV) chloride and cesium nitrate in sulphamic–nitric acid medium at 0°C [10]. The sample was dried in vacuo and kept in an air-tight vial.

All IR spectra were taken as a Nujol mull of the solid product on a Perkin–Elmer grating spectrophotometer, model 579, using cesium iodide plates. The phase identification of solids was obtained with XRD using Cu K_α radiation. Thermogravimetric measurements were done both in air and in nitrogen (2–3 l h^{-1}) using a thermomicrobalance. The details of the thermomicrobalance have been described elsewhere [11]. In addition, a few decomposition experiments under vacuum (10^{-2} Torr) at selected temperatures followed by the XRD of the products were also carried out. The samples were always handled inside a dry box of flowing argon.

RESULTS AND DISCUSSION

The sample of $Cs_2U(NO_3)_6$ on programmed heating underwent a change in its colour from straw-white to pale yellow and finally to orange. Above 525 K, there was frothing, especially at a reduced pressure of 10^{-2} Torr, indicating the formation of a melt. When a cold finger was introduced above the sample at or above 685 K, a white crystalline deposit was observed on the cold finger; XRD examination of this deposit showed the presence of only $CsNO_3$.

Figure 1A and B shows the TG curves of $Cs_2U(NO_3)_6$ obtained under different experimental conditions. It can be seen that within the experimental temperature range of investigation, air or nitrogen atmospheres appear to have an insignificant effect on TG curves. The slower heating rate of 2 K min^{-1} (Fig. 1B) gave a little better resolution of the step around 575 K but did not substantially alter the decomposition reaction. Similarly, altering the sample size from 30 mg to 8 mg also did not affect the reaction.

TG curves show three distinct steps in the thermal decomposition of this compound (Fig. 1A and B). There was no observable mass loss below 373 K and at this temperature, a sharp mass loss begins. This decomposition reaction was completed by about 428 K and the next sharp mass loss was observed to commence at 544 K and terminates around 663 K. The last step

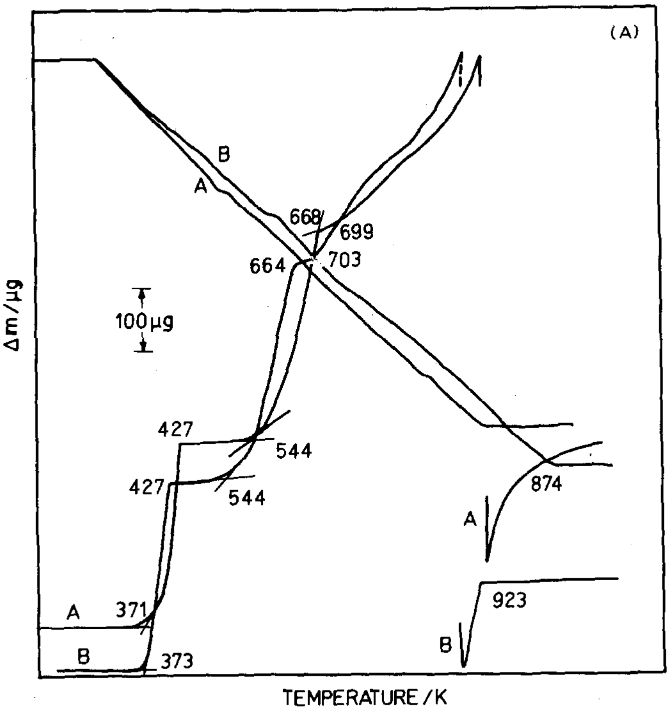

Fig. 1A. TG curves of $Cs_2U(NO_3)_6$ in N_2 and air. A, 27.36 mg, N_2, 4 K min^{-1}; B, 27.60 mg air, 4 K min^{-1}.

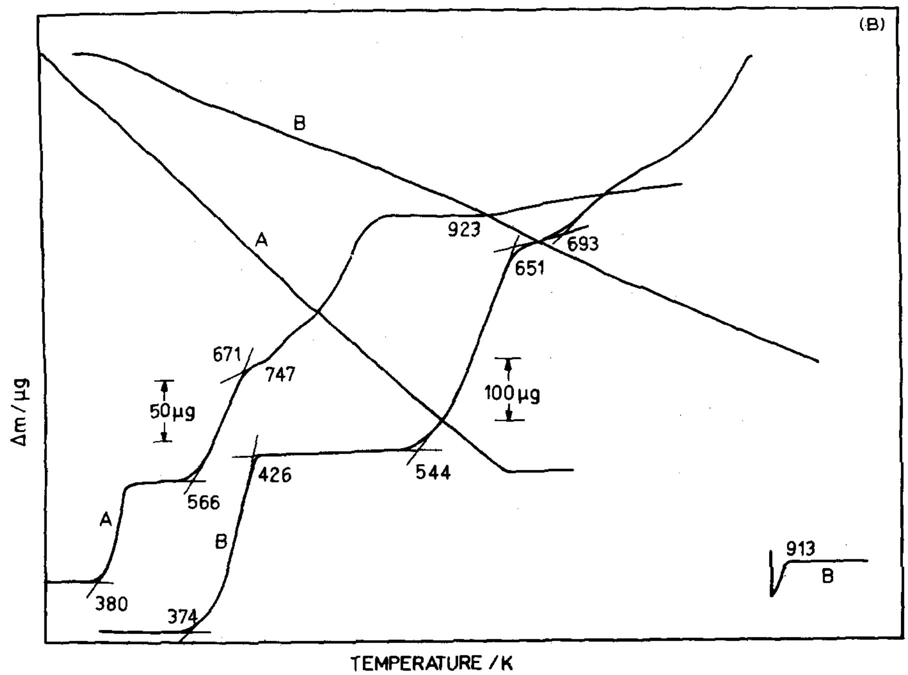

Fig. 1B. TG curves of $Cs_2U(NO_3)_6$ in N_2. A, 8.10 mg, 4 K min^{-1}; B, 28.10 mg, 2 K min^{-1}.

TABLE 1

Thermogravimetric data of $Cs_2U(NO_3)_6$

Experiment number	Sample size (m/mg)±0.05	Decomposition temperature range (T/K)±10		Mass loss % $(\Delta m/m)\times 100$	Remarks
1	28.10	(i)	374–426	10.32	N_2, 2 K min^{-1}
		(ii)	544–651	12.46	
		(iii)	693–883	13.17	
2	27.36	(i)	371–427	10.60	N_2, 4 K min^{-1}
		(ii)	544–668	12.43	Heated for
		(iii)	699–933	15.72	24 h at 933 K
3	27.60	(i)	373–427	10.87	Air, 4 K min^{-1}
		(ii)	544–664	12.68	
		(iii)	703–973	17.03	
4	8.10	(i)	380–433	10.49	N_2, 4 K min^{-1}
		(ii)	566–670	12.35	
		(iii)	747–923	20.37	
5	29.30	(i)	372–434	10.58	N_2, 4 K min^{-1}
		(ii)	544–563	12.63	Heated for 12 h at 563 K
6	30.26	(i)	379–440	10.58	N_2, 4 K min^{-1}
		(ii)	566–688	17.52	Heated for 42 h at 688 K

of mass loss was shown to begin around 700 K and reach a constant weight by about 875 K. This last step in the TG curves was not as sharp as the other two. In Table 1, the results of the TG runs are summarized.

The accrued data (TG, IR, and XRD) were sufficient to establish unambiguously the first step of the decomposition of $Cs_2U(NO_3)_6$ as follows

$$Cs_2U(NO_3)_6 \xrightarrow{373-428\ K} Cs_2UO_2(NO_3)_4 + NO_2 + \tfrac{1}{2}O_2 + NO \tag{1}$$

The calculated mass loss of reaction (1) is 10.50% of the initial sample while the observed mass loss for the first step of the TG curves was 10.49–10.87 %. (Table 1). Though the IR spectra of the starting sample, as well as that obtained on heating it at 423 K in nitrogen, showed the presence of coordinated nitrato bands [12], the latter, in addition, showed the characteristic bands of the uranyl group in the range 800–1000 cm^{-1} (Fig. 2). Further, the two X-ray diffraction patterns were distinctly different from each other (Table 2). Thus, reaction (1) was assigned to the first decomposition step. This conclusion is in good agreement with that of DuPreez et al. [13] except that we did not observe any decomposition of the cesium hexanitratouranium(IV) at ambient temperature even after 1 yr stored in a tightly closed vial.

The TG curves of the mass loss step above 685 K (Fig. 1A and B) were not as sharp as the other two steps and, in fact, there is an indication that there must be more than one mass loss reaction in this temperature interval.

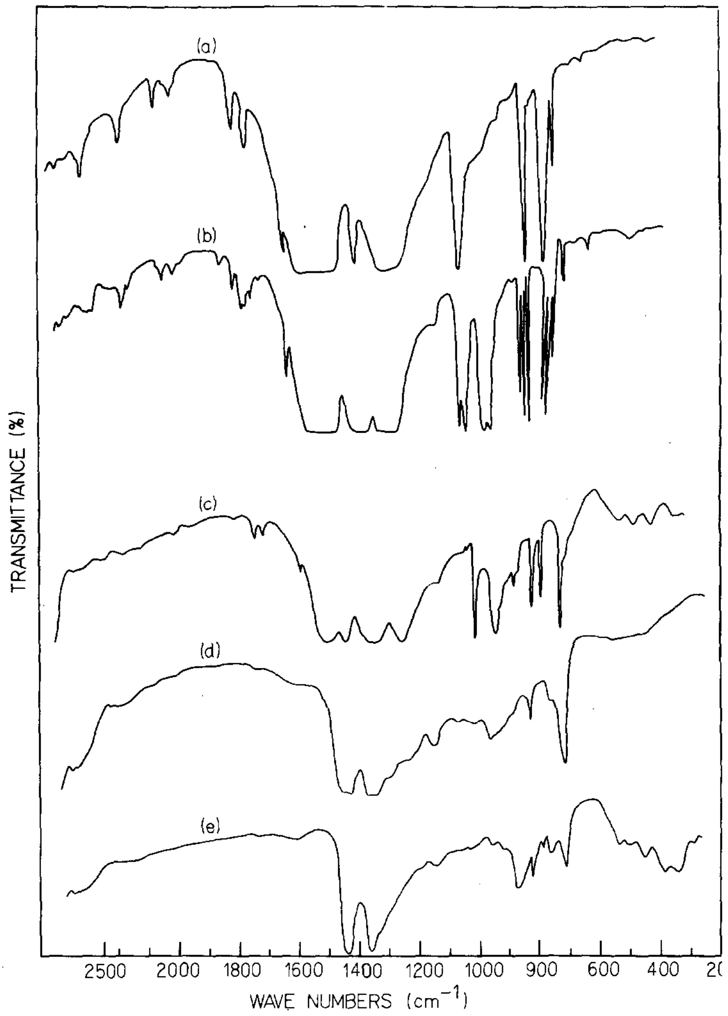

Fig. 2. IR results. (a), $Cs_2U(NO_3)_6$; (b), product at 422 K; (c), product at 588 K; (d), $CsNO_3$; and (e), product at 600 K.

As cesium nitrate is known to evaporate above 685 K [10], it is probable that between 685 K and 925 K, both the evaporation of a part of the cesium nitrate and the formation of cesium uranates would be taking place simultaneously and the observed TG curve of this step is an overlap of these two processes. Hence, the net mass loss for the step will depend both on the time interval of heating and also the temperature. The observed irreproducibility of the mass loss for this step (Table 1) is thus explained.

The characterization of the solid products formed between 544 K and 663 K and delineating the reactions responsible for the observed data in this temperature interval proved to be an arduous task. The fractional mass loss observed for this step was reproducible (12.35–12.68% of $Cs_2U(NO_3)_6$).

TABLE 2

XRD data of $Cs_2U(NO_3)_6$ and $Cs_2UO_2(NO_3)_4$

$Cs_2U(NO_3)_6$			$Cs_2UO_2(NO_3)_4$			Residue at 560 K		
2θ	d_{hkl}	I/I_0	2θ	d_{hkl}	I/I_0	2θ	d_{hkl}	I/I_0
12.65	6.997	9	13.15	6.732	11	13.40	6.607	100
14.00	6.326	65	14.00	6.326	24	18.50	4.796	35
16.40	5.405	33	16.20	5.471	54	20.00	4.439	35 [a]
17.70	5.001	26	17.50	5.068	13	21.20	4.191	33
18.00	4.928	13	18.50	4.796	7	27.00	3.302	22
21.15	4.201	14	21.10	4.210	100	28.30	3.153	100 [a]
21.35	4.162	11	22.45	3.960	20	32.30	2.772	16
21.85	4.068	9	23.40	3.802	12	34.00	2.637	14
22.50	3.952	13	24.30	3.663	55	34.90	2.571	30 [a]
22.70	3.917	10	27.90	3.198	75	37.50	2.398	13
23.35	3.513	38	29.10	3.069	58	40.50	2.227	20 [a]
26.20	3.401	6	33.00	2.714	25	41.00	2.201	8
28.70	3.110	100	36.00	2.495	25	43.00	2.103	8
29.60	3.018	9	36.35	2.471	25	45.50	1.993	32 [a]
35.95	2.498	20	36.65	2.452	12			
36.40	2.468	16	38.80	2.320	19			
38.50	2.338	24	39.60	2.276	6			
39.50	2.281	9	40.32	2.238	24			
40.15	2.246	28	40.75	2.214	16			
41.85	2.159	13	42.80	2.112	22			
42.10	2.146	10	43.25	2.089	20			
42.60	2.122	6	43.88	2.062	14			
43.10	2.099	11	45.80	1.981	7			
43.50	2.080	5	49.00	1.859	9			
44.65	2.029	7	49.30	1.848	11			
46.45	1.955	7	49.90	1.828	7			
47.00	1.933	5	50.50	1.807	6			
48.60	1.873	6	51.20	1.783	7			
49.00	1.859	5	54.4	1.687	7			
52.00	1.758	18	55.1	1.667	5			
54.00	1.698	9	55.70	1.650	9			
57.50	1.600	20						

[a] $CsNO_3$ lines

Even when the sample (29.30 mg) was heated isothermally at 563 K for 12 h (experiment number 5, Table 1), the observed mass loss was 12.63% only. XRD examination of the products obtained at the end of this step in the TG runs were not unambiguous. To obtain a better insight, a series of decomposition experiments at selected temperatures in flowing dry nitrogen or in vacuo were carried out. A known amount of the sample was taken for each experiment in a fused silica container and heated at the desired temperature isothermally for 4–12 h and then quenched to room temperature by quickly removing the sample container from the hot zone. The resultant solid residue was examined by the XRD technique.

All the products obtained when heated to 875 K or higher gave diffraction lines of only the $Cs_2U_2O_7$ phase. The gaseous environments, namely nitrogen, dry air or vacuum did not significantly change the diffraction pattern. The products obtained on heating the nitrate sample at 775 K after sublimation of the $CsNO_3$ was a mixture of $Cs_2U_2O_7$ and $Cs_4U_5O_{17}$. In other words, this product was a mixture of unreacted cesium nitrate, $Cs_4U_5O_{17}$, and $Cs_2U_2O_7$. The XRD patterns obtained for the products obtained on heating the nitrate samples at 585 K and 688 K were very similar and both showed the presence of $CsNO_3$ and $Cs_4U_5O_{17}$ phases. The XRD spectra of the products obtained by heating the original sample at $T \leqslant 560$ K in vacuo did not show the presence of any cesium uranates. In addition to $CsNO_3$, there was another "new" phase whose exact identification could not be made. The IR spectrum of the product obtained at $T \leqslant 560$ K was different from that obtained at 688 K (Fig. 2). Both spectra showed bands due to the presence of $CsNO_3$. However, in the sample prepared at $T \leqslant 560$ K, there were additional absorption bands of the uranyl group in the 800–1000 cm^{-1} region which were totally absent in the other sample. Without any phase identification data, Gelman et al. [14] have stated (probably based on their mass loss information) that above 533 K, they obtained a mixture of $CsNO_3$ and UO_3 as the decomposition product. Our search for the presence of any of the known crystalline UO_3 phases was in vain, though our observed mass loss for this step (Table 1) was in agreement with the formation of a mixture of $CsNO_3$ and UO_3. Therefore, the UO_3 phase formed must be the amorphous trioxide.

Based on these results, the following scheme is proposed for the thermal decomposition of cesium hexanitratouranium(IV)

$$Cs_2U(NO_3)_6 \xrightarrow{373-428\ K} Cs_2UO_2(NO_3)_4 + NO + NO_2 + \tfrac{1}{2}O_2 \tag{1}$$

$$Cs_2UO_2(NO_3)_4 \xrightarrow{428-544\ K} 2\ CsNO_3 + UO_2(NO_3)_2 \tag{2}$$

$$2\ CsNO_3 + UO_2(NO_3)_2 \xrightarrow{544-688\ K} 2\ CsNO_3 + UO_3 + NO + NO_2 + O_2 \tag{3}$$

$$CsNO_3(s) \xrightarrow{T > 688\ K} CsNO_3(g) \tag{4}$$

$$UO_3 + \tfrac{4}{5}CsNO_3 \xrightarrow{585-775\ K} \tfrac{1}{5}Cs_4U_5O_{17} + \tfrac{2}{5}NO + \tfrac{2}{5}NO_2 + \tfrac{2}{5}O_2 \tag{5}$$

$$\tfrac{1}{5}Cs_4U_5O_{17} + \tfrac{1}{5}CsNO_3 \xrightarrow{T \geqslant 775\ K} \tfrac{1}{2}Cs_2U_2O_7 + \tfrac{1}{10}NO + \tfrac{1}{10}NO_2 + \tfrac{1}{10}O_2 \tag{6}$$

Reaction (1) has already been discussed and all the experimental observations support this conclusion. TG data do not indicate reaction (2) as it involves no mass loss. XRD observation of the presence of a "new" phase in addition to $CsNO_3$ for cases where the original sample was heated only to $T \leqslant 560$ K and the fact that this solid product gave an IR spectrum containing bands characteristic of a coordinated nitrato group suggest that reaction (2) takes place in the range 428–560 K. The exothermic DSC peak at 451 K reported by DuPreez et al. [13] may be due to reaction (2). Further work is necessary to eliminate or confirm an alternate reaction (2a) for this step.

$$Cs_2UO_2(NO_3)_4 \rightarrow CsNO_3 + CsUO_2(NO_2)_3 \qquad (2a)$$

The mass loss calculated for reaction (3) is 12.34% of $Cs_2U(NO_3)_6$ which is in very good agreement with the observed mass loss of 12.35–12.68% (Table 1). Above 688 K, reactions (4), (5) and (6) are taking place almost simultaneously. The extent of each reaction depends on several experimental parameters and hence the non-producibility of the mass loss observed in TG curves for the last step is not surprising.

The powder diffraction data of the two nitrate compounds, namely, $Cs_2U(NO_3)_6$ and $Cs_2UO_2(NO_3)_4$, are summarized in Table 2. The $Cs_2UO_2(NO_3)_4$ was indexed on the basis of monoclinic symmetry and the resultant cell parameters are also given in Table 2.

CONCLUSION

In principle, the Cs_2UO_4 phase could be prepared by the thermal decomposition of suitable cesium–uranium oxycomplex compounds of proper Cs : U stoichiometry. Though $Cs_2U(NO_3)_6$ satisfied this criterion, the volatility of $CsNO_3$ formed as an intermediate product changed this stoichiometry and only $Cs_2U_2O_7$ could be prepared. However, thermal decomposition of a proper mixed carbonate complex should result in the formation of pure Cs_2UO_4.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. R.M. Iyer, Head, Chemistry Division, and Dr. K.S. Venkateswarlu, Head, Reactor Chemistry Section, Chemical Group, for their interest and to Dr. S.R. Dharwadkar for his assistance in carrying out some experiments.

REFERENCES

1 T.B. Lindemer, T.M. Besmanand and C.E. Johnson, J. Nucl. Mater., 100 (1981) 178.
2 D.C. Fee and E.E. Johnson, J. Nucl. Mater., 78 (1978) 219; 96 (1981) 80.
3 D.C. Fee and C.E. Johnson, J. Inorg. Nucl. Chem., 40 (1978) 1375.
4 E.A. Aitken, M.G. Adamson, D. Dutina and S.K. Evans, Thermodynamics of Nuclear Materials, Symp. Proc. IAEA, Vienna, Vol. I, 1975, p. 187.

5 R. Loranzelli, R. LeDudal and R. Atabeck, Thermodynamics of Nuclear Materials, Symp. Proc. IAEA, Vienna, Vol. I, 1980, p. 539.

6 M.G. Adamson, E.A. Aitken, R.W. Caputi, R.E. Potter and M.A. Mignanelli, Thermodynamics of Nuclear Materials, Symp. Proc. IAEA, Vienna, Vol. I, 1980, p. 503.

7 M. Shyamala, S.R. Dharwadkar and M.S. Chandrasekharaiah, J. Nucl. Mater., 114 (1983) 344.

8 M. Shyamala, M.Sc. Thesis, Bombay University, 1981.

9 K.M. Efremova, E.A. Lappalitove, Yu. Simanov and L.M. Rovba, in V.I. Spitsyn (Ed.), ANL-Transl-33, Issled, V. Obl. Khim. Urana, (1961) 59.

10 K.W. Bagnall, P.S. Robinson and M.A. Stewart, J. Chem. Soc., (1961) 4060.

11 M. Shyamala, S.R. Dharwadkar, M.D. Karkhanavala, V.V. Deshpande and M.S. Chandrasekharaiah, Thermochim. Acta, 44 (1981) 249.

12 S.C. Jain, M.S. Gill and G.S. Rao, J. Indian Chem. Soc., 58 (1981) 210.

13 J.G.H. DuPreez, C.P.J. Van Vuuran and W.J. McGill, J. Coord. Chem., 5 (1976) 231.

14 A.D. Gelman, N.N. Krot and N.P. Ermolaev, Russ. J. Inorg. Chem., 7 (1962) 1051.