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Note

STUDIES ON SELENATES. IX. THERMAL DECOMPOSITION OF DOUBLE SELENATES OF CERIUM(III) WITH RUBIDIUM AND CAESIUM *

M.A. NABAR and V.R AJGAONKAR

Department of Chemistry, University of Bombay, Vidyanagari, Bombay-400 098 (India)

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Gomez Madrazo et al. [1] have recently synthesised the double selenates of cerium(III) with alkali metals and studied some of their physico-chemical properties. The present communication is devoted to the study of the thermal behaviour of rubidium cerium(III) and caesium cerium(III) selenates, which has not been attempted so far.

EXPERIMENTAL

The double selenates were prepared by crystallisation, from solutions containing equimolar quantities of cerium selenate pentahydrate and rubidium or caesium selenate. The salts obtained were analysed chemically for cerium and selenate ions. The thermal decomposition was studied using a Mettler thermoanalyser, as detailed previously [4].

RESULTS AND DISCUSSION

The analytical results (Table 1) show that rubidium cerium selenate is an anhydrous compound, while caesium cerium selenate crystallises as a dihydrate. The latter compound effloresces to give its anhydrous form. The thermoanalytical curves of anhydrous rubidium cerium(III) selenate and caesium cerium(III) selenate are reproduced in Figs. 1 and 2, respectively. The results are given in Table 2.

The DTA curves of these compounds exhibit two endothermic activities. The first, associated with the major weight loss on the TG curve, appears at 560°C for both $RbCe(SeO_4)_2$ and $CsCe(SeO_4)_2$. The observed weight loss for this stage is in fair agreement with that calculated for the decomposition resulting in the mixture of cerous oxide (Ce_2O_3) and $M(I)_2SeO_4$. The second endotherm, appearing at 982 and

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* For Part VIII, see ref. 5.

TABLE 1

Analytical results

Compound	Ce%		SeO_4%	
	Calcd	Obsd.	Calcd.	Obsd.
$RbCe(SeO_4)_2$	27.39	26.22	55.90	55.69
$CsCe(SeO_4)_2 \cdot 2\ H_2O$	23.55	23.42	48.05	47.69

TABLE 2

Thermoanalytical Results

Compound	TG temp range (°C)	Wt loss		Reaction
		Calcd	Obsd	
$RbCe(SeO_4)_2$	450–900	37.23	38.38	$RbCe(SeO_4)_2 \rightarrow Rb_2SeO_4 + Ce_2O_3$
$CsCe(SeO_4)_2$	450–950	34.07	33.54	$CsCe(SeO_4)_2 \rightarrow Cs_2SeO_4 + Ce_2O_3$

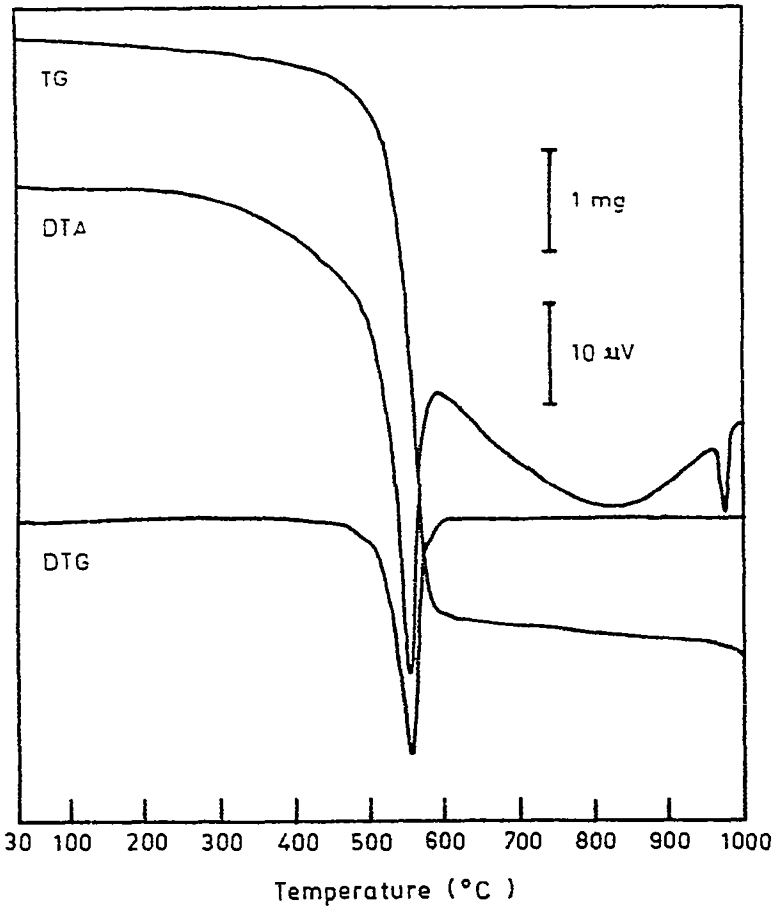

Fig 1 Thermoanalytical curves of $RbCe(SeO_4)_2$. Sample weight, 14.95 mg; heating rate, 10°C min^{-1}.

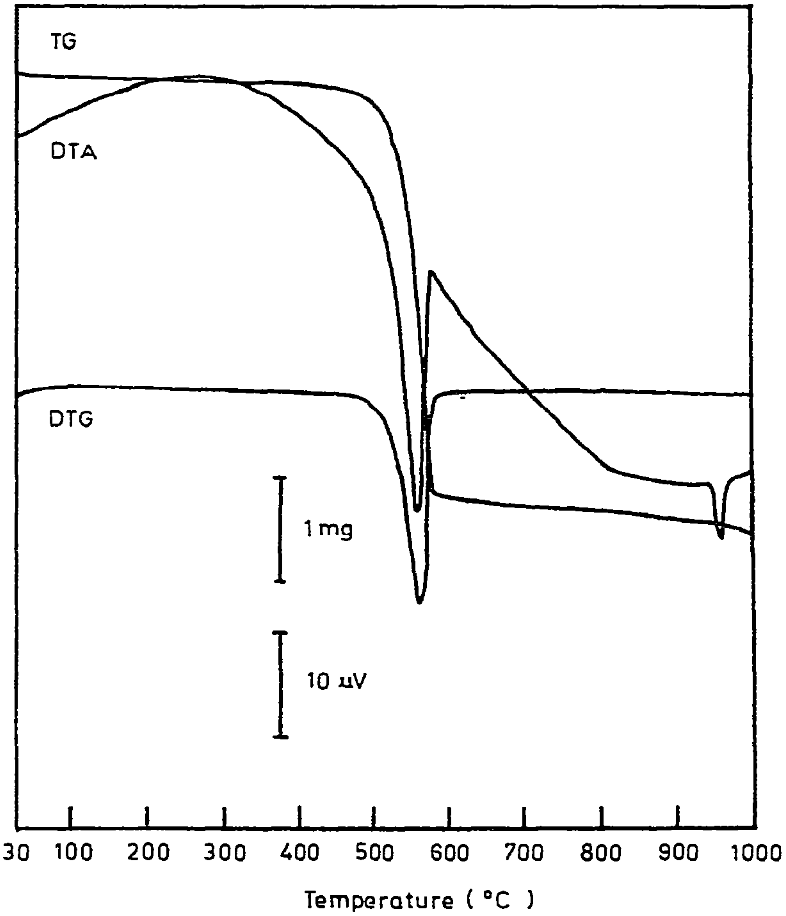

Fig 2 Thermoanalytical curves of $CsCe(SeO_4)_2$ Sample weight, 12 94 mg, heating rate, 10°C min^{-1}

960°C, respectively, for the rubidium and caesium compounds, can be accounted for by the melting of Rb_2SeO_4 and Cs_2SeO_4. These are in conformity with the reported melting points [6]. The continuous weight losses observed on the TG curves beyond these temperatures are evidently due to the evaporation of the molten alkali selenates.

The final residuum, on X-ray analysis, showed the presence of CeO_2 and not Ce_2O_3, as was expected from the weight losses on the TG curves. It may thus be concluded that the thermal decomposition of the parent compounds probably yields Ce_2O_3 in an atmosphere of nitrogen which is subsequently oxidised to CeO_2 when exposed to air.

The weight losses on isothermal heating of the parent compounds at 650°C in air (see Table 3) correspond to decomposition to $CeO_2 + M(I)_2SeO_4$.

It is interesting to note here that the double cerium selenates studied presently decompose in one stage, in contrast to the multi-stage decompositions observed in the other rare earth double selenates studied earlier [2–5,7]. Further, the formation of the oxide in these cases takes place at a much lower temperature as compared to that of the other rare earth oxides from their corresponding double selenates.

TABLE 3

Results of isothermal heating at 650°C

Compound	Wt. loss	
	Obsd	Calcd. for decomposition to $M(I)_2SeO_4 + CeO_2$
$RbCe(SeO_4)_2$	36 01	35 67
$CsCe(SeO_4)_2$	32 61	32 64

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REFERENCES

1 L A Gomez Madrazo, J G. Ribas Bernat and F J Arnaiz Garcia, Ion (Madrid), 33 (1973) 242
2 M A Nabar and S V Paralkar, Thermochim Acta, 35 (1980) 287
3 M A Nabar and S V Paralkar, in W Heminger (Ed) Proc 6th ICTA, Vol 2, Bayreuth, Birkhauser, Basel, Boston, Stuttgart, 1980, p 175
4 M A Nabar and V R Ajgaonkar, Thermochim Acta, 47 (1981) 309
5 M A Nabar and V R Ajgaonkar Thermochim Acta, 51 (1981) 381
6 M Ionashiro and I Giolito, Thermochim Acta, 38 (1980) 341.
7 M Ionashiro and I Giolito, Thermochim Acta, 38 (1980) 285