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THERMAL DECOMPOSITION OF EUROPIUM FORMATE AND OXALATE *

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ABSTRACT

A complete and consistent scheme of the thermal decomposition of europium(III) formate and europium(III) oxalate was elucidated from the results of microthermogravimetry supplemented by DTA, evolved gas analysis, IR and X-ray powder diffraction examination of the products. In addition to the previously known oxycarbonate, namely $Eu_2O_2CO_3$, another oxycarbonate, $Eu_2O(CO_3)_2$, was shown to be an additional intermediate of the decomposition reaction. The sequence of the decomposition reaction of the formate was shown to be

$2\ Eu(HCOO)_3 \rightarrow Eu_2(C_2O_4)_3 \rightarrow Eu_2O(CO_3)_2 \rightarrow Eu_2O_2CO_3 \rightarrow Eu_2O_3$

INTRODUCTION

Europium sesquioxide is considered as an alternate material to B_4C for fast breeder reactor control rod applications [1,2]. The thermal decomposition of its oxysalts, especially oxalate or formate, is the commonly practised method of preparing Eu_2O_3. But the decomposition reactions of the oxalate as well as the formate are poorly understood as yet and, in view of the said importance, a reinvestigation of the decomposition of a few europium salts, including the oxalate and the formate, was undertaken to obtain an unambiguous scheme of decomposition reaction.

The thermal decompositions of $Eu_2(C_2O_4)_3$ and $Eu(HCOO)_3$ have been reported but agreement among different investigators is lacking [3–7]. Glasner et al. [3,4] proposed reaction (1) as the first step in the Eu(III) oxalate decomposition

$$Eu_2(C_2O_4)_3 \rightarrow 2\ EuC_2O_4 + 2\ CO_2 \qquad (1)$$

Gallagher et al. [5], however, having failed to detect any Eu(II) compounds from the decomposition products in air from Mössbauer spectroscopy or

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[*] Taken from the M.Sc. thesis of M. Shyamala, Bombay University, 1981.

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fluorescence measurements, suggested the following decomposition scheme with a carbonyl carbonate as the first decomposition product.

$$Eu_2(C_2O_4)_3 \rightarrow Eu_2O_2COCO_3 + 2\,CO + 2\,CO_2 \tag{2}$$

$$Eu_2O_2COCO_3 \rightarrow Eu_2O_2CO_3 + CO \tag{3}$$

$$Eu_2O_2CO_3 \rightarrow Eu_2O_3 + CO_2 \tag{4}$$

For europium formate decomposition to Eu_2O_3, $Eu_2O_2CO_3$ has been proposed as the only intermediate [6,7]. In view of the complex sequences of decomposition steps for the decomposition of $La(HCOO)_3$ established recently [8] in this laboratory, it was thought that the same may be true of europium formate. Hence a reinvestigation of the decomposition of $Eu(HCOO)_3$ was carried out.

EXPERIMENTAL

All europium salts were prepared from 99.5% pure Eu_2O_3. Europium(III) formate and oxalate samples were prepared in the usual way. $EuC_2O_4 \cdot H_2O$ and $EuCO_3$ were prepared from $EuSO_4$. Details of the preparative procedure are described elsewhere [9].

All solids, namely, the initial starting compounds as well as all intermediate products obtained during the thermal decomposition, were examined by X-ray powder diffraction method using $Cu\,K_\alpha$ radiation, and their IR spectra were recorded on a Perkin-Elmer Model 577 spectrophotometer in a KBr matrix. ESR spectra of these solid samples were recorded on a Varian V-4502 spectrometer in order to detect whether or not any Eu^{2+} ions were present in the sample.

The TG and DTG curves were recorded (~ 2–2.5 mg) in flowing air or carbon dioxide (~ 2.5 dm^3 h^{-1}) at a heating rate of 2 K min^{-1} using the microthermobalance system described previously [10]. Similarly, DTA curves in air and CO_2 were obtained at 6 K min^{-1} using about 60 mg of sample each time and calcined alumina as reference [8].

Evolved gas analysis was carried out in two steps. First, 10–20 mg of the formate or anhydrous oxalate samples were taken in evacuated, sealed pyrex tubes and heated for about 2 weeks at preselected temperatures. The samples were then quenched and the gas compositions were determined by gas chromatography.

RESULTS

Figures 1 and 2 show the TG, DTG and DTA curves of $Eu(HCOO)_3$ and $Eu_2(C_2O_4)_3$ obtained in air and carbon dioxide. For clarity, the dehydration

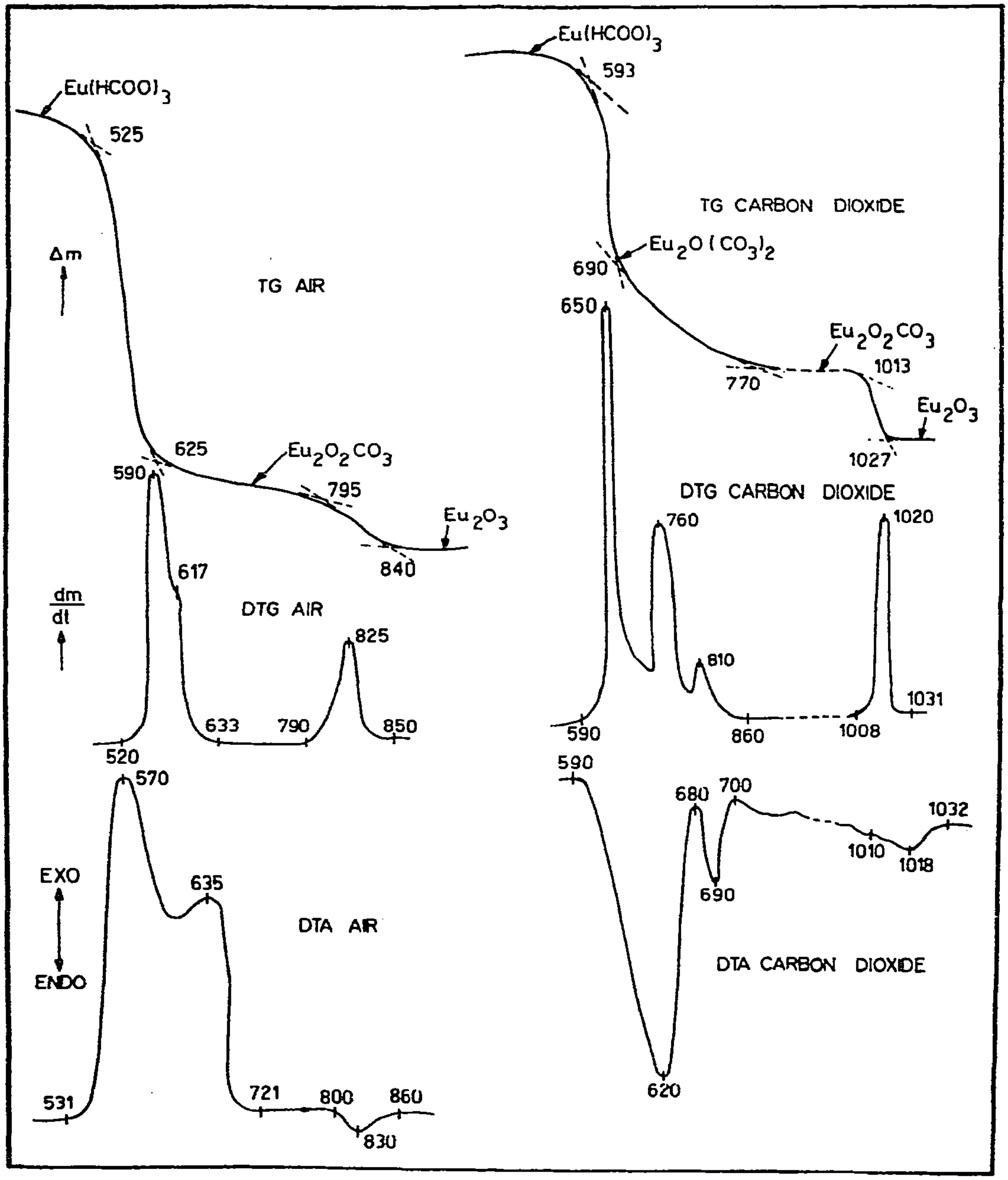

Fig. 1. TG, DTG and DTA curves for the decomposition of $Eu(HCOO)_3$ in air and carbon dioxide.

steps of Eu(III) oxalate are omitted in Fig. 2. The TG and DTG data are summarized in Tables 1 and 2.

In the decomposition of both $Eu(HCOO)_3$ and $Eu_2(C_2O_4)_3$, a new oxycarbonate phase of composition $Eu_2O(CO_3)_2$ was isolated in addition to the previously reported dioxycarbonate, $Eu_2O_2CO_3$. The products obtained in the usual TG runs were rather amorphous and hence a separate annealing

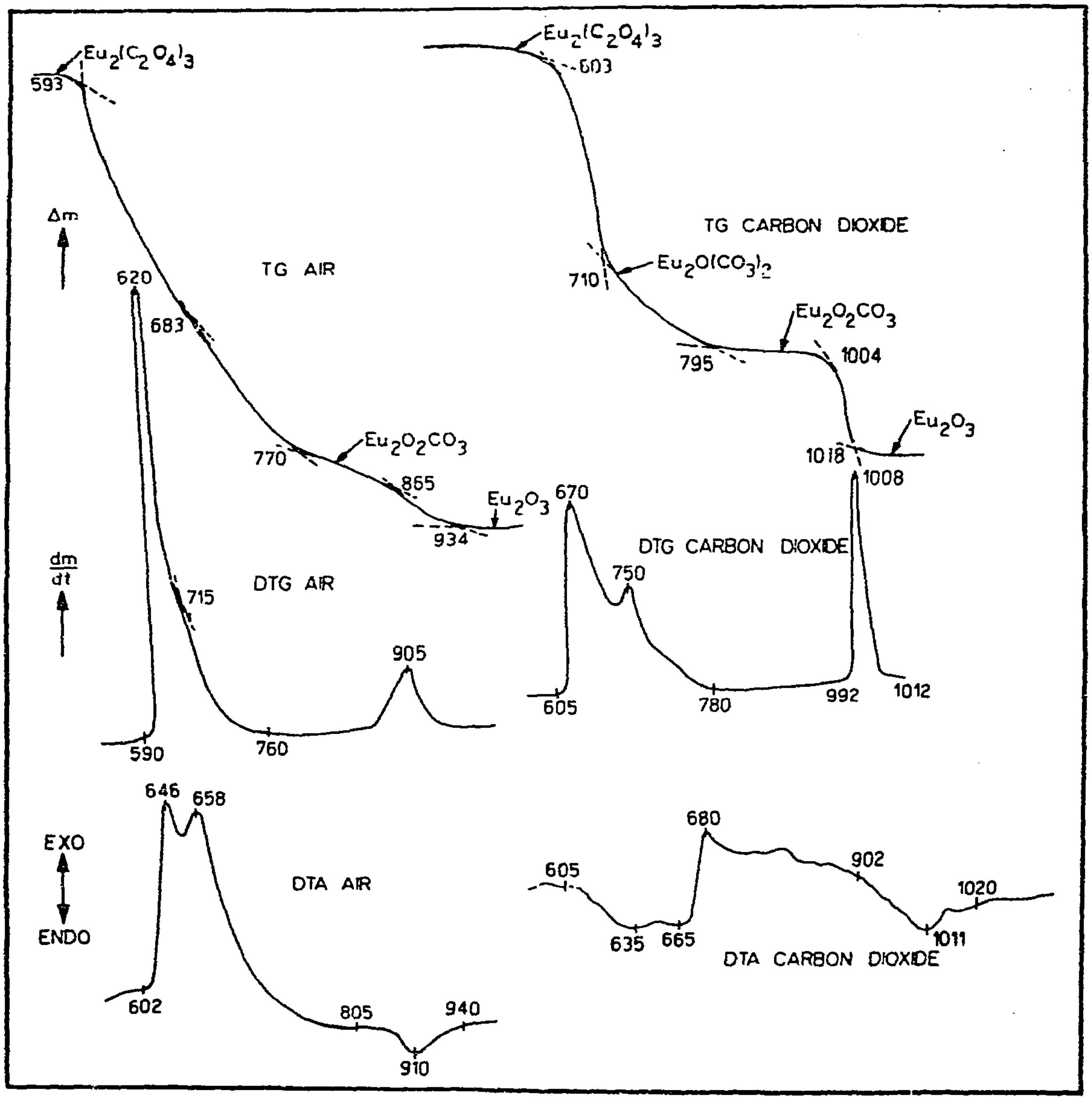

Fig. 2. TG, DTG and DTA curves for the decomposition of $Eu(C_2O_4)_3$ in air and carbon dioxide.

procedure was followed to prepare its crystalline phase. For this, a sample of europium formate (10–15 mg) was heated on the microbalance pan for 20–22 h at 600 K in a stream of dry carbon dioxide until constant weight was reached corresponding to $Eu_2O(CO_2)_2$ stoichiometry. This was quickly quenched to room temperature, transferred to a glass vial and sealed under 2–3 atmospheres of carbon dioxide. These sealed tubes were heated for a further 3 weeks at 600 K and quenched. The resultant product, of composition $Eu_2O(CO_3)_2$, was sufficiently crystalline to give good X-ray powder diffraction spectra (Fig. 3). This was then indexed on the basis of a hexago-

TABLE 1

TG data for the decomposition of $Eu(HCOO)_3$ in air and carbon dioxide

	Air	Carbon dioxide
(1) Temp. interval for the first decompn. step (K)	525–625	593–690
Net reaction	$2\ Eu(HCOO)_3 \rightarrow Eu_2O_2CO_3 + 3\ H_2 + 3\ CO + 2\ CO_2$	$2\ Eu(HCOO)_3 \rightarrow Eu_2O(CO_3)_2 + 3\ H_2 + 3\ CO + CO_2$
Obsd. mass loss (%)	31.5	23.59
Calcd. mass loss (%)	31.01	23.34
(2) Temp. interval for the 2nd decompn. step (K)		690–770
Net reaction		$Eu_2O(CO_3)_2 \rightarrow Eu_2O_2CO_3 + CO_2$
Obsd. mass loss (%)		9.55
Calcd. mass loss (%)		10.00
(3) Temp. interval for the 3rd decompn. step (K)	795–840	1013–1023
Net reaction	$Eu_2O_2CO_3 \rightarrow Eu_2O_3 + CO_2$	$Eu_2O_2CO_3 \rightarrow Eu_2O_3 + CO_2$
Obsd. mass loss (%)	10.94	10.65
Calcd. mass loss (%)	11.11	11.11

TABLE 2

TG data for the decomposition of $Eu_2(C_2O_4)_3$ in air and carbon dioxide

	Air	Carbon dioxide
(1) Temp. interval for the 1st decompn. step (K)	593–683	603–710
Net reaction	$Eu_2(C_2O_4)_3 \rightarrow Eu_2O(CO_3)_2 + 3\ CO + CO_2$	$Eu_2(C_2O_4) \rightarrow Eu_2O(CO_3)_2 + 3\ CO + CO_2$
Obsd. mass loss (%)	22.38	22.22
Calcd. mass loss (%)	22.53	22.53
(2) Temp. interval for the 2nd decompn. step (K)	683–770	710–795
Net reaction	$Eu_2O(CO_3)_2 \rightarrow Eu_2O_2CO_3 + CO_2$	$Eu_2O(CO_3)_2 \rightarrow Eu_2O_2CO_3 + CO_2$
Obsd. mass loss (%)	10.42	10.20
Calcd. mass loss (%)	10.00	10.00
(3) Temp. interval for the 3rd decompn. step (K)	865–934	1004–1018
Net reaction	$Eu_2O_2CO_3 \rightarrow Eu_2O_3 + CO_2$	$Eu_2O_2CO_3 \rightarrow Eu_2O_3 + CO_2$
Obsd. mass loss (%)	10.95	11.36
Calcd. mass loss (%)	11.11	11.11

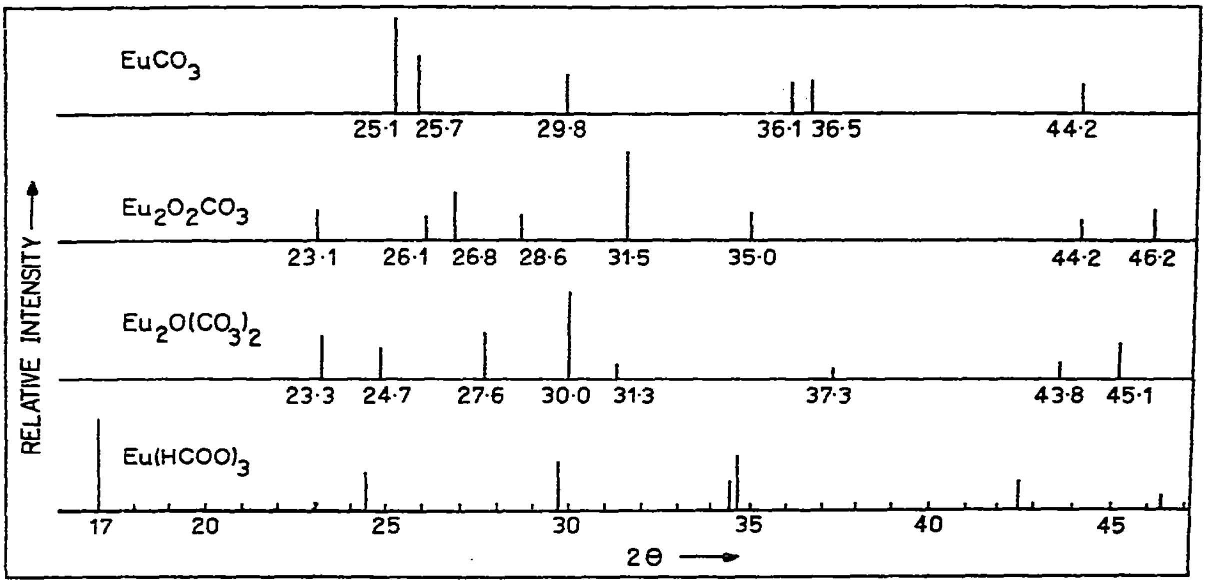

Fig. 3. X-Ray diffraction patterns of Eu(HCOO)$_3$, Eu$_2$O(CO$_3$)$_2$, Eu$_2$O$_2$CO$_3$ and EuCO$_3$.

nal unit cell. The results are given in Table 3.

Infrared spectra of Eu(HCOO)$_3$, Eu$_2$O$_2$CO$_3$, Eu$_2$O(CO$_3$)$_2$ and EuCO$_3$ are shown in Fig. 4. Both the oxycarbonate intermediate products obtained in

TABLE 3

X-Ray powder diffraction data for Eu$_2$O(CO$_3$)$_2$ [a]

d_{hkl} (nm)	Relative intensity (visual) [b]	*hkl*
0.382	S	102
0.360	S	110
0.323	S	003
0.297	VS	201
0.286	W	103
0.262	VW	202
0.241	W	004
0.224	M	203
0.208	M	300
0.201	S	114
0.193	M	005
0.180	M	220
0.177	M	221
0.169	S	222

[a] Lattice parameters calculated on the basis of a hexagonal unit cell: $a = 0.7205 \pm 0.004$ nm; $c = 0.9654 \pm 0.0015$ nm.

[b] VS = very strong; S = strong; VW = very weak; W = weak; M = medium.

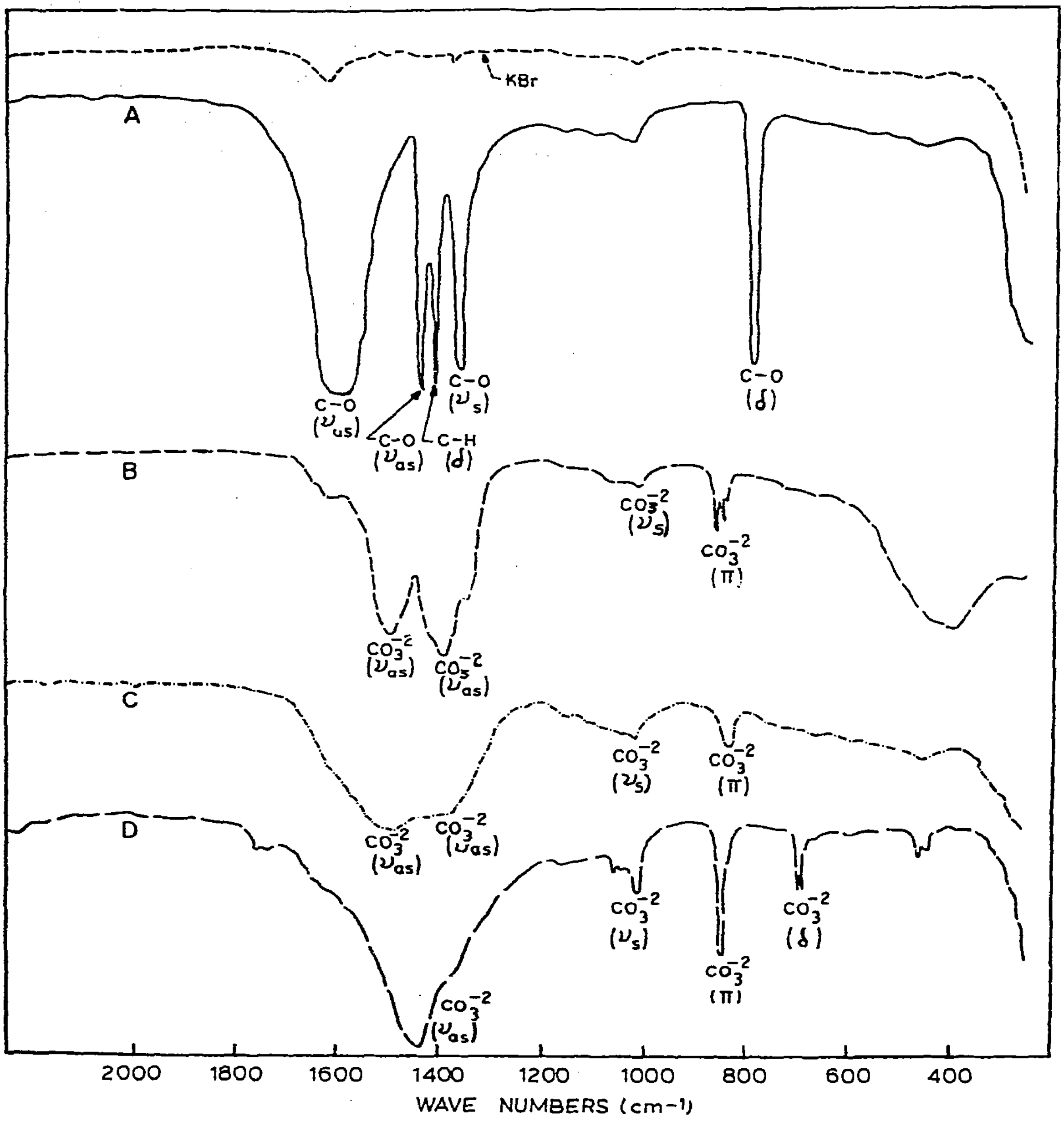

Fig. 4. Infrared patterns of A, $Eu(HCOO)_3$; B, $Eu_2O_2CO_3$; C, $Eu_2O(CO_3)_2$; and D, $EuCO_3$.

the thermal decomposition of the formate and oxalate show the presence of absorption bands due to the CO_3^{2-} group but none due to the carbonyl group. Thus these intermediate products are carbonates but not carbonyl carbonates as predicted by Gallagher et al. [5].

The decomposition products of europium formate and oxalate obtained by heating the samples in air or carbon dioxide at 600 K [corresponding to the stoichiometry of $Eu_2O(CO_3)_2$] and quenched did not show the characteristic ESR absorption band due to Eu(II) ions when examined by ESR spectra. Thus these products were not europous salts.

As described earlier, the evolved gases could not be analyzed directly during the TG or DTA runs in flowing air or carbon dioxide. However, the gas phase compositions formed during modified sealed tube experiments were analyzed by gas chromatography. The relative concentrations of gases thus determined are presented in Table 4.

DISCUSSION

TG curves of Eu(III) formate (Fig. 1) and Eu(III) oxalate (Fig. 2) in air show only one unambiguous intermediate step preceding the formation of Eu_2O_3, though the TG curves for the oxalate suggest another step around 683 K. However, the TG curves taken in flowing CO_2 and the DTG curves in air and CO_2 clearly show that another intermediate step in the decomposition of the formate and the oxalate exists. The overlapping of the two intermediate steps involving the oxycarbonates is such that it was not possible to establish the stoichiometry of the new oxycarbonate unambiguously form the TG curves obtained at 2 K min^{-1} heating rate. The exact composition of this product was obtained in a separate experiment as follows. As seen in Fig. 1, the Eu(III) formate begins to lose weight in CO_2 at 593 K and the formation of the dioxycarbonate, $Eu_2O_2CO_3$, does not commence till 690 K. Hence a sample of 2–3 mg of Eu(III) formate (accurately weighed) was heated in flowing CO_2 at the same 2 K min^{-1} heating rate until a temperature of 600 ± 1 K was reached. The sample was then maintained at this temperature isothermally until the decomposition reaction was complete and a constant weight was recorded. This isothermal heating was continued sometimes as long as 20–22 h. From such runs, the composition of the resulting product was calculated as $Eu_2O(CO_3)_2$.

The difference in the calculated Δm for $Eu_2O(CO_3)_2$ and $Eu_2O_2COCO_3$ is so small that TG studies alone could not resolve this dilemma. The IR spectra (Fig. 4) of this product showed the presence of only the CO_3^{2-} group, not the carbonyl group. It was therefore concluded that the product was oxycarbonate, $Eu_2O(CO_3)_2$. As the ESR spectra of this sample did not show the characteristic absorption peaks due to Eu(II) ions, the formula $Eu_2O(CO_3)_2$ was assigned to this intermediate phase. The powder diffraction spectrum of this product (Fig. 3) was quite distinct from that of $Eu_2O_2CO_3$. The X-ray powder diffraction spectrum was indexed on the basis of a hexagonal lattice. These data are given in Table 3. From Figs. 1 and 2 it is seen that the TG curves of Eu(III) formate and Eu(III) oxalate are quite similar, the oxalate decomposition curves exhibit a higher temperature in all cases. But for this difference in temperature, one can almost superimpose one set of TG curves on the other. These observations were interpreted in that the europium formate first decomposes to europium oxalate which subsequently undergoes further decomposition, similar to the decomposition sequence observed in the case of lanthanum formate [8].

This conclusion was further strengthened from the evolved gas data shown in Table 4. A large amount of molecular hydrogen was observed in the gases evolved on heating the formate in closed tubes at 523 K as well as at 673 K. This could not be accounted for on the basis of the decomposition of moisture impurity in the sample. The only way to reconcile the observed quantities of hydrogen was to consider hydrogen as one of the primary gaseous products of the decomposition of europium(III) formate. Although the gaseous composition obtained by decomposing the sample in a sealed tube will be somewhat different from that formed during the TG run in air or in carbon dioxide, this difference will amount to minor changes only.

Although no europium(II) compounds could be isolated in either TG or DTG experiments, under highly reducing conditions prevailing in the sealed tube experiment (Table 4) some reduction took place. Thus the products formed in the sealed tube experiments showed the presence of $EuCO_3$ (Table 4). However, EuC_2O_4 could not be identified in any of the products. $EuCO_3$ was probably formed through the reduction of $Eu_2O(CO_3)_2$ or $Eu_2O_2CO_3$.

To unravel this dilemma further, thermogravimetric investigations of EuC_2O_4 and $EuCO_3$ were carried out in atmospheres of air and CO_2 (Fig. 5). Both these compounds decompose first to $Eu_2O_2CO_3$ and then the oxide; even the corresponding temperatures are similar. Except for a small change in the inception temperatures of decomposition in CO_2, namely 740 K for the EuC_2O_4 compared to 793 K for $EuCO_3$, the others, such as the temperatures of the completion of formation of $Eu_2O_2CO_3$ and that of Eu_2O_3, are almost the same. Neither the oxalate nor the carbonate gave $Eu_2O(CO_3)_2$ as an intermediate product.

TABLE 4

Results of evolved gas analysis

Compound	Temp. (K)	Solid residue	Percentage of the gas by volume		
			H_2	CO	CO_2
$Eu(HCOO)_3$	523	$EuCO_3$	30.0	26.0	44.0
$Eu(HCOO)_3$	673	$EuCO_3 + Eu_2O_2CO_3$	26.4	31.6	42.0
$Eu_2(C_2O_4)_3$	573	(Eu^{2+} ion present)[a]		14.4	45.6
$Eu_2(C_2O_4)_3$	673	$EuCO_3 + Eu_2O_2CO_3$		20.9	79.1
EuC_2O_4	673	$EuCO_3 + Eu_2O_2CO_3$		46.0	54.0

[a] The product was amorphous and could not be identified by X-ray powder diffraction technique. The ESR spectrum showed the presence of Eu^{2+} ions.

The results of the DTA investigation of the formate as well as the oxalate (Figs. 1 and 2) do not provide any additional information. In air, both formate and oxalate decompositions exhibit two exothermic peaks followed by a last endotherm due to decomposition of the oxycarbonate to the sesquioxide, while in carbon dioxide all DTA peaks are endothermic. These endothermic peaks in carbon dioxide are the result of the decomposition steps of the formate or oxalate. The decomposition steps of the formate to the oxalate and then to $Eu_2O(CO_3)_2$ are not sufficiently resolved and only one DTA peak could be observed. In air, as soon as the decomposition of formate (or oxalate) begins forming hydrogen and carbon monoxide, these gases simultaneously react with oxygen in the air. Thus there will be a superposition of the endothermic decomposition reaction and highly exothermic oxidation process resulting in the exothermic DTA peaks. The larger first peak in the case of the formate compared to that of the oxalate (for about the same sample size) may be due to an additional energy contribution from the oxidation of hydrogen. It was not possible to draw any quantitative conclusions from the DTA investigations.

In a series of separate thermogravimetric experiments, the dehydration reaction of the europium oxalate decahydrate was investigated with the microthermobalance in flowing air. The dehydration was observed to take place in three distinct steps: decomposition to the hexahydrate followed by the tetrahydrate and finally to anhydrous oxalate, in good agreement with previous results [5,11].

Based on the results obtained in the present investigation and previously

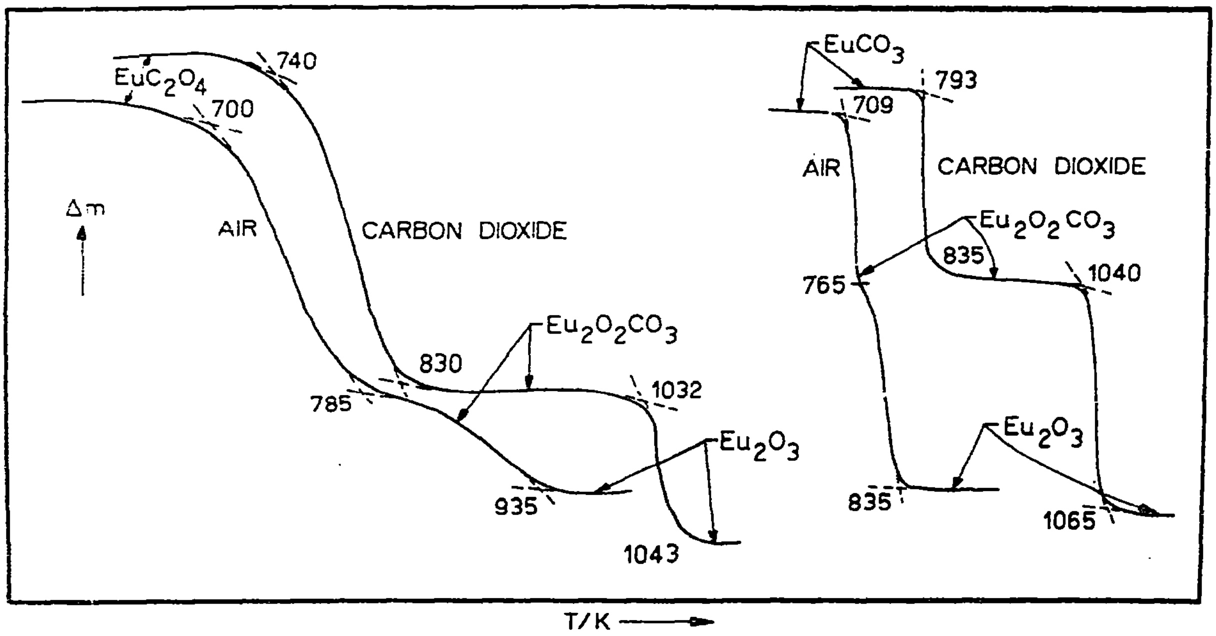

Fig. 5. TG curves for the decomposition of EuC_2O_4 and $EuCO_3$ in air and carbon dioxide.

published data, the following scheme of reactions is proposed for the thermal decomposition of europium(III) formate and europium(III) oxalate

$$2\ Eu(HCOO)_3 \rightarrow Eu_2(C_2O_4)_3 + 3\ H_2 \quad (5)$$

$$Eu_2(C_2O_4)_3 \rightarrow Eu_2O(CO_3)_2 + 3\ CO + CO_2 \quad (6)$$

$$Eu_2O(CO_3)_2 \rightarrow Eu_2O_2CO_3 + CO_2 \quad (7)$$

$$Eu_2O_2CO_3 \rightarrow Eu_2O_3 + CO_2 \quad (8)$$

and

$$Eu_2(C_2O_4)_3 \cdot 10\ H_2O \rightarrow Eu_2(C_2O_4)_3 \cdot 6\ H_2O + 4\ H_2O \quad (9)$$

$$Eu_2(C_2O_4)_3 \cdot 6\ H_2O \rightarrow Eu_2(C_2O_4)_3 \cdot 4\ H_2O + 2\ H_2O \quad (10)$$

$$Eu_2(C_2O_4)_3 \cdot 4\ H_2O \rightarrow Eu_2(C_2O_4)_3 + 4\ H_2O \quad (11)$$

$$Eu_2(C_2O_4)_3 \rightarrow Eu_2O(CO_3)_2 + 3\ CO + CO_2 \quad (12)$$

$$Eu_2O(CO_3)_2 \rightarrow Eu_2O_2CO_3 + CO_2 \quad (13)$$

$$Eu_2O_2CO_3 \rightarrow Eu_2O_3 + CO_2 \quad (14)$$

CONCLUSION

Although thermogravimetry with a microthermobalance and differential thermal analysis are powerful experimental methods for the investigation of the thermal decomposition of solids, the present investigation has reiterated the fact that these techniques by themselves, even when carried out in different gaseous environments, are insufficient to establish the complete decomposition scheme. Several supplementary measurements, such as evolved gas analysis, X-ray powder diffraction analysis, IR and other measurements to characterize the intermediate products, etc., are essential.

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