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A STUDY OF THE THERMAL DECOMPOSITION OF HYDRATED EUROPIUM(III) CHLORIDE AND EUROPIUM(III) BROMIDE

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ABSTRACT

The thermal decompositions of $EuCl_3 \cdot 6\ H_2O$ and $EuBr_3 \cdot 6\ H_2O$ have been studied and compared in the temperature range ambient to 900°C. The techniques used were thermogravimetric analysis supported by chemical analysis, Mössbauer spectroscopy, mass spectrometry and infrared spectrophotometry applied to intermediate decomposition products. When heated in a slow stream of nitrogen, water is lost in stages, which are better defined in the chloride than in the bromide system, up to 350° and 390°C, respectively, above which temperatures the corresponding oxide halide is the only major product. At least part (about 30%) of the europium undergoes a valence change to europium(II) in the bromide system but not in the chloride system in the course of removal of water which occurs by dehydration and hydrolytic processes. The bromide system is thus intermediate between the corresponding chloride and iodide systems since the latter appears to undergo a complete, or near complete, transformation to europium(II). The oxide chloride and oxide bromide are converted to europium(III) oxide at 900 and 910°C, respectively.

INTRODUCTION

The thermal decompositions of hydrated trivalent chlorides of the lanthanoid elements have been the subject of several investigations [1–6]. However, there is a lack of agreement concerning the number, composition and nature of the intermediate compounds formed in the course of decomposition to europium(III) oxide. The corresponding bromide system has received much less attention, having only been studied on one previous occasion [7].

In the work described here, the thermal decompositions of $EuCl_3 \cdot 6\ H_2O$ and $EuBr_3 \cdot 6\ H_2O$ have been studied initially using thermogravimetry under nitrogen and then by independent examination of products prepared by heating samples in a furnace to predetermined temperatures selected from the thermograms. The residual products were characterised by chemical analysis and by Mössbauer and infrared spectroscopy. The Mössbauer technique is particularly useful for the detection of valency changes in

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europium compounds. Volatile products were examined mass spectrometrically.

EXPERIMENTAL

Hydrated europium(III) halide samples were prepared from europium(III) oxide (99.9% pure) obtained from Rare Earth Products, England. The oxide was treated with concentrated hydrochloric or hydrobromic acid and the resulting solution carefully evaporated to near dryness at temperatures $\leqslant 70°C$. Finally, each sample was dried at room temperature.

The thermogravimetric analyses were performed using a duPont 990 thermal analysis system. Samples (5–10 mg) were heated at 10°C min^{-1} in a stream of nitrogen at 50 ml min^{-1}.

Intermediate products in the thermal decomposition of the hexahydrates were prepared by placing about 200 mg of the starting material, thinly spread, in a sealed combustion tube (Fig. 1) under nitrogen (1 atm pressure) for 30 min at a temperature selected from the appropriate thermogram. Then, the sample was cooled rapidly and the tube evacuated to remove any displaced water which had condensed at the cold end. The sample was recovered under dry argon in a glove box as some end-products are known to be air-sensitive.

The product was analysed chemically for europium and halogen by

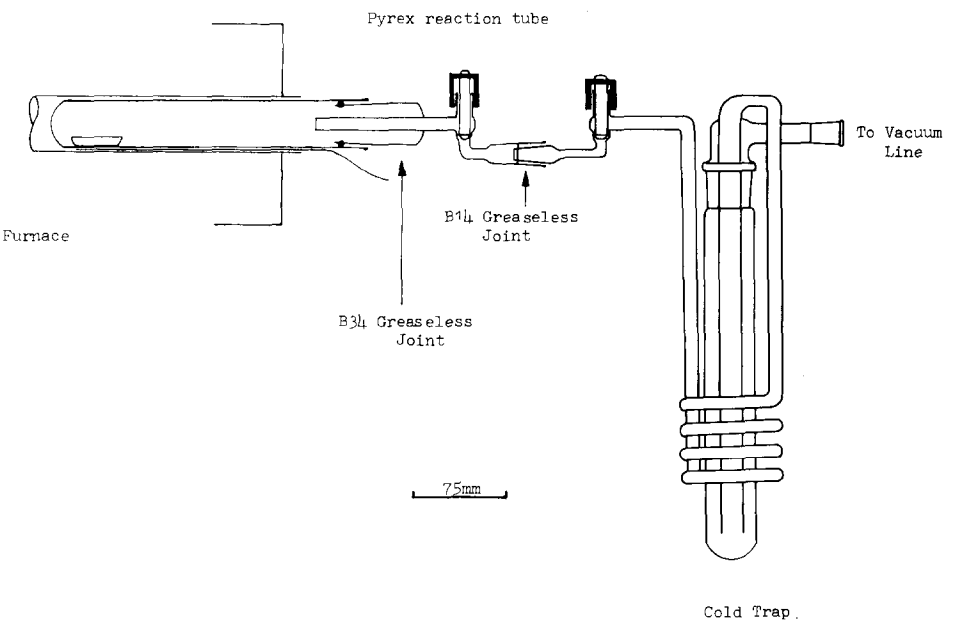

Fig. 1. Apparatus used for the thermal decomposition of 200 mg samples under nitrogen or nitrogen + oxygen.

titration with EDTA [8] and mercury(II) nitrate [9], respectively.

The Mössbauer spectrometer described previously [10] was used in conjunction with a 50 mCi samarium-151 source incorporated in a samarium(III) fluoride matrix. The source was supplied by The Radiochemical Centre, Amersham, England. Both source and absorber were held at the same temperature in a cryostat operating at preselected temperatures between ambient and 77 K.

All Mössbauer isomer shifts were measured relative to anhydrous europium(III) fluoride; errors quoted are standard deviations of the mean values.

Information about the volatile products of the decomposition reactions was obtained from mass spectrometry. Products were identified by heating small samples to temperatures selected between ambient and 250°C in an AEI MS902 mass spectrometer operated under standard conditions with a source temperature of 250°C.

RESULTS

The thermogram for hydrated europium(III) chloride is presented in Fig. 2, curve A. Some slight weight loss occurs at a temperature just above ambient after which the weight remains constant until around 75°C. Above 75°C there is a steady weight loss until a second plateau at 138–200°C is reached. Chemical analysis of the residue produced in the furnace (Fig. 1) by

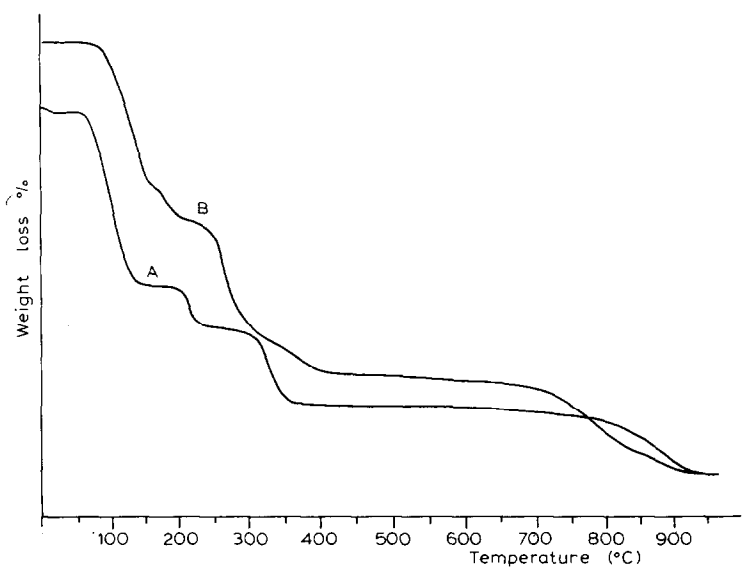

Fig. 2. Thermograms for hydrated samples of (A) europium(III) chloride and (B) europium(III) bromide.

TABLE 1

Comparison of calculated and observed thermogravimetric weight losses for formation of the products

Product, suggested composition	Weight loss	
	Calcd. (%)	Found (%)
$EuCl_3 \cdot n\ H_2O + 5\%$ EuOCl $0.5 \leqslant n \leqslant 1$	25.6–27.9	26.5–27.5
$0.53\ EuCl_3 \cdot n\ H_2O \cdot 0.47$ EuOCl	34.5	32.5–34.0
$EuBr_3 \cdot n\ H_2O + 10\%$ EuOBr $0 \leqslant n \leqslant 0.5$	19.8	21.0
$(EuBr_3 \cdot n\ H_2O)_x \cdot (EuOBr)_y$ $x/y \approx 4, 0 \leqslant n \leqslant 0.5$	25.0	25.0–27.0

heating within the temperature range 140–200°C as described in the experimental section, indicated that the ratio of chlorine to europium is slightly less than three, suggesting the presence of some europium(III) oxide chloride. The main component is $EuCl_3 \cdot n\ H_2O$, where $0.5 \leqslant n \leqslant 1$, with about 5% by weight of EuOCl found in all samples produced in this temperature interval. The calculated weight loss (Table 1) for such a composition agrees well with that found from the thermogram (Fig. 2, curve A). Mössbauer spectra of these samples prove that only europium in the trivalent state is present; the isomer shift, δ, is 0.42 ± 0.03 mm s^{-1} and the peak width at half-height, Γ, is 2.21 ± 0.03 mm s^{-1} at 0°C.

Another horizontal region occurs on the thermogram at 230–258°C beyond which there is a gradual weight loss with increasing temperature to 308°C. The chemical analysis of samples produced in the temperature range 230–308°C show that further loss of chlorine has occurred. The Mössbauer spectra indicate that only europium(III) is present in the products; spectral data can be fitted to two overlapping peaks with maxima about 1 mm s^{-1} apart. One fitted peak gives $\delta \simeq 0$ mm s^{-1} and the other $\delta \approx 1$ mm s^{-1}; these isomer shifts are consistent with those expected for $EuCl_3 \cdot n\ H_2O$ and EuOCl, respectively. The composition of this intermediate decomposition system can be written as $(EuCl_3 \cdot n\ H_2O)_x(EuOCl)_y$. From 230 to 258°C, the ratio $x : y \simeq 2 : 1$ but above 258°C the EuOCl content increases so that the ratio $x : y$ approaches 1 : 1. Chemical analysis indicates that $0.5 \leqslant n \leqslant 1$ and the calculated weight losses are in good agreement with those found (Table 1). An absorption peak at 1600–1630 cm^{-1} attributable to the H–O–H bending mode was present in the infrared spectra. Above 350°C, EuOCl is the only product and it decomposes to Eu_2O_3 at about 900°C.

From the mass spectrometric study, it could be deduced that the major volatile products of decomposition are water and hydrogen chloride; free chlorine is not observed. The release of hydrogen chloride increases with

decomposition temperature to a maximum at 230°C corresponding to the temperature range resulting in major depletion of the original compound in chlorine. The onset of production of hydrogen chloride observed in the mass spectra corresponds to the initial formation of EuOCl as deduced from chemical analysis and Mössbauer spectrometry.

The thermogram for hydrated europium(III) bromide (Fig. 2, curve B) suggests that the temperature ranges for relative stability of products are less well defined than for the corresponding chloride system. The hexahydrate is stable up to a temperature of about 75°C above which a steady weight loss occurs with increasing temperature up to about 165°C. A sloping plateau (165–175°C) follows. Samples prepared in the furnace (Fig. 1) and analysed chemically provide evidence that there is no loss of bromine up to 160°C but from 160 to 175°C and at higher temperatures depletion occurs with

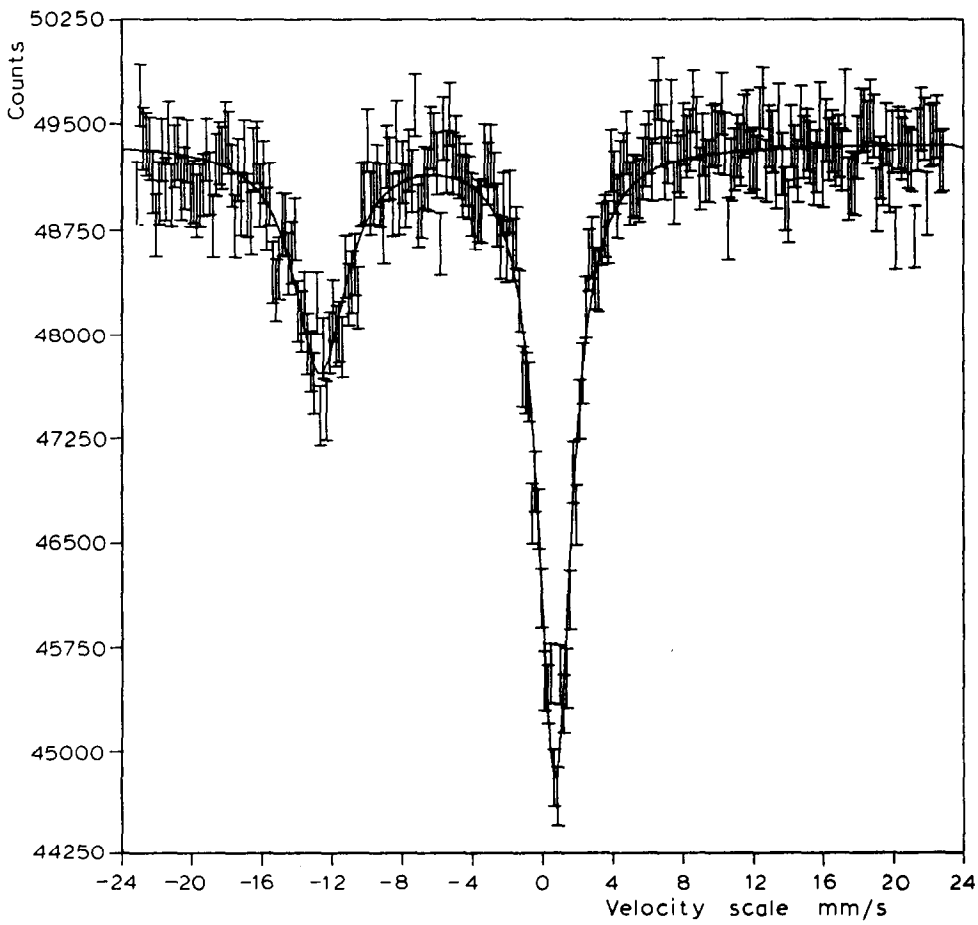

Fig. 3. Mössbauer spectrum of hydrated europium(III) bromide heated for 30 min at 364°C in the apparatus depicted in Fig. 1.

ultimate formation of europium(III) oxide bromide. The infrared spectra show that water of hydration is still present up to 175°C. The composition for this temperature region suggests the presence of $EuBr_3 \cdot n\ H_2O$ with $0 \leqslant n \leqslant 0.5$ and about 10% by weight of EuOBr. The calculated weight loss (Table 1) for this suggested composition is consistent with that found from the thermogram. The Mössbauer spectra have a single peak with $\delta = 0.60 \pm 0.03$ mm s^{-1} and $\Gamma = 2.59 \pm 0.08$ mm s^{-1} showing that only trivalent europium is present.

The rate of weight loss from 195 to 235°C is relatively small (Fig. 2) compared to that at temperatures above or below this range. Products prepared in the furnace within this temperature interval contain only europium(III) as deduced from Mössbauer spectra. Chemical analysis of these products show that further depletion in bromine has occurred with consequent increase in EuOBr at the expense of $EuBr_3 \cdot n\ H_2O$ where $0 \leqslant n \leqslant 0.5$. The ratio of $EuBr_3 \cdot n\ H_2O$ to EuOBr decreases from 4 : 1 to 2 : 1 as the temperature increases over this range. A decrease in weight loss occurs again at 305°C and continues to 390°C above which the product is entirely EuOBr. Mössbauer spectra of samples prepared within this temperature interval show the presence of europium(II). The spectra consist of two peaks (Fig. 3), one having $\delta = -12.47 \pm 0.20$ mm s^{-1} and $\Gamma = 3.6 \pm 0.2$ mm s^{-1} and the other having $\delta = 0.89 \pm 0.04$ mm s^{-1} and $\Gamma = 2.3 \pm 0.1$ mm s^{-1}. Assuming the recoil-free fractions to be the same, the ratio of europium(II) to europium(III) is 1 : 1.8. Some water is also present (infrared spectra). Involatile decomposition products prepared in an atmosphere of oxygen mixed with nitrogen within this temperature range did not contain europium(II). The Mössbauer spectrum consists only of a single peak with $\delta = 0.76 \pm 0.05$ mm s^{-1} and $\Gamma = 2.7 \pm 0.1$ mm s^{-1}.

Only water and hydrogen bromide were observed mass spectrometrically among the volatile products up to the maximum temperature attainable in the instrument, namely 250°C.

DISCUSSION

The results of the study of the decomposition of hydrated europium(III) chloride agree with those of Wendlandt [2] except that he did not observe water in the intermediate $2\ EuCl_3 \cdot EuOCl$ phase. Matthes and Haeseler [5] dispute the existence of this phase claiming that the reaction

$$2\ EuCl_3 \cdot 1.5\ H_2O \rightarrow 2\ EuOCl + 4\ HCl + H_2O$$

describes the decomposition with no other intermediate species formed.

For the decomposition of hydrated europium(III) bromide, Mayer and Zolotov [7] claim that the reaction follows the course

$$EuBr_3 \cdot 6\ H_2O \rightarrow EuBr_3 \cdot H_2O \rightarrow EuBr_3 \rightarrow EuOBr$$

with no temperature interval over which $EuBr_3$ and EuOBr coexist. From their results, it is evident that the calculated and observed weight losses for their proposed stages $EuBr_3 \cdot H_2O$ and $EuBr_3$ are not in good agreement. They claim that the discrepancies are due to the premature formation of EuOBr arising from the high vapour pressure of the water present thus lowering its temperature of formation. The fact that europium(II) is produced in the decomposition points to the existence of some anhydrous europium(III) bromide since this is the only likely substance to give divalent europium by a thermal reaction [11]

$$EuBr_3 \rightarrow EuBr_2 + \tfrac{1}{2}\, Br_2$$

(Bromine was not detected from the mass spectrometric study because decomposition temperatures in excess of 250°C could not be attained in the instrument and the threshold temperature for the reaction is around 300°C). This reaction will not lead to europium(II) in the presence of oxygen and the availability of oxygen from the sample atmosphere will also affect the formation of EuOBr. Thus, when oxygen is absent from this atmosphere the only oxygen-containing species is water and it leads exclusively to formation of EuOBr, presumably by hydrolytic reactions since hydrogen bromide was detected mass spectrometrically.

In the present work, it has been shown that up to the temperature at which europium(III) oxohalide is the sole europium compound, water is present in the solid decomposition products. The following chemical transformations, with relevant appended data, summarise the results.

Chlorides

$$\underset{T \leqslant 70°C}{EuCl_3 \cdot 6\, H_2O} \rightarrow \underset{138°C \leqslant T \leqslant 200°C}{EuCl_3 \cdot n\, H_2O} \rightarrow \underset{230°C \leqslant T \leqslant 308°C}{(EuCl_3 \cdot n\, H_2O)_x (EuOCl)_y} \xrightarrow{350°C} EuOCl \xrightarrow{900°C} Eu_2O_3$$

$\frac{1}{2} \leqslant n \leqslant 1,\ 1 \leqslant x/y \leqslant 2$

Bromides

$$\underset{T \leqslant 75°C}{EuBr_3 \cdot 6\, H_2O} \rightarrow \underset{160°C \leqslant T \leqslant 175°C}{EuBr_3 \cdot n\, H_2O} \rightarrow \underset{195°C \leqslant T \leqslant 235°C}{(EuBr_3 \cdot n\, H_2O)_x (EuOBr)_y} \rightarrow \underset{305°C \leqslant T \leqslant 390°C}{\left\{\begin{matrix} EuBr_3 \cdot n\, H_2O \cdot EuBr_2 \cdot EuOBr \\ \text{or } EuBr_3 \cdot n\, H_2O \cdot EuOBr \end{matrix}\right\}} \xrightarrow{390°C} EuOBr \xrightarrow{910°C} Eu_2O_3$$

$0 \leqslant n \leqslant \frac{1}{2}, \quad 2 \leqslant x/y \leqslant 4$

It is interesting to note that the behaviour of hydrated europium(III) bromide is intermediate between that of the corresponding chloride and iodide systems in that the chloride does not give rise to measurable fractions of europum(II) species whereas the iodide probably goes entirely through divalent europium in its thermal decomposition [12].

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