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THERMAL ANALYSIS OF THE OXALATE HEXAHYDRATES AND DECAHYDRATES OF YTTRIUM AND THE LANTHANIDE ELEMENTS

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Summary

Simultaneous thermogravimetry and differential thermal analysis data are presented for yttrium and the tervalent lanthanide oxalate decahydrates (Y, La - Er excluding Pm) and hexahydrates (Y, Er - Lu). The dehydration and the oxalate and intermediate dioxycarbonate decomposition of these two series of isomorphs show systematic trends which are discussed with reference to the stereochemical and bonding effects resulting from the lanthanide contraction. Anomalies in behaviour primarily arise from changes in the oxidation states of the cations during decomposition. Thermal analyses of co-precipitated cerium–terbium and yttrium–europium oxalate decahydrates indicate that the crystalline solid solutions so formed are thermally distinct species which show non-additive decomposition behaviour intermediate between those of the parent oxalates.

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1. Introduction

The very low solubilities of oxalates of the tervalent rare earth metals are utilized both in their extraction from minerals, particularly xenotime, and in their gravimetric analytical determination [1]. In addition, these oxalates can be convenient reactants for the thermal preparation of oxide lattices containing rare earths, an example being certain inorganic photoluminescent and cathodoluminescent phosphors.

Because of their importance there has been considerable interest over the years in their thermal decomposition behaviour. However, the more comprehensive thermal studies on these compounds have involved only thermogravimetry (TG) [2 - 5], in one case [2] on materials with widely varying hydration numbers and in all cases without crystallographic identification of the phases involved. In addition, the general tendency has been to discuss the thermal behaviour of these compounds individually without attempting to relate variations in behaviour to crystallographic differences or to the possible consequences of the lanthanide contraction. More detailed thermal studies, particularly those involving differential thermal analysis (DTA), have tended to concentrate on individual compounds [6 - 12] or small groups [13 - 16].

We therefore investigated the simultaneous TG–DTA behaviour of hydrated oxalates of yttrium and all the lanthanide elements except promethium under identical conditions, and we attempt to discuss the results collectively rather than individually. An effort is also made to review and collate the diverse and often contradictory published thermal data on the decomposition of these compounds.

Some data are presented on the effect of crystalline solid solution formation in modifying the thermal behaviour of these oxalates.

2. Experimental

2.1. Materials

The oxalates were precipitated by the rapid addition, with stirring, of 0.8 M AnalaR oxalic acid to an equal volume of a neutral 0.4 M solution of the rare earth nitrate. With the exception of Ce(III), where 99.9% Ce(III) nitrate hexahydrate (Rare Earth Products) was used, the nitrate solutions were prepared by dissolving the corresponding 99.99% oxide (Rare Earth Products) (R_2O_3 except for Pr_6O_{11} and Tb_4O_7) in a slight stoichiometric deficiency of 4 - 12 M AnalaR HNO_3; this procedure was followed by dilution and filtration. The precipitates were filtered, washed and dried to constant weight over saturated NH_4Cl at 25 °C (79% relative humidity).

2.2. Instrumentation

X-ray powder diffraction data were obtained using Cu $K\alpha$ radiation with a 19.0 cm Unicam camera and a Hilger microfocus generator. The relative intensities of the reflections were obtained from densitometric measurements of the films.

Simultaneous TG–DTA data were obtained on 100 - 150 mg of undiluted samples using a Stanton MF-H5 thermobalance with a Stanton 661 DTA attachment. A heating rate of 4 °C $\min^{-1}$ was used with alumina as the DTA reference material; unless otherwise stated the atmosphere was static air.

3. Results

3.1. Structural

X-ray diffraction studies of the oxalates precipitated at 95 °C showed that the elements Y and La - Ho formed an isomorphous series which was

TABLE 1

X-ray powder data for $Y_2(C_2O_4)_3 \cdot nH_2O$ (highest d lines only)

$n = 10$		$n = 6$		$n = 2^a$		$n = 2^b$	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
6.95	13	6.43	34	7.27	14	7.25	33
6.60	76	6.19	34	5.94	43	5.92	80
6.49	100	6.00	99	5.88	100	5.86	100
4.98	23	5.48	81	4.81	26	4.79	31
4.89	42	4.88	41	4.66	14	4.67	33
4.81	36	4.79	84	4.44	6	4.42	16
4.72	37	4.66	5	3.87	3	3.87	3
4.43	5	4.28	20	3.60	12	3.64	8
4.34	8	4.22	100			3.59	12
4.23	5	3.96	16	3.50	28	3.50	42
3.98	7	3.89	8	3.36	3	3.22	5
3.67	2	3.83	17	3.12	4	3.12	6
3.62	8	3.74	4	3.00	5	3.01	10
3.46	15	3.52	10	2.91	15	2.91	18

[a] Broad pattern obtained by arresting the thermal analysis of the decahydrate at 270 °C.

[b] Sharp pattern obtained by arresting the thermal analysis of the hexahydrate at 270 °C.

identified from thermal analysis and comparison with published X-ray powder diffraction data [14, 17 - 20] as being that of the decahydrates. The elements Er - Lu formed a second isomorphous series under these precipitation conditions which was similarly identified [14, 19] as being that of the hexahydrates. In all cases these appeared to be single uncontaminated phases.

The pure hexahydrate of yttrium was obtained by precipitation under conditions of vigorous boiling, and the decahydrate of erbium was obtained by precipitation at 15 °C. In the latter case very weak X-ray reflections due to a third unidentified phase were present, but its concentration was obviously very low and the thermal analysis data were consistent with those expected of the pure compound. Attempts to prepare the pure decahydrate phases of Tm - Lu using low temperature precipitation proved unsuccessful as mixed phases were produced. For example ytterbium showed no evidence of decahydrate formation and yielded both the hexahydrate and, predominantly, a further unidentified phase.

Table 1 includes the X-ray powder diffraction data of the yttrium oxalate decahydrates and hexahydrates.

3.2. *Thermal analysis*

Simultaneous TG–DTA data for decomposition of the oxalate hydrates in static air are shown in Figs. 1 - 3. The numbered lines refer to the TG curves and signify the total numbers of water molecules of crystallization

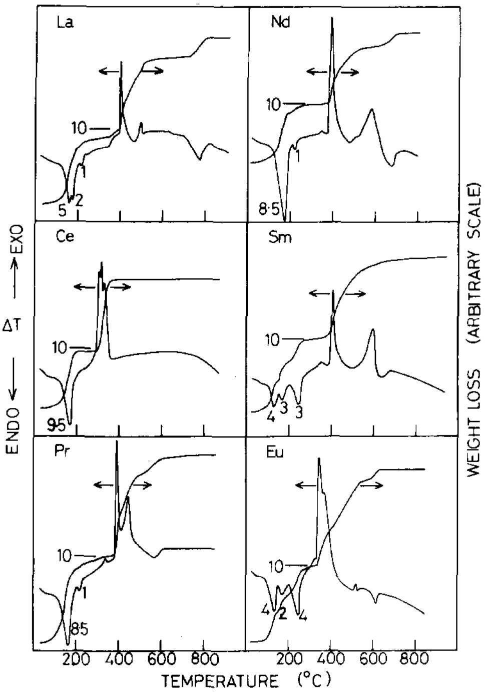

Fig. 1. TG–DTA curves for the oxalate decahydrates of La - Eu (Pm excepted).

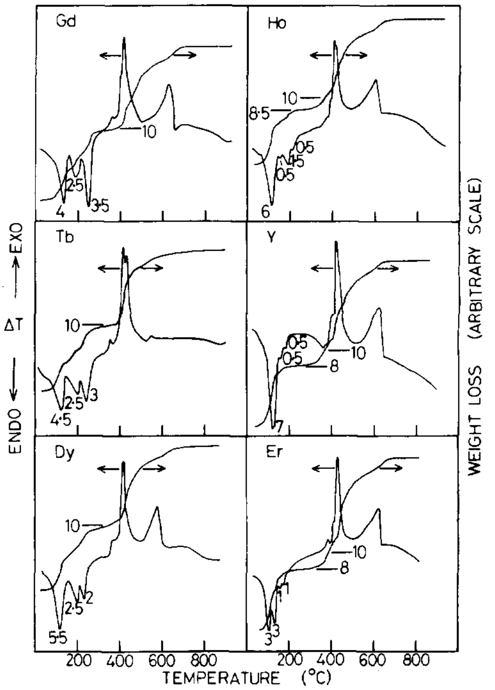

Fig. 2. TG–DTA curves for the oxalate decahydrates of Y and Gd - Er.

lost at that stage; the figures beside the endothermal dehydration peaks are estimated waters of crystallization lost under the peaks. Whilst the latter were estimated both from inflection points in the TG curves and/or from derived DTG curves they must be considered only approximate in certain cases, particularly where significant overlap in the dehydration peaks occurs. In cases where the TG curves showed clear evidence of intermediate hydrates, their estimated hydration numbers are shown in Table 2.

For convenience, discussion of the thermal data is divided into dehydration and oxalate decomposition, and the decahydrates and hexahydrates are also dealt with separately.

In the relevant figures and tables yttrium is positioned between holmium and erbium in accordance with the tervalent ionic radii of the series.

4. Discussion

4.1. *Dehydration of the decahydrates*

Figures 1 and 2 show that thermal dehydration of the lanthanide oxalate decahydrates follows a systematic trend over the series La - Er. The first four (La - Nd) are characterized by loss of the bulk of the water of

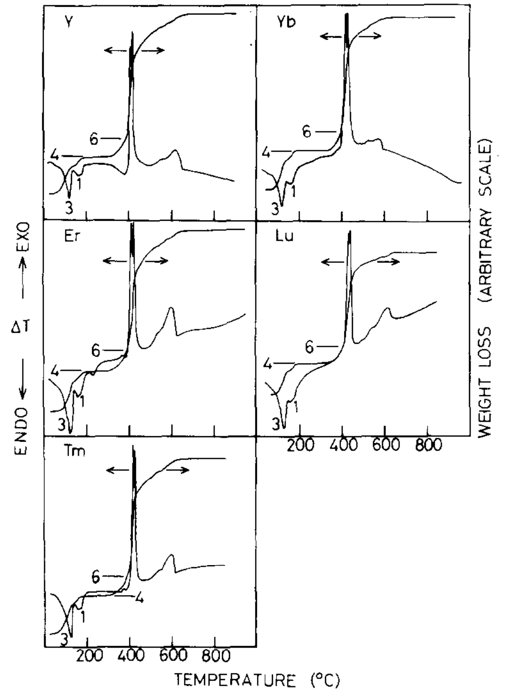

Fig. 3. TG–DTA curves for the oxalate hexahydrates of Y and Er - Lu.

TABLE 2

Intermediate hydrates observed during the thermal dehydration of $R_2(C_2O_4)_3 \cdot 10H_2O$

R	*Hydration number*												
	0		*1*		*2*		*3*		*4*		*5*		*6*
La	X		X				X						
Ce		(X)											
Pr	X	X		X									
Nd	X	X		X									
Sm	(X)						X						X
Eu	X								X				X
Gd	(X)							X					X
Tb	X						X					X	
Dy					X					X			
Ho				(X)	X			X	X				
Y					(X)		X						
Er					(X)		X		X				

(X), air-stable species.

crystallization (75 - 95%) in a single-peaked (Ce, Pr, Nd) or double-peaked (La) endotherm centred at 160 - 173 °C. The lanthanum, praseodymium and neodymium salts also show a further loss of one molecule of water of crystallization at a peak temperature of 210 - 230 °C. Amongst the light lanthanide oxalate decahydrates (La - Tb) cerium is atypical in not showing complete dehydration before the onset of oxalate decomposition. The TG plateau between 220 and 290 °C which corresponds to a hemihydrate is better defined than that reported for dynamic heating by other workers [2, 3, 5, 20 - 23], although Caro and Loriers [2] have observed a well-defined plateau corresponding to a hemihydrate between about 190 and 230 °C under essentially equilibrium heating conditions and Möbius and Matthes [5] have quoted this as being the approximate water content at the onset of oxalate decomposition. The present work thus tends to confirm the non-existence of anhydrous cerium(III) oxalate.

The lanthanum salt is also uncharacteristic of the light lanthanide decahydrates in retaining a significant amount of water at 350 °C (about one water molecule), this being released in a low energy reaction between 350 °C and the onset of oxalate decomposition at 380 °C. In this respect the lanthanum salt more closely resembles the heavier holmium and erbium decahydrates discussed later. The TG evidence for lanthanum suggests the existence of an intermediate trihydrate and monohydrate. This compares with the essentially equilibrium thermal data of Caro and Loriers [2], who observed the intermediate formation of tri-, di- and monohydrates from a salt reported to be a heptahydrate. From dynamic studies other workers have reported variously the existence of intermediate mono-, sesqui-, di- and trihydrates (refs. 11, 2, 24 and 21 respectively) or no intermediate hydrates [3, 23].

Dehydration of the praseodymium and neodymium decahydrates shows a remarkable similarity with evidence of intermediate sesqui- and hemihydrates, the loss of this final water coinciding with the onset of oxalate decomposition. This implies that these anhydrous oxalates, together with those of lanthanum and cerium, are unstable, in agreement with the observations of Subba Rao *et al.* [23]. Most previous dynamic TG studies on the praseodymium and neodymium decahydrates have failed to indicate the existence of intermediate hydrates [3, 4, 23, 25], exceptions being the sesquihydrate for praseodymium (but not neodymium) observed under equilibrium heating conditions [2] and sesquihydrates for both salts and a 3.5-hydrate for the neodymium salt [5].

An abrupt change in the decahydrate dehydration behaviour occurs between the salts of neodymium and samarium; possibly this is attributable to the larger decrease in cationic size due to the missing element promethium. The Sm - Dy salts all show three well-defined dehydration endotherms and in all cases except europium, where premature oxalate decomposition occurs, complete dehydration occurs at a temperature below that marking the onset of oxalate decomposition. In fact the heavier lanthanide salts within this group, particularly that of dysprosium, show a weight loss between complete dehydration and the onset of the main oxalate decomposition, as also occurs for the holmium, yttrium and erbium decahydrates (see later).

The approximate hydration numbers corresponding to the three endothermal decompositions for the Sm - Dy salts are shown in Table 2. The existence of intermediate penta- to hexahydrates and tri- to tetrahydrates for Sm - Tb agree with the more recent thermal data published for some [12, 16] or all [5] of these salts. Wendlandt [4] has found no evidence of intermediates for samarium and europium but has found a hexahydrate for gadolinium, penta- and monohydrates for terbium and tetra- and dihydrates for dysprosium, whereas other workers [5, 16] have postulated intermediate penta-, 2.6- and monohydrates for the dysprosium salt. In addition, Gallagher *et al.* [7] have observed a 4–2–4 dehydration mode for the europium salt, in agreement with our findings.

A further significant change in the dehydration behaviour occurs between the decahydrate salts of dysprosium and those of holmium, yttrium and erbium; only the first 8 - 8.5 waters of crystallization are lost in four endothermal stages followed by a TG plateau region between about 220 and 300 °C corresponding to the formation of apparently stable sesqui-, di- and dihydrates for holmium, yttrium and erbium respectively. The formation of a stable dihydrate from the yttrium salt is well established [3 - 5, 21] and other studies have tended to suggest that holmium forms a stable sesqui- [16] or dihydrate [3 - 5] from the decahydrate. The stability of the intermediate yttrium oxalate dihydrate has been established using X-ray diffraction (Table 1). The hydrate intermediates observed by Möbius and Matthes [5] for the holmium and yttrium salts were also observed in the present work, together with the other intermediates shown in Table 2.

The further decomposition of these stable lower hydrates of holmium, yttrium and erbium is interesting in that the weight loss before the onset of extensive oxalate decomposition exceeds that required for complete dehydration, as was also observed for the dysprosium salt. This excess weight loss is accompanied by an exothermal shoulder on the low temperature side of the oxalate decomposition peak; the TG plots also show a clear inflection point marking the transition between these two decompositions. Only in the case of the yttrium salt is there initial evidence of a characteristic dehydration endotherm. A possible explanation for this behaviour arises when the oxalate decomposition of the hexahydrates is considered (see later).

For most of the decahydrates which do not exhibit premature oxalate decomposition there is evidence of a small exothermal peak or shoulder at 340 - 390 °C; examination of the simultaneous TG plots indicates that this is accompanied by a small weight loss. This peak is also evident in published DTA plots for the Tb - Ho and Y salts [16]. From reported thermal data [26] it is unlikely to be the result of traces of adsorbed oxalic acid, but may possibly be attributable to adsorbed nitrate. However, extensive washing did not eliminate this peak and its origin is at present unresolved.

In summary, it is evident that the lanthanide oxalate decahydrates show a systematic dehydration trend with decreasing cationic radius, particularly amongst the oxalate decahydrates of the true rare earths Ce - Er. With increasing atomic number and decreasing ionic radius the initial tendency for the majority of the water to be evolved over a narrow temperature region centred at 160 - 170 °C changes and the waters are lost over a wider temperature range with an increasingly large number (4 - 6) being evolved at progressively lower temperatures (140 - 110 °C) and with the final 2 - 3 molecules being increasingly strongly retained. This becomes particularly apparent for the holmium, yttrium and erbium salts which form stable lower (sesqui- to di-) hydrates.

Since all the decahydrates are isomorphous it is reasonable to assume that the water is structurally bonded in the same way in all of them and that the differences in dehydration behaviour are a consequence of the lanthanide contraction. The most complete published structural analysis of lanthanide oxalate decahydrates is probably that for the La - Nd salts [27, 28]. These are monoclinic and consist of metal oxalate layers perpendicular to the *b* axis in which each oxalate ligand is bidentately coordinated to two metal ions and each metal ion is coordinated by three oxalate ligands. Three water molecules are coordinated to each metal atom and a further one [28] or two [27] water molecules per formula weight are hydrogen bonded to an oxalate oxygen. The remaining two or three water molecules are unlocated but are presumed to reside in cavities between the layers and to be hydrogen bonded to each other and to surrounding water oxygen atoms.

Significant structural changes occur during dehydration of the oxalate decahydrates, as evidenced by the low degree of crystallinity of the dehydration intermediates [22, 23]; thus complete dehydration behaviour cannot reasonably be expected to be quantitatively related to this initial structure. However, from the purely qualitative viewpoint it would be expected that the larger the metal cation in this isomorphous series the more easily could the larger lattice accommodate the ten water molecules, but the less strongly bonded they would be, particularly those coordinated directly to the cation. The fact that oxalate decahydrates of the heavy rare earths Tm - Lu cannot be obtained suggests that the small lattice sterically excludes the accommodation of ten water molecules. Thus, as the lattice size decreases from cerium to erbium the hydrogen-bonded water might be expected, from lattice stability and stereochemical considerations, to be more readily evolved whereas the water directly coordinated to the cations would be more strongly retained owing to the stronger metal—oxygen bonds.

4.2. Dehydration of the hexahydrates

In contrast with the decahydrates, dehydration of the oxalate hexahydrates of Y and Er - Lu are all very similar. There are presumably no steric limitations to the accommodation of six water molecules; three of these are lost in a single endothermal reaction peaking at 120 - 130 °C, followed by the loss of a further water molecule in an apparently two-stage process at 160 - 180 °C. In the case of the erbium salt a third endothermal reaction centred at 230 - 240 °C is observed. This is not accompanied by weight loss and is presumably attributable to a structural rearrangement, although the reason for its occurrence only for this salt is not obvious.

The resulting dihydrates are stable and X-ray examination of the yttrium salt has shown that it possesses a high degree of crystallinity (Table

1). The formation of trihydrate intermediates [5, 16] and stable dihydrates [3 - 5, 16] from thermal decomposition of the hexahydrates has been reported previously.

With the exception of the yttrium salt the stable dihydrates decompose by low energy reactions to the apparently unstable anhydrous salts, the formation of which marks the onset of oxalate decomposition. There is TG evidence of increased stability of the dihydrates along the series Er - Lu; the temperature at the onset of decomposition increases from 300 °C for erbium to 340 °C for lutetium.

4.3. *Oxalate decomposition of the decahydrates*

Figures 1 and 2 show that the predominant features in the decomposition of most of the "anhydrous" rare earth oxalates in air are a sharp exotherm followed by a broader exotherm followed by, in most cases, an endothermal reaction. The first exotherm is typical of oxalate decompositions in air, although in inert atmospheres these tend to be far less exothermal or even endothermal [26]. This difference in oxalate decomposition behaviour in inert atmospheres has also been observed for the oxalate decahydrates of europium (weakly [6] or very weakly [7] exothermal), cerium (endothermal [26]) and, in the present work, yttrium (very weakly exothermal).

The final endothermal reaction is also well established for oxalate decompositions [26] and is attributable to the decomposition of an intermediate carbonate.

The second exothermal peak is not generally observed during oxalate decompositions [26]; although it has been reported for rare earth oxalates [13 - 16] its origin is not well established. Bezdenezhnykh *et al.* [16] have attributed it to the oxidation of carbon monoxide produced during decomposition of the oxalate groups. However, we consider this highly unlikely (1) because of its appearance at a temperature more than 100 °C higher than that of oxalate decomposition and (2) because of its lack of appearance for other oxalates. Blum and Maguire [15] have attributed it to crystallization of the oxide produced during the decomposition. Again this is unlikely because it often precedes the endothermal decomposition of the intermediate carbonate. All our studies indicate that it is caused by carbon burn-off. It is well known that, unlike most oxalates, those of the rare earth metals deposit carbon during their decomposition [2, 7, 11, 16, 22, 29]. We have also observed this (1) on examination of various samples subjected to thermal analysis at temperatures up to 900 °C in inert atmospheres where, incidentally, this peak is not observed and (2) from visual observation of the decomposition of larger batches in air at 400 - 500 °C.

Dollimore and Griffiths [26] have postulated that the highly exothermal nature of the oxalate decomposition in air is attributable either to oxidation of the initial solid product or to oxidation of the carbon monoxide formed. This latter reaction would obviously require catalytic involvement of the solid surface because of the unfavourable kinetics of the gas phase reaction at about 400 °C. The majority of the rare earths, with the possible exceptions of cerium, europium and ytterbium, would not be expected to form oxidizable solid intermediates during oxalate decomposition; thus carbon monoxide oxidation is the most likely cause of the exothermal peak. Savitskaya *et al.* [13] have analysed the gases evolved during the various stages of the decomposition of yttrium and lanthanum oxalate decahydrates and have found that, during the oxalate decomposition reaction between about 350 and 500 °C, only very small amounts of free carbon monoxide are observed (less than 5% relative to carbon dioxide). However, it is also apparent that not all the evolved carbon monoxide is oxidized, since the deposition of carbon is probably attributable to disproportionation of a significant proportion of this carbon monoxide [7, 11, 29, 30].

The thermal data for the oxalate decompositions are thus discussed with reference to the following reaction scheme:

$$R_2(C_2O_4)_3 \longrightarrow R_2O_2CO_3 + 2CO_2 + 3CO \qquad (1)$$

$$2xCO \longrightarrow xCO_2 + xC \qquad (2)$$

$$(3-2x)CO + (1.5-x)O_2 \longrightarrow (3-2x)CO_2 \qquad (3)$$

$$xC + xO_2 \longrightarrow xCO_2 \qquad (4)$$

$$R_2O_2CO_3 \longrightarrow R_2O_3 + CO_2 \qquad (5)$$

In the absence of oxygen reactions (1) and (2) typically occur essentially simultaneously at 390 - 420 °C with little overall thermal effect. In the presence of air the strongly exothermal catalysed reaction (3) is the largest thermal effect. The exothermal carbon burn-off reaction (4), which does not proceed in the absence of oxygen, typically occurs at 500 - 600 °C and the endothermal carbonate decomposition reaction (5) sets in above 500 °C.

It is most likely that reaction (1) represents a simplification of the formation of the dioxycarbonate species; intermediates, such as dioxyoxalates or carbonylcarbonates [7, 31], have been postulated as possibly occurring during oxalate pyrolyses. Indeed, the data presented in this work for the lanthanide oxalate hexahydrates show clear evidence of a two-stage oxalate decomposition in these compounds.

Excluding the cerium, europium and terbium compounds, the general oxalate decomposition trend appears to be a broadening of the exothermal peak with increasing atomic number; in the case of the gadolinium, holmium and yttrium compounds there is clear TG evidence of an inflection point during oxalate decomposition. Figure 4 shows plots both of the peak temperature of oxalate decomposition and of the temperature at onset of the main oxalate decomposition as functions of the cationic radius. On both criteria there is clear evidence of the expected increase in thermal stability with decreasing ionic radius. Oxalate decomposition thus appears to be a good example of the chemical effect of the lanthanide contraction over an isomorphous series.

The obvious exceptions to the above trend are the cerium and europium compounds, both of which have been extensively studied in the past.

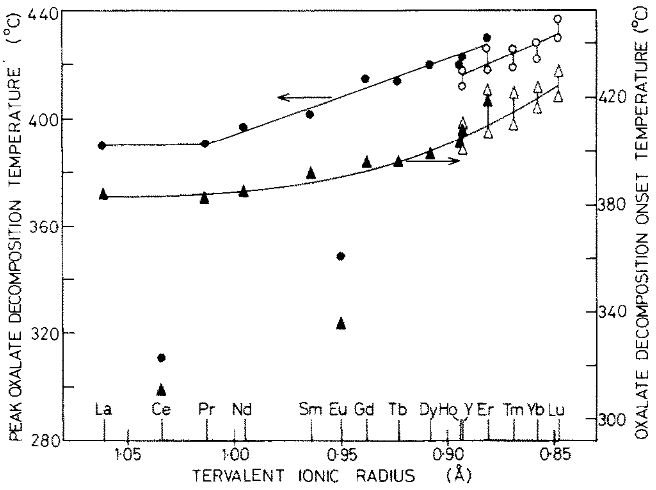

Fig. 4. Oxalate decomposition temperatures of the lanthanide oxalate decahydrates (filled symbols) and hexahydrates (open symbols).

In the case of Ce(III) oxalate decomposition it is well known that CeO_2 is formed even at the moderately low temperature of 350 °C [2 - 5, 20 - 23]. Our DTA plot shows clear evidence of a three-stage exothermal process occurring over the temperature range 290 - 360 °C after which the weight remains constant. Thus oxalate decomposition, Ce(III) oxidation and carbon burn-off all occur within this temperature range. It has been shown that carbon burn-off does occur with Ce(III) oxalate [22], and it is reasonable to assume that the third exothermal peak represents this. That it occurs at a temperature well below the 600 ± 30 °C observed for all the other oxalates except lanthanum, praseodymium, europium and terbium is probably attributable to the fact that it is accelerated by the oxidation of the lattice. Interestingly, of the above exceptions both praseodymium and terbium also form oxides richer in oxygen than the normal sesquioxides after thermal decomposition of the oxalates, these being approximately Pr_6O_{11} and Tb_4O_7 respectively. Thus it is likely that the relatively sharp and premature carbon burn-off reaction observed for these oxalates is also attributable to a similar effect.

Which of the first two sharp exothermal peaks represents Ce(III) oxidation and which represents oxalate decomposition is of interest in explaining the anomalously low Ce(III) oxalate decomposition temperature. Some indication of this is obtained from the simultaneous TG–DTA data. For all the other oxalate decompositions the DTA peak coincides with the maximum rate of weight loss in the TG curve; in the case of Ce(III) oxalate this clearly coincides with the second peak. Thus it appears that the first peak corresponds to the air oxidation of Ce(III) to a basic Ce(IV) oxalate species; presumably this species is unstable and decomposes immediately.

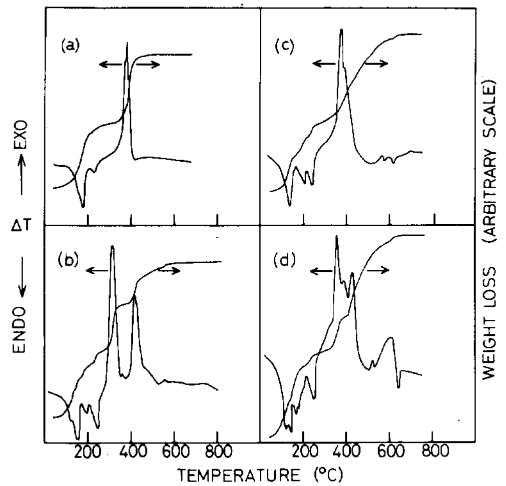

Fig. 5. TG–DTA curves of (a) a $CeTb(C_2O_4)_3 \cdot 10H_2O$ solid solution, (b) a 1:1 mixture of $Ce_2(C_2O_4)_3 \cdot 10H_2O$ and $Tb_2(C_2O_4)_3 \cdot 10H_2O$, (c) a $YEu(C_2O_4)_3 \cdot 10H_2O$ solid solution and (d) a 1:1 mixture of $Y_2(C_2O_4)_3 \cdot 10H_2O$ and $Eu_2(C_2O_4)_3 \cdot 10H_2O$.

The stability of the Ce(III) ion in the oxalate lattice is improved when it is in a crystalline solid solution with another rare earth. For example a co-precipitated 1:1 cerium–terbium oxalate decahydrate, which was found from X-ray diffraction studies to be a crystalline solid solution, showed the same three exotherms as the pure Ce(III) oxalate but these occurred at 377, 381 and 390 °C compared with 307, 311 and 322 °C for the pure Ce(III) compound (Fig. 5(a)). Interestingly, the dehydration behaviour of this solid solution was essentially identical with that of the praseodymium and neodymium oxalate decahydrates, indicating that solid solution formation produces a distinct entity with characteristic thermal properties intermediate between those of the parent compounds. For comparison Fig. 5(b) illustrates the purely additive thermal behaviour observed for an intimately ground and sieved 1:1 mixture of the pure parent compounds, although it is apparent that the grinding process destroys the fine detail in the DTA curves observed during oxalate decomposition of the original pure compounds.

The anomalous oxalate decomposition behaviour of europium oxalate has also received attention in the past [6, 7]; it is interesting to note that, of the lanthanide metals, cerium and europium are those which most commonly exist in an oxidation state other than 3+. Ce^{3+} ($4f^1$) has a tendency to lose its single electron to form the 4+ state, whereas Eu^{3+} ($4f^6$) has a tendency to acquire the stable f^7 configuration with consequent reduction to the 2+ state. By analogy with the cerium oxalate system, it is tempting to attribute the anomalously low Eu(III) oxalate decomposition temperature to instability of its anhydrous salt and its tendency to form a Eu(II) species. A mechanism of this type has in fact been posulated by Glasner *et al.* [6], who have proposed the reaction

$$Eu_2(C_2O_4)_3 \longrightarrow 2EuC_2O_4 + 2CO_2$$

as the first stage in the oxalate decomposition although, unlike ourselves and Gallagher *et al.* [7], they observed an initial endothermal effect to account for this reaction. They attributed the onset of exothermal decomposition to oxidation of the Eu(II) to Eu(III) with the formation of $(EuCO_3)_2O$, which subsequently decomposed endothermally to the oxide. They also cited the similarity in the DTA behaviour of Eu(II) and Eu(III) oxalates above 310 °C as further evidence of this initial reduction step. In contrast, however, Gallagher *et al.* [7] could find no evidence of Eu(III) reduction during oxalate decomposition either from Mössbauer spectroscopy or from fluorescence measurements. They proposed the following reaction scheme involving a Eu(III) carbonylcarbonate species:

$$Eu_2(C_2O_4)_3 \xrightarrow{(310-490\ ^\circ C)} Eu_2O_2OCOCO_2 + 2CO + 2CO_2 \quad (6)$$

$$Eu_2O_2OCOCO_2 \xrightarrow{(490-560\ ^\circ C)} Eu_2O_2CO_3 + CO \quad (7)$$

$$Eu_2O_2CO_3 \xrightarrow{(560-925\ ^\circ C)} Eu_2O_3 + CO_2 \quad (8)$$

Only in the presence of oxygen are reactions (6) and (7) significantly exothermal, presumably owing to the catalytic oxidation of the carbon monoxide produced.

Thus in the case of the Eu(III) salt the precise oxalate decomposition route is unresolved. However, apart from invoking some degree of reduction to Eu(II) it is difficult to explain the anomalous oxalate decomposition behaviour of Eu(III) relative to its rare earth oxalate neighbours.

As for Ce(III) oxalate, crystalline solution incorporation of other cations with the Eu(III) enhances thermal stability. Figure 5(c) shows that 1:1 crystalline solid solution formation with yttrium causes increases in the oxalate decomposition peak and the subsequent exothermal shoulder from 349 and 365 °C to 377 and 396 °C respectively. Once again the dehydration behaviour shows that expected of a rare earth oxalate decahydrate intermediate between the parent compounds, and is totally different from the additive effect observed for a thoroughly ground and sieved 1:1 mixture of the pure parent compounds (Fig. 5(d)).

The carbon burn-off exotherms during pyrolysis of the rare earth oxalate decahydrates have been mentioned earlier. These typically occur at 500 - 650 °C with a peak at 600 ± 30 °C; this is in the temperature range where non-catalysed burn-off would be expected. The premature burn-off of the cerium, praseodymium, terbium and, arguably, europium compounds can be attributed to oxidation of the solid intermediates formed during the oxalate decompositions. The premature carbon burn-off of the lanthanum compound is not obviously explained, but might tentatively be attributed to a catalytic acceleration by the very stable $La_2O_2CO_3$ surface.

The endothermal dioxycarbonate decomposition is well established for certain rare earths, and in particular for lanthanum [2 - 5, 11, 13, 20, 21, 23] where it is sufficiently stable to have been isolated and an X-ray diffraction pattern obtained [2]. Of the other rare earths, only in the cases of praseodymium, europium and possibly terbium, where premature carbon burn-off occurs, does the dioxycarbonate decomposition occur under dynamic heating as a well-separated endothermal DTA peak accompanied by a distinct inflection point in the TG trace. The dioxycarbonate decomposition is also evident for samarium, gadolinium and possibly dysprosium as a weak endothermal effect immediately following carbon burn-off. There is no DTA evidence for dioxycarbonate decomposition for holmium, yttrium and erbium, but the effect may be masked by carbon burn-off. Bezdenezhnykh *et al.* [16] have presented IR spectroscopic evidence for the formation of $R_2O_2CO_3$ at 490 - 510 °C for the holmium and yttrium salts.

The stabilities of the dioxycarbonates would be expected to decrease with decreasing cationic radius (*i.e.* decreasing basicity) and this is what is observed qualitatively. By using very carefully controlled heating of the oxalates Caro and Loriers [2] have been able to detect weight loss plateaux corresponding to the pure dioxycarbonates for several of the rare earths. These occurred at 620 - 780 °C for lanthanum, 400 - 530 °C for praseodymium, 620 - 730 °C for neodymium, 400 - 430 °C for samarium and 400 - 470 °C for gadolinium. No evidence for stoichiometric $R_2O_2CO_3$ could be found for erbium or yttrium. From the data of Figs. 1 and 2 the peak dioxycarbonate decomposition temperatures under our dynamic conditions can be put at 770 °C for lanthanum, 570 °C for praseodymium, 680 °C for neodymium, below about 630 °C for samarium, 620 °C for europium, less than 660 °C for gadolinium and, arguably, 520 °C for terbium.

The anomalously low thermal stability of $Pr_2O_2CO_3$ has also been observed by other workers [23]. However, it has been shown that the oxidation of Pr_2O_3 to Pr_6O_{11} occurs below about 500 °C [2]; therefore premature dioxycarbonate decomposition is probably attributable to the onset of this reaction.

4.4. Oxalate decomposition of the hexahydrates

The oxalate decomposition temperatures of the lanthanide oxalate hexahydrates show a similar increase with decreasing cationic radius to that observed for the decahydrates (Fig. 4). However, one significant difference is that in all cases the main oxalate decomposition peak is split into two very sharp exotherms; the relevant temperatures for both peaks are shown in Fig. 4. Interestingly, the carbon burn-off exotherms peaking at 580 - 610 °C also show a low temperature shoulder at 520 - 550 °C in all cases; this is possibly attributable to the different reactivities of the carbon deposited in the two oxalate decomposition stages.

The reason for this difference in the oxalate decomposition behaviour compared with that for the decahydrates is surprising in view of the fact that, at least in the case of the two yttrium salts, we found that the stable dihydrates formed at 200 - 300 °C are crystallographically identical (Fig. 1).

However, that formed from the hexahydrate was found to be far more highly crystalline, which presumably accounts for its sharper and better resolved oxalate decomposition behaviour. The previously mentioned exothermal shoulders on the low temperature sides of the main oxalate decomposition peaks of the holmium, yttrium and erbium decahydrates thus probably represent a broadened and poorly resolved version of this two-stage decomposition.

Whether this two-stage decomposition represents two distinct oxalate decompositions or whether the second peak is an oxidative decomposition of a carbonate intermediate formed during the first decomposition is unresolved, although the extremely sharp nature of the second peak suggests the former alternative as being more likely. In crystallographic studies of ytterbium oxalate hexahydrate, Hansson [32] has observed that one of the three bidentate oxalate ligands coordinated to each ytterbium ion in the metal oxalate layers has significantly different bonding from the other two. Two of these ligands have metal—oxygen distances in the range 2.28 - 2.34 Å with oxalate "bites" of 2.62 - 2.73 Å, whereas the third has distances of 2.37 - 2.41 and 2.80 Å respectively. Comparable behaviour has not been observed for the neodymium oxalate decahydrate [28] where the ligand bonding is much more equal.

An oxalate "bite" of 2.80 Å is very large for a coordinated oxalate and is similar to the distance expected for the non-chelating part of oxalate ions in mononuclear complexes (2.75 - 2.90 Å). The highly crystalline nature of the dihydrates suggests that severe structural rearrangement has not occurred at this stage; thus the two-stage nature of the subsequent oxalate decomposition might reflect the slightly different thermal stabilities of these oxalate ligands.

In agreement with the trends observed during decomposition of the oxalate decahydrates, there was no DTA evidence of dioxycarbonate decomposition during pyrolysis of the Y and Er - Lu oxalate hexahydrates.

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