

DETERMINATION OF SOLID STATE BASICITY OF RARE EARTH OXIDES BY THERMAL ANALYSIS OF THEIR CARBONATES

A. M. Maitra

CSIRO DIVISION OF COAL TECHNOLOGY, P.O. BOX 136, NORTH RYDE, N.S.W. 2113, AUSTRALIA

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Relative basicities of the rare earth oxides (M_2O_3) were determined from the measurement by TG - DTA of decomposition temperatures of the carbonates of Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er and Yb. From the comparison of this data with that published by Head and Holley, a sequence of basicity has been proposed for the entire range of rare earth oxides. This sequence in decreasing basicities is : La > Pr ~ Nd > Sm > Gd ~ Eu > Tb ~ Ho ~ Er > Dy ~ Tm ~ Yb ~ Lu > Ce. Basicity of rare earth oxides, therefore, does not decrease progressively with an increase in atomic number.

Present investigations form a part of our Division's research program into new routes for the production of transport fuels from natural gas. An important feature of this is the need to develop and understand the catalysts necessary for promoting the desired reactions.

Active catalysts usually include strongly basic oxides of alkali, alkaline earth and the rare earth elements [1-5]. To date there has been no systematic study examining the role of oxide-basicity on the catalytic activity. Usual methods [6] to measure solid basicity include acid titrations (viz. benzoic acid) using indicators, and acidic gas adsorption. Other methods based on measurements of catalytic activity, viz., dehydrogenation of isopropyl alcohol to acetone [7], and the binding energy calculations, viz., O_{1s} in oxides, by X-ray photoelectron spectroscopy [8] have been employed. We have considered the measurement of thermal stability of carbonates as a means of determining relative basicities of the metal oxides. To our knowledge no complete basicity studies on the rare earth (RE) oxides have ever been carried out.

*John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest*

In the present study the stability of the carbonates of the rare earth (REC) elements Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er and Yb was investigated in some detail by thermogravimetry (TG) and differential thermal analysis (DTA). Although a number of similar studies have been conducted by other workers [9-18], the published literature contains conflicting information. This arises from the choice of various experimental parameters and the use of starting materials which varied in terms of the degree of hydration and carbonation. Further, apart from Head & Holley [14, 15], other workers studied only a limited number of the compounds from which to determine a sequence of stability for the entire series of elements. This study aimed to be more comprehensive so as to enable us to examine whether the sequence of thermal stability for the lanthanide carbonates could be employed as a measure of relative basicity of the RE oxides. Assessment of catalytic potentials of these oxides will be discussed in a separate note to the Journal of Applied Catalysis.

Experimental

Reagents and samples

$\text{Ce}_2(\text{CO}_3)_3$ was used as received from a commercial source (Ajax, 95% purity having 0.05% other REC). Carbonates of Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Yb were prepared by precipitation from nitrate solutions with sodium carbonate (Ajax, Univar). The method was similar to that used by Savin *et al.* [11]. Metal nitrates were obtained by dissolving in nitric acid (Ajax, Univar) 1-2 g of the following metal oxides (99.9% purity): Pr_6O_{11} (BDH), Sm_2O_3 (BDH), Eu_2O_3 (BDH), Gd_2O_3 (Union Molycorp, 20 g of this material was used), Tb_2O_3 (BDH), Dy_2O_3 (BDH), Ho_2O_3 (BDH), Er_2O_3 (Fluka) and Yb_2O_3 (BDH). The carbonate precipitates were filtered, washed with hot water and boiled in water. This washing sequence was repeated 3 times to rid the precipitate of sodium before drying in an oven at 150° . TG-DTA work was carried out in CO_2 using these oven-dried materials. From these results it was apparent that the carbonates were partially hydrated and therefore, the samples were subsequently treated at 200° in a tube furnace for 6 hours in a stream of pure carbon dioxide prior to TG-DTA in N_2 . These samples were analyzed for sodium by atomic absorption spectrometry, and for carbonate purity by rapidly heating the samples to 1350° and measuring the evolved CO_2 in a LECO CR12 carbon analyzer. These results together with that of sodium analysis are given in Table 1.

Table 1a Analytical data for the REC's

Formula	CO ₂ , wt. %		H ₂ O, wt. %		Total wt. loss, %		Na Content wt. %
	Expected	Found	Expected	Found	in N ₂	in CO ₂	
Ce ₂ (CO ₃) ₃	28.7		0.0		28.7		
Ce ₂ O ₃ .2CO ₂ .2H ₂ O	19.5	16.9	8.0		27.4	23.3	1.6
Ce ₂ O ₃ .2.5CO ₂ .3.5H ₂ O	21.9		12.6		34.5		
Pr ₂ (CO ₃) ₃	28.6		0.0		28.6		
Pr ₂ O ₃ .2CO ₂ .2H ₂ O	19.4	22.0	7.9		27.3	27.8	0.4
Pr ₂ O ₃ .2.5CO ₂ .3.5H ₂ O	21.9		12.5		34.4		
Sm ₂ (CO ₃) ₃	27.5		0.0		27.5		
Sm ₂ O ₃ .2CO ₂ .2H ₂ O	18.6	22.0	7.6		26.4	25.9	<0.1
Sm ₂ O ₃ .2.5CO ₂ .3.5H ₂ O	21.1		12.1		33.2		
Eu ₂ (CO ₃) ₃	27.3		0.0		27.3		
Eu ₂ O ₃ .2CO ₂ .2H ₂ O	18.5	21.3	7.6		26.0	28.6	0.1
Eu ₂ O ₃ .2.5CO ₂ .3.5H ₂ O	20.9		12.0		33.0		
Gd ₂ (CO ₃) ₃	26.7		0.0		26.7		
Gd ₂ O ₃ .2CO ₂ .2H ₂ O	18.1	20.2	7.4		25.5	26.3	4.8
Gd ₂ O ₃ .2.5CO ₂ .3.5H ₂ O	20.5		11.8		32.3		

Table 1b Analytical data for the REC's

Formula	CO ₂ , wt. %		CO ₂ , wt. % Found	H ₂ O, wt. % Expected	Total wt. loss, %		Na Content wt. %
	Expected	Found			in CO ₂		
					Expected	Found	
Tb ₂ (CO ₃) ₃	26.5			0.0	26.5		
Tb ₂ O ₃ .2CO ₂ .2H ₂ O	18.0	19.1		7.3	25.3	24.3	0.1
Tb ₂ O ₃ .2.5CO ₂ .3.5H ₂ O	20.4			11.7	32.1		
Dy ₂ (CO ₃) ₃	26.1			0.0	26.1		
Dy ₂ O ₃ .2CO ₂ .2H ₂ O	17.7	17.2		7.2	25.0	24.7	0.6
Dy ₂ O ₃ .2.5CO ₂ .3.5H ₂ O	20.2			11.5	31.7		
Ho ₂ (CO ₃) ₃	25.9			0.0	25.9		
Ho ₂ O ₃ .2CO ₂ .2H ₂ O	17.5	17.6		7.2	24.7	23.9	0.1
Ho ₂ O ₃ .2.5CO ₂ .3.5H ₂ O	20.0			11.4	31.4		
Er ₂ (CO ₃) ₃	25.6			0.0	25.6		
Er ₂ O ₃ .2CO ₂ .2H ₂ O	17.4	16.9		7.1	24.5	21.5	0.1
Er ₂ O ₃ .2.5CO ₂ .3.5H ₂ O	19.8			11.3	31.1		
Yb ₂ (CO ₃) ₃	25.1			0.0	25.1		
Yb ₂ O ₃ .2CO ₂ .2H ₂ O	17.0	15.4		7.0	23.9	22.2	1.0
Yb ₂ O ₃ .2.5CO ₂ .3.5H ₂ O	19.4			11.1	30.5		

XRD analyses were unsuccessful as all but the Sm compound appeared amorphous. In the FTIR spectra the carbonate samples (both oven-dried and CO₂-roasted) contained some non-carbonate features, such as, oxide and water; the residues after TG runs showed only oxide features. Note that the carbonates of La, Nd, Tm and Lu were not included in the study as the materials of suitable purity were unavailable.

TG-DTA

Thermal analyses (TG-DTA) were carried out in a Rigaku Thermoflex PTC-10A instrument interfaced to an Apple II+ computer. Samples were ground thoroughly in an agate mortar to produce particle sizes of less than 5 μm . Analyses were performed on 15 mg samples using Pt cups and alpha-alumina as a reference at a heating rate of 10 deg/min to 1250° in a stream (100 ml/min) of high purity, dry, CO₂-free N₂ and also in a stream of dry CO₂ (food grade, CIG). Reproducibility in TG was found to be within 5%. Table 1 contains the total weight loss observed for each carbonate during thermal analysis from ambient to 1250°. Each decomposition step shown in TG has been described in the text in terms of $T_{0.5}$ at the temperature corresponding to 50% weight loss in a certain temperature range (T_{range}). T_{max} has been used to represent the temperature of peak maxima in DTA and DTG.

Results and discussions

It is now generally agreed [9] that the REC's decompose to M₂O₃ via the decomposition product M₂O₂CO₃ with the decomposition of M₂O₂CO₃ proceeding in further intermediate stages. MO(CO₃)₂ as the first step decomposition product was mentioned only in two reports [12, 13]. Data published by various workers often differ from each other in terms of the temperature regions at which decompositions take place indicating that individual investigators saw slightly different thermal events. It is likely that the purity of starting materials significantly contributes to the confusion [19].

There are two ways the REC are usually prepared:

a) by rapid precipitation of REC from a solution of lanthanide nitrates or chlorides with a solution of an alkaline metal carbonate [10, 11, 19] or ammonium carbonate [12]

b) by the method of Salutsky and Quill [20] involving a slow precipitation from the hydrolysis of trichloroacetate salts.

Both methods produce hydrated carbonates which are susceptible to hydrolysis forming oxycarbonates ($M_2O_3 \cdot 2CO_2 \cdot 2H_2O$ or $M_2O_3 \cdot 2.5CO_2 \cdot 3.5H_2O$) [18]. Sastry *et al.* [18] from their own results and earlier literature argued that, irrespective of the precipitation method employed, the carbonates are hydrolyzed to the oxycarbonates. This hydrolysis usually takes place during the purification and preservation of the carbonates in a moist medium low in CO_2 , especially, at an elevated temperature.

Thus, it is likely that the condition used for the preparation of REC in the present study would favour oxycarbonates. From the data presented in Table 1, $M_2O_3 \cdot 2CO_2 \cdot 2H_2O$ appears to be a reasonable representation of these carbonates. However, some variation in the molecular formula, due to varying degrees of hydrolysis, are apparent in cases such as Ce, Pr, Sm and Eu.

Thermal analysis: TG

Table 2 gives a summary of the thermogravimetric (TG and DTG) and DTA data collected from TG curves in Figs 1 and 2 for the carbonates of Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Yb under an inert environment of N_2 . Table 3 presents a similar data set collected under the influence of an interactive atmosphere of CO_2 and the corresponding TG curves are illustrated in Figs 3 and 4. In the Tables the steps shown in numerical order primarily indicate the number of distinctly identifiable TG events. However, as will be seen later, they are implicitly associated with the formation of various intermediate decomposition products. Summation of weight losses in these steps is usually less than the total weight loss over the whole range of temperatures studied since some of these steps slowly run into other domains. Table 1 gives the total weight loss as determined from the weight of residues after the thermal run which is similar to the total weight loss that was observed in the TG curve in both N_2 and CO_2 . (This similarity implies that the oxide residues are resistant to recarbonation when left to cool in the stream of CO_2). From Table 1 and Figs 1-4 it is apparent that higher weight losses are usually observed in CO_2 than in N_2 with the exception of Gd and, to a lesser extent, Ce and Yb samples which contained some sodium impurities. It may be recalled that the samples used in the thermal studies in N_2 were pretreated in CO_2 . This treatment is likely to minimize the degree of hydration.

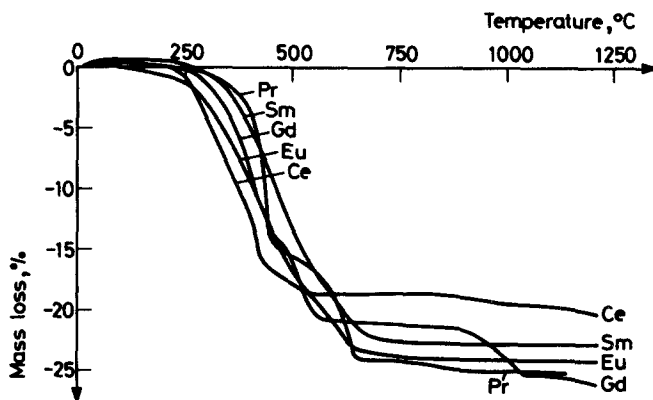


Fig. 1 Weight loss (%) as a function of dynamic furnace temperature for the carbonates of Ce, Pr, Sm, Eu and Gd in N₂

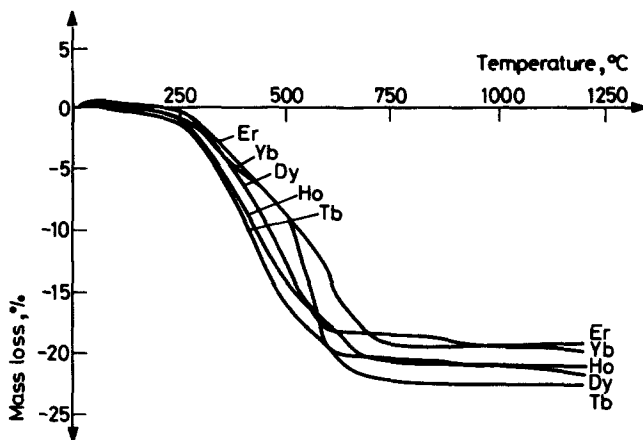


Fig. 2 Weight loss (%) as a function of dynamic furnace temperature for the carbonates of Tb, Dy, Ho, Er and Yb in N₂

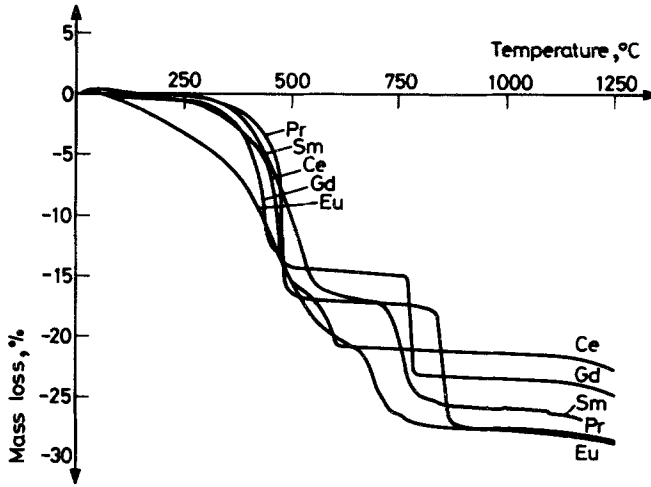


Fig. 3 Weight loss (%) as a function of dynamic furnace temperature for the carbonates of Ce, Pr, Sm, Eu and Gd in CO_2

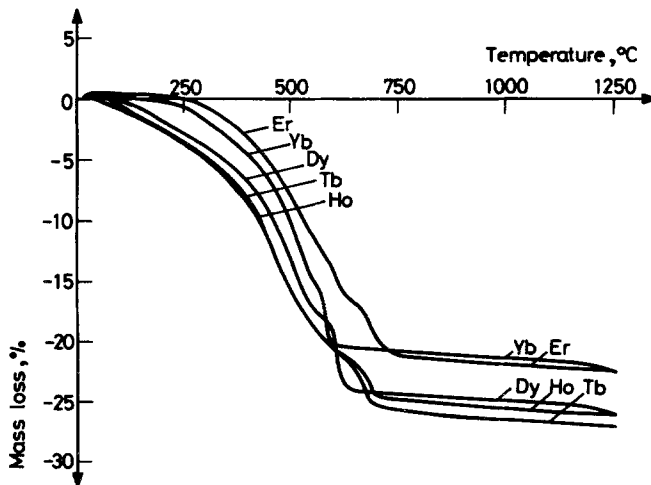
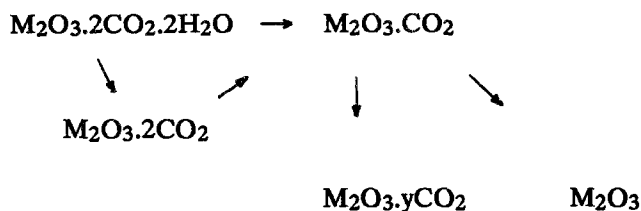


Fig. 4 Weight loss (%) as a function of dynamic furnace temperature for the carbonates of Tb, Dy, Ho, Er and Yb in CO_2

The observed decomposition pattern can be broadly expressed by the following scheme:



where, $\text{M}_2\text{O}_3 \cdot y\text{CO}_2$ is to be considered when a non-stoichiometric step is observed before complete decomposition to metal oxides. According to the above pathway the decomposition proceeds via the main step involving $\text{M}_2\text{O}_3 \cdot \text{CO}_2$ and its subsequent degradation(s) to oxides. Although the existence of the intermediate $\text{M}_2\text{O}_3 \cdot 2\text{CO}_2$ has not been confirmed by any worker (but the formation was indeed speculated [9]), the weight ratio in the three-step decomposition of Yb-carbonate in N_2 (in Table 2) is a good indication of the involvement of $\text{M}_2\text{O}_3 \cdot 2\text{CO}_2$ in the direct decomposition process. Decomposition of the other carbonates proceeds according to the general pattern described above with y being normally less than one and the step leading to the formation of $\text{M}_2\text{O}_3 \cdot y\text{CO}_2$ lying close to the formation of $\text{M}_2\text{O}_3 \cdot \text{CO}_2$ under a single TG event. Thus, in Table 2 (and Table 3), steps 1, 2 and 3 for Yb are tentatively assigned to the formation of $\text{Yb}_2\text{O}_3 \cdot 2\text{CO}_2$, $\text{Yb}_2\text{O}_3 \cdot \text{CO}_2$ and Yb_2O_3 , respectively. For other carbonates steps 1 and 2 were generally considered as being due to the formation of $\text{M}_2\text{O}_3 \cdot \text{CO}_2$ and M_2O_3 , respectively, despite some low weight losses being observed for step 2, notably Ce. Obviously, in these instances step 2 is more correctly associated with the decomposition to M_2O_3 from the non-stoichiometric basic carbonate $\text{M}_2\text{O}_3 \cdot y\text{CO}_2$ as shown in the above scheme.

Apart from Eu, Gd and Er the degradation pattern in CO_2 remains unchanged and generally the thermal events shift towards higher temperatures (Table 3). However, sensitivity of $T_{0.5}$ to CO_2 is much less pronounced with heavier elements, such as, Dy, Er or Yb in contrast to Head and Holley's data (discussed later) which shows larger differences in $T_{0.5}$ values in CO_2 relative to that observed under vacuum. Europium carbonate under CO_2 appeared to decompose in four steps; the last minor step(s) may also indicate the formation of solid solution of the carbonate containing species with the newly formed oxide phase. For Er the decomposition of dioxycarbonate to Er_2O_3 appears to proceed in two steps via the non-stoichiometric basic carbonate $\text{Er}_2\text{O}_3 \cdot y\text{CO}_2$ as shown in the scheme. For gadolinium carbonate a

Table 2 Thermoanalytical data of the REC's in N₂. Key: $T_{0.5}$, temperature (°C) corresponding to 50% weight loss of a decomposition step shown by TG; T_{range} , range of temperatures (°C) for a particular decomposition step; T_{max} , the peak maximum temperature in a DTA or DTG event; exothermic peaks in DTA are indicated by "x"

Carbonate	Step 1				
	$T_{0.5}$	T_{range}	T_{max}		wt. loss, %
			DTA	DTG	
Ce	355	192-460	325	285	17.2
			425	420	
Pr	433	210-460	442	436	14.7
Sm	444	180-570	330	437	18.3
			~435		
Eu	410	70-560	~425	422	19.6
Gd	390	200-463	320	413	14.4
			415		
Tb	390	70-510	~310	313	15.9
			~430	419	
Dy	418	175-530	~315	312	14.7
			523	514	
Ho	~405	70-565	~315	~315	17.1
				437	
Er	480	180-630	~310	307	15.5
			615	606	
Yb	~335	110-430	315	312	6.2
Step 2					
Ce	500	460-547		~500	1.5
Pr	603	460-660	635	628	9.6
Sm	616	570-730	560	540	4.7
			610	607	
Eu	610	560-715	590	605	4.2
Gd	515	463-595	515	505	6.6
			532		
Tb	590	510-740		~610	6.0
Dy	580	530-620	585	587	5.3
			603		
Ho	635	565-705	600	648	3.7
			645x		
Er	670	630-790			3.9
Yb	510	430-540	530	529	6.2
Step 3					
Yb	570	540-650	580	571	6.0

Table 3 Thermoanalytical data of the REC's in CO₂. Key as in Table 2

Carbonate	$T_{0.5}$	T_{range}	Step 1		wt. loss, %
			T_{max}		
			DTA	DTG	
Ce	460	110-488	470	466	14.8
Pr	478	220-525	472	478	16.3
Sm	480	280-593	510	495	15.9
Eu	425	60-565	450	456	19.0
			530		
Gd	420	110-455	432	431	12.6
Tb	445	165-615	~460	449	19.6
Dy	440	150-540	466	485	16.1
			520		
Ho	450	140-660	~470	460	21.5
Er	480	200-600	295	~500	14.1
			~500	600	
Yb	430	150-510	~480	~300	11.8
				~490	
Step 2					
Ce	565	488-610	500	595	5.9
			600		
Pr	856	790-920	862	860	10.2
Sm	764	710-858	767	732	8.5
				762	
Eu	~680	565-705	695	691	5.6
Gd	473	455-515	475	470	1.9
Tb	660	615-765	665	665	4.4
Dy	600	540-640	605	604	7.1
Ho	678	660-780	675x	678	2.6
Er	605	600-640		600	2.8
Yb	525	510-545	523	521	3.1
Step 3					
Eu	720	705-740	723	720	1.6
Gd	775	755-800	777	774	8.4
Er	684	640-790	667x	674	4.6
Yb	575	545-670	583	577	5.8
Step 4					
Eu	770	740-815	765	766	1.0

relatively low weight loss in the first step creates some uncertainty as to its decomposition pattern. In all cases, the residues obtained after decomposition in CO_2 and cooling to room temperature in the same gas stream showed little or no carbonate features in FTIR or gravimetric studies, again indicating a very poor capacity of these heated oxides for recarbonation. Loss of basicity due to changes in crystal structure after high temperature treatments is not uncommon.

The Na impurity in Gd, Ce, and traces in Yb and Pr can be seen in Figures 1 & 2 as steps with $T_{0.5}$ values (not shown in Table 2) at 970, 955, 890 and 820°, respectively, under N_2 . These $T_{0.5}$ values appear at 1240° when the decomposition is carried out in CO_2 . Only the Gd-carbonate sample exhibited the presence of Na_2CO_3 strongly in its DTG and DTA curves, viz., T_{max} in N_2 at 998° in DTG and at 1020° in DTA. The $T_{0.5}$ value for pure Na_2CO_3 in air was found at 1002°. It is hard to assess from the present data what the effect of the low levels of Na_2CO_3 impurity would be on the thermal behaviours of these lanthanide carbonates. Comparison of these mixed systems with the solid solutions of the alkaline-earth carbonates examined in this laboratory indicates that Na_2CO_3 has not significantly influenced these data.

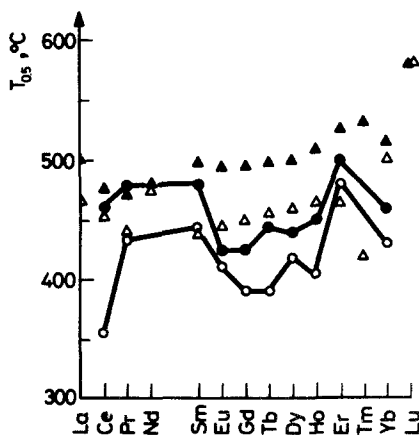


Fig. 5 Observed $T_{0.5}$ values for the first decomposition step of RECO₃ approaching the formation of $\text{M}_2\text{O}_3\cdot\text{CO}_2$: (o) data in N_2 ; (●) data in CO_2 (101 kPa). Data published by Head and Holley [14, 15] obtained in vacuo and CO_2 (67 kPa) given in Table 4 are also shown by (Δ) and (▲), respectively

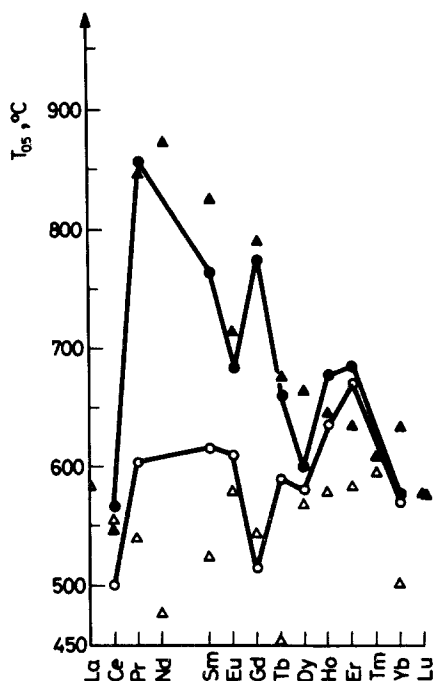


Fig. 6 Observed $T_{0.5}$ values for the last major decomposition step of the REC's approaching the formation of RE oxides: (o) data in N_2 , (●) data in CO_2 . Head and Holley's data given in Table 4 are also shown by (Δ) and (▲), respectively

It is relevant to make reference to the study of Head and Holley [14, 15] and Table 4 presents $T_{0.5}$ values derived from their published TG curves determined under vacuo and 67 kPa of CO_2 (cf. N_2 and 101 kPa CO_2 used in present study). $T_{0.5}$ values for the steps leading to $M_2O_3 \cdot CO_2$ (or $M_2O_3 \cdot 2CO_2$ as in Yb) and M_2O_3 are also shown in Figs 5 & 6. Note that for Eu the $T_{0.5}$ of Fig. 6 in CO_2 is for the second step since the two subsequent steps represent a small weight loss. There are evidently similar trends in both sets of data. In CO_2 good agreement is found for the lighter REC's. However, significant differences occur with the heavier elements, especially, in the temperature of the first decomposition step (see Fig. 5). Head and Holley's data indicate a rather constant decomposition temperature for the first step irrespective of any particular element in the series. Data from the present study show more variations without any distinct trend across the series. This difference may well represent some effect of the simultaneously occurring dehydration with the carbonate decomposition process. Com-

parison of Head and Holley's vacuum data with the data generated under N₂ also shows marked differences, with their $T_{0.5}$ values for the first step being generally higher (Fig. 5) and for the oxide-formation step being lower (Fig. 6). It is not easy to explain these differences unambiguously but they may be attributed to varying rates of CO₂ removal associated with decomposition under vacuum or in N₂ resulting in variable decomposition kinetics.

DTG, DTA and phase transformation

Comparison of DTA, DTG and $T_{0.5}$ values in Tables 2 & 3 shows that under both N₂ and CO₂, most thermal events are associated with concomitant weight changes. However, under the experimental conditions used only the Ce, Pr, and Gd-carbonates showed sharp features. DTA curves for other carbonates contained less definitive information. DTA peaks around 315° (under N₂) are indicative of dehydration. DTG in N₂ also shows this event although the suspected dehydration can not be so clearly separated from the decarbonation process in the TG curves.

As noted above, there are few DTA features that can be attributed to thermodynamic changes due to phase transformations because of the concurrent TG events. In the case of Ho carbonate an exothermic peak at 645° (in N₂) and 675° (in CO₂) may allow some speculation about a probable transformation of tetragonal Ho₂O₂.CO₃ to the hexagonal form based only on the unusual exothermicity. In general, three polymorphic forms of dioxymonocarbonate M₂O₂.CO₃ have been recognized [9, 21] for the lighter lanthanides. Phase modification of these dioxymonocarbonates has been the subject of an elaborate study by Turcotte *et al.* [21]. Briefly, the transition from the tetragonal to the hexagonal modification takes place around 400° although the hexagonal form has not been confirmed for the heavier RE elements. The intermediate monoclinic form has been observed with Pr and Nd-compounds only.

These transformations



were described [9, 21] as irreversible as are the cubic → hexagonal modifications for the corresponding M₂O₃ oxides. However, in the review of Touret and Queyroux [22] reversible transformations were emphasized. They also mentioned two additional polymorphic phases *H* and *X* for the lanthanide oxides. Phase modifications will not only influence the thermal property (of

carbonates) which is directly related to crystal packing, but also change the M - O bond distances and hence the acid - base properties.

Basicity of the carbonates and oxides

Since the decomposition of the REC is not a single step process the question arises as to which step one should select for a comparison of oxide basicities. The decomposition temperature of the second or the final major step which is free from the uncertainty in composition of the starting hydrated carbonates, would appear to represent a more appropriate parameter for this purpose. However, the temperature of the first decomposition step may also be considered as providing a measure of minimum (or a lower limit of) basicity.

It may be recalled from Fig. 6 that the $T_{0.5}$ values for the final step in N_2 are usually close to 600° except for some low values in Ce and Gd, and higher values for Ho and Er. As in the first decomposition temperature the $T_{0.5}$ values for the final step also bear no apparent relationship with the atomic number of the elements.

On changing the reaction environment to CO_2 one should expect to see an enhanced difference in the decomposition temperatures (over that in N_2) across the RE series. This is usually the case for the first step decomposition temperatures as can be seen in Fig. 5. $T_{0.5}$ values for the final step do also show this, although the heavier elements Tb through Yb, and the lighter elements Ce and Eu exhibit lesser sensitivities to CO_2 as will be further discussed later. Overall these $T_{0.5}$ values in CO_2 appear to suggest a more regular trend of decreasing decomposition temperatures (hence basicities) as one moved from left to right across the periodic table (Ce is certainly out of place). It may be fortuitous but, as depicted in Fig. 7, this trend is also similar to the increase of the electrostatic potential experienced by an outermost electron in an M^{3+} ion, expressed as z^*/r ; where z^* is the effective nuclear charge calculated using Slater's rules [23] and r is the ionic radius [24] for M^{3+} . According to this consideration the higher the z^*/r value the lower the expected basicity. Only lanthanum falls out of the continuity shown in Fig. 7 and is expected to be comparable in basicity to that of Eu or Sm. If the thermal stability of the carbonate is used as a measure of the oxide basicity then lanthanum certainly shows an opposite trend in the data of Head & Holley where La-carbonate appeared as the most stable carbonate.

Ionic radius coupled with the fourth ionization potential may be an alternative parameter for judging the basicity although the fourth ionization

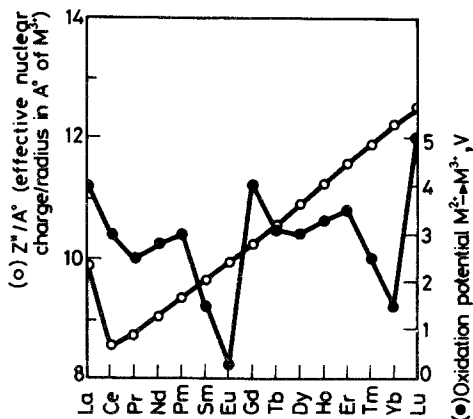


Fig. 7 (○) Electrostatic potential experienced by an outermost electron in an M^{3+} RE-cation (see text) and (●) Oxidation potential [25] for the electrode reaction $M^{2+} \rightarrow M^{3+} + e$ for the lanthanides

potential data is not available for all of these elements. Figure 7 also shows the experimentally determined oxidation potential [25] for the divalent cations $M^{2+} \rightarrow M^{3+} + e$. Very stable f_0 , f_7 and f_{14} electronic configurations in the trivalent cations La, Gd and Lu provide a rationale for their high oxidation potentials, and a low value for Eu or Yb can be understood in this light. Overall this curve demonstrates the importance of the contribution of orbital symmetry to the overall energy of these ions which is rather poorly represented in potential energy calculations based on z^*/r . It is not surprising, therefore, to see the lack in a uniform pattern of the change in thermal stabilities (hence basicity) among this series of carbonates. Rather, in analogy with the oxidation potential curve, lower stabilities for Eu or Yb, and higher stabilities for La, Gd, Er or Lu carbonates may be expected. In general, this trend is reflected in our results shown in Figs 5 & 6. Further variations in oxidation states in such cases as Ce will again influence the sequence in stability or basicity. Thus the predilection of Ce, Pr and Tb to higher oxidation states is expected to suppress basicities. On the other hand augmented basicity should result from the ability of Eu^{3+} , Yb^{3+} or Sm^{3+} to be reduced to the lower 2+ oxidation state [26]. It should be remembered that although the oxidation potential values indicate a good correlation with our thermal stability data the former includes such terms as solvation energy

of the hydrated cations which are, of course, irrelevant to thermal stability considerations, and therefore, must be used only as a qualitative guide. It is of interest to compare also the oxidation potentials (in volts) for the alkaline earth metals ($M \rightarrow M^{2+} + 2e$) which are 1.97, 2.36, 2.87, 2.89 and 2.90 for Be, Mg, Ca, Sr and Ba, respectively. These are in the same sequence as the increasing thermal stabilities of the carbonates although the actual stability difference between any two carbonates is much greater than the difference in the oxidation potentials suggests.

Lack of sensitivity of the carbonate decomposition temperatures of the heavier elements (Dy through Lu) to the presence of CO_2 is notable and is suggestive of the existence of irreversible polymorphic phases in the oxides or the oxycarbonates. This may also indicate that the oxide of these elements assumes a high temperature crystal form/phase which is different to that for the lighter lanthanides. This implies a dependence of basicity on the particular polymorphic phase, and hence the thermal history.

Therefore, in order to frame a basicity series (applicable to reactions at elevated temperatures) for the RE oxides, the $T_{0.5}$ values of the final step in CO_2 (Fig. 6) appears a reasonable yardstick to adopt. This would be equivalent to the temperature maxima in the case of a temperature programmed adsorption - desorption experiment using CO_2 as probe. Thus the series in order decreasing basicities is:

La > Pr ~ Nd > Sm > Gd ~ Eu > Tb ~ Ho ~ Er > Dy ~ Tm ~ Yb ~ Lu > Ce

Note that Head & Holley's data for La, Nd, Tm and Lu have been incorporated in the series. Note also that Eu and Gd have been grouped together because of the latter's low $T_{0.5}$ value in N_2 and the existence of additional decomposition steps at higher temperatures for Eu (Table 3) subsequent to the one shown in Fig. 6. Obviously further work in crystal structure determination of various oxides and oxycarbonates is required before more precise correlation of basicity with the thermal stability can be established.

* * *

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Table 4 Thermoanalytical data of the REC's collected from the TG curves of Head and Holley [14, 15]. Key as in Table 2

Anhydrous carbonate	$T_{0.5}$ under CO_2 (67 kPA)				$T_{0.5}$ under vacuum			Wt loss ratio steps 1:2
	Step 1	Step 2	Step 3	Step 4	Step 1	Step 2	Step 3	
La	501	956			466	583		2:1
Ce	477	547			456	555		2:1
Pr	473	847			442	540		uncertain
Nd	300	481	802	873	476			one step
Sm	498	746	826		440	525		3:2
Eu	495	716			445	580		3:2
Gd	495	717	790		450	545		5:2
Tb	499	676			456			one step
Dy	500	665			460	569		1:1
Ho	509	646			465	580		2:1
Er	526	637			465	585		1:1
Tm	531	610			420	600		1:1
Yb	515	636			500			one step
Lu	580				580			one step

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Zusammenfassung – Die relative Basizität der Seltenerdenoxide (M_2O_3) wurde mittels der durch TG-DTA-Untersuchungen festgestellten Zersetzungstemperaturen der Karbonate folgender Metalle bestimmt: Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er und Yb. Aufgrund eines Vergleiches der hier ermittelten Daten mit denen von Head und Holley wird für die Basizität der Seltenerdenoxide folgende Reihenfolge aufgestellt: La > Pr ~ Nd > Sm > Gd ~ Eu > Tb ~ Ho ~ Er > Dy ~ Tm ~ Yb ~ Lu > Ce. Wie ersichtlich nimmt die Basizität der Seltenerdenoxide mit ansteigender Ordnungszahl nicht progressiv ab.