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Thermal Decomposition of Lanthanide, Yttrium, and Scandium Oxalates and Carbonates

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Data concerning the thermal decomposition of lanthanide, yttrium, and scandium oxalates and carbonates are surveyed. The complexity of the process, the large number of stages involved, and the dependence of the composition of the intermediates in the thermal transformations on the experimental conditions is noted. Certain process characteristics have been discovered and it is concluded that the decomposition process depends on the ionic radius of the metal. The bibliography includes 83 references.

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I. INTRODUCTION

In the review an attempt is made to survey the existing data on the thermal decomposition of lanthanide, yttrium, and scandium oxalates and carbonates. The principal studies in this field have been carried out in the last 2–3 decades.

In the thermal decomposition of hydrated lanthanide oxalates it is possible to distinguish two stages: dehydration and decomposition of anhydrous oxalates. The available literature data for each stage are not unambiguous due to the dependence of the results on the experimental conditions (the rate of heating, the size of the specimen sample, the sensitivity of the apparatus, etc.). From a critical examination of the available data, we have attempted to reach certain conclusions about the compositions of the intermediate hydrates and about the changes in the nature and strength of the bonds in the series of compounds considered.

II. DEHYDRATION OF OXALATES

The dehydration of lanthanide oxalates proceeds with formation of intermediate hydrates. The dehydration process has been investigated by derivatographic methods in various media (air, argon, and CO_2) and *in vacuo* and also by infrared spectrophotometry and diffractometry.

In the first studies[1,2] of the dehydration of lanthanide oxalates at heating rates of 6, 2.5, and 0.33 K min^{-1} it was already observed that the composition and the region of stability of the intermediate hydrates depend on the heating rate of the specimen, the size of the sample, and the sensitivity of the apparatus. Systematic treatment of the result of subsequent studies confirmed this conclusion[3–27]. In this connection studies of the dehydration of all the lanthanide oxalates under the same conditions are of greatest interest for the elucidation of the characteristics of the dehydration process.

The first attempt to subdivide all the lanthanide oxalates into groups based on their ability to form intermediate hydrates of definite composition was made by Wendlandt[4,28]. He assigned to the first group lanthanum, praseodymium, and neodymium oxalates, for which the formation of intermediate hydrates has not been observed: the decahydrates decompose to the anhydrous compounds. For the oxalates of the second group (Sm–Dy) for formation of various hydrates and anhydrous oxalates has been observed. The oxalates of the third group (Y, Sc, Ho–Lu) give rise to stable dihydrates. Cerium oxalate does not belong to any of these groups.

Möbius and Matthes[7,8] divided the hydrated oxalates into three groups on the basis of very careful investigations. The thermogravimetric (TGA) and differential thermographic (DTA) curves for the decomposition of the oxalates of the first group (La, Ce, Pr) do not indicate the formation of lower hydrates. The oxalates of the second group (Sm–Tb) split off water in three stages, forming hexahydrates, 3,5-water oxalates, and anhydrous oxalates. Water is given up by the oxalates of the third group (Y, Er, Lu) in two stages with formation of trihydrates and dihydrates without any sign of the formation of anhydrous oxalates. Neodymium and holmium oxalates constitute transitions between two groups, while dysprosium oxalate does not form part of any of the above groups. The authors carried out their investigations at heating rates of 2, 1.1, 0.7, and 0.48 K min^{-1} and also by the isothermal heating method. In all cases decrease of the heating rate made it possible to discover the intermediates more effectively. For example, decrease of the rate of heating of the oxalate nonahydrate from 2 to 0.6 K min^{-1} showed that a relatively unstable trihydrate is formed in addition to the stable dihydrate.

The dependence of the dehydration process on the specimen sample size at a heating rate of 5 K min^{-1} has been investigated[24] for the yttrium compound. For a 500 mg sample, the curve describing the dehydration of yttrium oxalate has a single maximum, for a 318 mg sample it has three maxima, and for a 13.3 mg sample it has five maxima; the compositions of the intermediates are also correspondingly different.

Thus the temperatures of the formation and the temperature ranges corresponding to the existence of the hydrates cannot be regarded as definite constant quantities.

Data concerning the possibility of obtaining anhydrous oxalates in air are also contradictory[7,11,12,16,18,19]. On the other hand, investigators agree unanimously that *in vacuo* complete dehydration of the oxalate hydrates is attained[13,29–31].

Whereas much attention has been devoted in the literature to the composition of the intermediate hydrates of rare earth oxalates, no conclusions have been reached on the basis of the stepwise elimination of water. For example, it has been

shown clearly[2,4] that the number of dehydration stages increases in the oxalates of the elements ranging from lanthanum to dysprosium. According to these authors, this is because with increase of the atomic number of the element, the strength of the hydrogen and coordinate bonds involving the water molecules in the rare earth oxalate hydrates changes. In other words the activation energies for the elimination of water molecules linked by hydrogen (E_h^a) and coordinate (E_c^a) bonds are approximately the same for hydrated lanthanum oxalate, while $E_h^a < E_c^a$ for dysprosium oxalate.

It is also known[7,8,25,32-35] that the oxalate decahydrates of the elements located at the beginning of the series (La–Nd) lose the entire outer-sphere water and most of the coordinate water in a single stage, while closer to the centre of the series (Sm–Tb) only the outer-sphere water is lost and at the end of the series the outer-sphere and approximately half of the inner-sphere water is lost (in a single stage) (Fig.1).

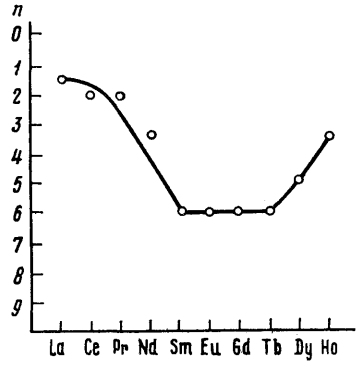


Figure 1. The first stage of the transition $Ln_2(C_2O_4)_3 \cdot 10H_2O \rightarrow Ln_2(C_2O_4)_3 \cdot nH_2O$ on heating. The curve has been plotted on the basis of the data of Bezdenezhnykh et al.[24,32]

It follows from Fig.1 that, on passing from La and Ce to Sm in the series of lanthanide oxalates, the strength of the bond between the lanthanide and the coordinated water increases; on passing from Sm to Tb, the bond strength hardly changes and subsequently weakens. There is not yet a molecular orbital scheme for the σ-bonds of complexes with a central ion having a coordination number of eight or nine. It is known only that the covalent bond between the rare earth ions and ligands is formed mainly as a result of the mixing of the occupied ligand orbitals with the partly filled 4*f* orbitals and the vacant 6*s*, 6*p*, and 5*d* orbitals of the rare earth ions[36]. An admixture of covalent character in an ionic bond should favour the formation of coordination polyhedra with vertices pointing in the directions of the maxima of the hybrid sp^3d^n orbital. This requirement is satisfied in the first place by the 9-coordination polyhedron with D_{3h} symmetry. For polyhedra with a coordination number of 8, the dodecahedron with D_{2d} symmetry is most preferred. However, the ionic contribution is greater than the covalent contribution[37].

It is interesting that the nature of the variation of the Ln-coordinated water bond strength in the rare earth oxalate decahydrates is the same as that of the variation of the stability of the octahedral complexes in the series of rare earths[38]. This justifies the hypothesis that the arrangement of the molecular orbitals (bonding, non-bonding, and the first antibonding) in polyhedra with coordination numbers of 6 and 9 is the same, the difference consisting in the number of lowest bonding orbitals (6 for an octahedron and 9 for a 9-coordination polyhedron), which are localised mainly at the ligands[38,39].

Using this orbital scheme, it is possible to explain the variation of the lanthanide-coordinated water bond strength in the series of lanthanide oxalate decahydrates (Fig.1). The increase in the strength of the Ln–H_2O bond on passing from Pm to Ce, Pr, Nd, and Sm is due to the enhancement of the bonding effect, which is determined by the possible increase of the overlap integrals (decrease of the Ln–H_2O distance) and the increase of the ionisation potential. On passing from Pm to Sm–Gd, the increase of the stability of the compounds slows down (or even ceases) because electrons appear in the antibonding t_{1u}^* orbital[38]. Beyond Tb, the Ln–H_2O bond weakens, since electrons fill the t_{1u}^* orbital.

The coordinated water in Nd–Er oxalates is split off stepwise. Its elimination temperature increases up to Tb–Dy and then falls (Fig.2), which is consistent with the above considerations concerning the nature of the variation of the Ln–H_2O (coordinated) bond strength.

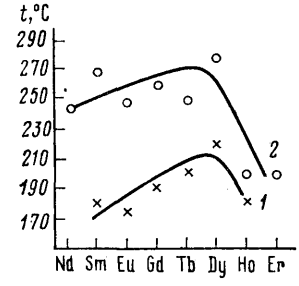


Figure 2. The minima on the DTA curves for the decomposition of the lanthanide oxalates corresponding to the loss of coordinated water: 1) first stage; 2) second stage[28].

The dehydration of terbium, ytterbium, and lutetium oxalate hexahydrates proceeds isotypically in two stages with formation of the relatively unstable trihydrate and the dihydrate, which is stable in the temperature range 200° to 350 °C.[7,8,24] It is therefore difficult to discover how the Ln–H_2O (coordinated) bond strength varies from Tm to Lu. Theoretically it should decrease, since the filling of antibonding orbitals with electrons is characteristic of Tm, Yb, and Lu.[38,39]

III. DECOMPOSITION OF OXALATES AFTER DEHYDRATION

In the study of the decomposition of rare earth, yttrium, and scandium oxalates in air, different workers obtained compounds having the following compositions:

$Ln_2(C_2O_4)_3$ 2, 11, 17, 23, 40 — 42 ; $Ln_2(C_2O_4)_2O$ 29 ;
LnC_2O_4 42 ; $Ln_2O_2(C_2O_4)_2$ 9,18 ; $Ln_2O_2OCOCO_2$ 23 ;
$Ln(CO_3)_2C_2O_4$ 22, 43 ; $Ln(CO_3)_2O$ 29 ; $(LnCO_3)_2O$ 22, 42 ;
$Ln_2(CO_3)_2$ 2, 17, 41, 44 ; $Ln_2O_3 \cdot 2CO_2$ 2, 14, 39, 41
$Ln_2O_3 \cdot CO_2$ 1, 2, 4, 9 — 12, 14,24, 40 — 42 ; $(LnO_2)CO_3$ 14, 15, 18, 22, 23, 29 ;
$2Ln_2O_3 \cdot CO_2$ 2, 17, 18 .

Apart from the products quoted, CO, CO_2, and free carbon are liberated in the thermolytic process. The formation of carbon was noted for lanthanum[5,9,14,15,42], cerium[14], praseodymium[9,45], neodymium[2,9,45,46], samarium, gadolinium[45], terbium[24], dysprosium, erbium[45], and yttrium[2,24] oxalates. Carbon was not found in the decomposition of cerium, scandium[2], erbium, thulium, ytterbium, and lutetium[24] oxalates.

The most stable intermediate proved to be the basic carbonate $Ln_2O_3.CO_2$. It has been established in recent years by X-ray diffraction[45,57] that the composition of this compound is $Ln_2O_2.CO_3$ and that it should be most correctly referred to as the dioxomonocarbonate. In the thermolysis of thulium, ytterbium, and lutetium oxalates, $Ln_2O_2.xCO_3$ ($x < 1$), which is a mixture of the dioxomonocarbonate and the oxide Ln_2O_3, was found as an intermediate[47].

The presence of three polymorphic forms of the dioxomonocarbonates $Ln_2O_2.CO_3$, namely (I), (Ia), and (II), has been demonstrated[45] on the basis of high-temperature X-ray diffraction and density data, TGA curves, and infrared spectra. They were obtained in the decomposition of the following oxalates:

La	Pr	Nd	Sm	Eu	Gd	Structure
(I)	(I)	(I)	(I)	(I)	(I)	tetragonal
	(Ia)	(Ia)				monoclinic
(II)	(II)	(II)	(II)		(II)	hexagonal

These are layer type structures made up of planar $(Ln_2O_2)_n^{+}$ polymers and CO_3^{2+} groups. Form (I) has square layers, as in LnOCl and related compounds, while form (II) is characterised by hexagonal $(Ln_2O_2)_n^{2+}$ layers, as in the A-forms of sesquioxides.

In all cases form (I) is formed in the first place from $Ln_2(CO_3)_3$. The transformation of form (I) into form (II) is observed above 400 °C without weight loss. There is no definite evidence for the formation of form (II) for heavy lanthanides. It is interesting that an analogous behaviour has been observed for the oxides of light lanthanides; the conversion of the C form (cubic) into the A form (hexagonal) requires an increase of temperature, while for the heavy lanthanides only the C form has been discovered. Since the carbonate of form (II) can be regarded as layers of the A form of Ln_2O_3 separated by C–O layers, the tendency towards the transition form (I) (tetragonal) → form (II) (hexagonal) as a function of temperature and the probable absence of form (II) for the heavy lanthanides are apparently caused directly by the known tendency towards the existence of polymorphic regions in Ln_2O_3.

By analogy with the irreversible transformation of the C form of the oxide into the A form, the transformation of form (I) into form (II) is not reversible. Nevertheless the rate of this transformation is evidently greatly influenced by the presence of carbon and (or) the particle size. The data presented by the authors[11,18,20,26,47,62,63] suggest that form (I) is characteristic of all the lanthanides: the corresponding compounds of the heavy lanthanides decompose at temperatures only slightly above the temperatures at which they are obtained from $Ln_2(CO_3)_3$.[45]

On the basis of their own studies, the authors[47] explained the available TGA curves in the literature for the decomposition of lanthanide oxalates and carbonates. Depending on which lanthanide is investigated, three types of generalised curves are obtained. For La and Pr at a heating rate of 0.6 K h^{-1}, there is a phase change to $Ln_2O_2.CO_3$ (II). The latter is formed before the dissociation temperature is attained. For Nd and Sm–Gd at a heating rate of 0.6 K h^{-1}, the phase transition from $Ln_2O_2.CO_3$ (I) or (Ia) to $Ln_2O_2.CO_3$ (II) does not reach completion, because the thermal decomposition of phases (I) and (Ia) to Ln_2O_3 begins. The length of the plateau on the TGA curves depends on the heating rate.

It is known[47] that the $Ln_2O_2.CO_3$ (II) phase is not encountered when the ionic radius of Ln^{3+} is smaller than for Gd^{3+}. The formation of the $Ln_2O_2.CO_3$ (I) or (Ia) phase is characteristic on heating Tb–Lu oxalates or carbonates. The $Tb_2O_2.CO_3$ (I) and (Ia) forms have a high thermal stability, while $Yb_2O_2.CO_3$ (I) and (Ia) begin to decompose immediately after formation.

The decomposition temperatures of $Ln_2O_2.CO_3$ have been published[45,48–50]. The Dy, Ho, Er, and Y dioxomonocarbonates have been obtained by a hydrothermal method and their X-ray diffraction patterns (the values of *h*, *k*, *l*, *d*, *I*) have been published[51].

The thermolysis has been studied by the DTA method[10,12,14,15,22,42,52,53], which is more sensitive to phase transitions than the TGA method. The decomposition of the hydrated La,[10,14,15,42,52] Nd, Sm–Gd,[52] Tb–Lu[24,54], Y,[10,24,52,54] and Sc [10] oxalates in the range 300–600 °C is accompanied by complex exothermic processes, which are a consequence of the decomposition of the oxalates and demonstrate the simultaneous occurrence of two reactions: the endothermic decomposition of the oxalate or carbonates of various compositions and an exothermic reaction involving the interaction of CO and O_2 with formation of CO_2 and the oxidation of free carbon[14,42,43,55]. This has been confirmed, firstly, by the fact that the total amount of the evolved gases is greater than the weight loss by the sample[10] and, secondly, by the observation that the decomposition of, for example, yttrium oxalate in a helium atmosphere[10] or of lanthanum oxalate in an argon atmosphere[23] is accompanied by endothermic effects. Above 600–700 °C, exothermic processes associated with the crystallisation of cryptocrystalline oxides[52] and the conversion of the metastable C form of the oxide into the B form[53] are observed for all the oxalates.

Since the decomposition temperatures of the anhydrous oxalates increase in the La–Lu series[28], an impression has been created that the Ln–C_2O_4 bond strength increases in this series. However, one should bear in mind here that the increase of the Ln–C_2O_4 bond strength entails a decrease of the thermal stability of the oxygen-containing salts[57,58]. Hence it follows that the Ln–C_2O_4 bond strength should be weakened in the La–Lu series, which is consistent with the weakening of the basic properties in the same series. This weakening occurs monotonically from La to Tb, but subsequently, from Tb to Lu, the Ln–C_2O_4 bond strength hardly changes. Thus the nature of the variation of the Ln–C_2O_4 bond strength in the series of lanthanide oxalates differs from that for the Ln–H_2O bond strength. To a first approximation, this can be explained by the fact that, in contrast to the water molecules, the C_2O_4 groups can be linked to the central ion via not only σ-bonds but also via π-bonds.[59]

The final products of the decomposition of the oxalates are the oxides CeO_2, Pr_6O_{11}, Ln_2O_3 (Ln = La, Nd, Sm, Eu, Gd, Dy, or Ho), and Tb_6O_{11} (converted into $TbO_{1.714}$ with an endothermic effect at 865 °C).

The thermal dissociation reactions of the lanthanide oxalates *in vacuo* and in inert media proceed differently. The vacuum thermal decomposition of the La–Eu oxalates[44,60] takes place with formation of the intermediates $Ln_2(C_2O_4)(CO_3)_2$, $Ln_2(CO_3)_3$, $Ln_2O_{0.6}(CO_3)_{2.4}$, and $Ln_2O(CO_3)_2$, the evolution of CO and CO_2, and the formation of free carbon. All the oxides formed are black due to the presence of free carbon. Studies have been made of the oxalates of Ce,[9,13] La,[61] Nd–Sm, Gd–Dy, and Er,[20] Eu,[22,23,29,30] Yb,[27,29,43] Y,[26,62,63] and Sc.[3]

An attempt has been made[62] at a qualitative explanation of the formation of intermediates in the decomposition of *s*, *p*, and *d* metals as a result of the combination of various radicals formed on dissociation of $-M-C_2O_4-M-$ linkages, where M is a metal. Free carbon is obtained as a result of the disproportionation of CO or the decomposition of the carbon–oxygen polymers C_4O_3, C_8O_3, and $C_{12}O_9$, which have been described in the literature. These polymers can be obtained as a consequence of the combination of carbon–oxygen radicals formed on dissociation of the bonds in the C_2O_4 groups.

An attempt may be made to reach a series of conclusions from the data presented above.

1. Since the basic properties of the lanthanide ions weaken with increasing atomic number (with decreasing ionic radius), the strength of the bond formed between Ln^{3+} and the oxalato- or carbonato-group should decrease. This has been confirmed by the majority of investigations[2,11,31,45,48,61], with the exception of that of Palei et al.[17]

2. The weakening of the $Ln-CO_3$ bond with increasing atomic number of the lanthanide explains the preferential formation of the normal carbonates and compounds of the type $Ln_2O(CO_3)_2$ by the light lanthanides[2,14,15,41,60]. The carbonates of the heavy lanthanides are unstable and rapidly decompose to the oxides[31,45].

3. The mechanism of the thermal decomposition of light lanthanide oxalates should have the following general form:

$$\underset{\text{(III)}}{Ln_2(C_2O_4)_3} \rightarrow \underset{\text{(IV)}}{Ln_2(C_2O_4)_x(CO_3)_y} \rightarrow \underset{\text{(V)}}{Ln_2(CO_3)_3} \rightarrow \underset{\text{(VI)}}{Ln_2O(CO_3)_2} \rightarrow \underset{\text{(VII)}}{Ln_2O_2CO_3} \rightarrow \underset{\text{(VIII)}}{Ln_2O_3}$$

It is difficult to establish from available literature data how the values of x and y vary throughout the lanthanide series. According to general considerations, an increase of the atomic number of the lanthanide should entail an increase of x and a decrease of y. This has been confirmed by the finding that the degree of disproportionation of CO diminishes from Ce to Lu. However, the opposite conclusion can also be reached, because the relative amount of CO increases in the same direction.

As a consequence of the proximity of the decomposition temperatures of compounds (III)–(VI), it has not been possible to detect all five stages in the case of the heavy lanthanides *in vacuo*, in air, and in CO_2 and N_2 atmospheres. Here the mechanism is usually restricted to compounds (III), (VII), and (VIII). This is evidently also true of scandium and ytterbium oxalates.

4. The formation of $Ln_2O_2CO_3$ has been demonstrated by hydrothermal synthesis, X-ray diffraction analysis, infrared spectroscopy, and the discovery of three polymorphic forms. In order to confirm the variation of the above compounds in the series of lanthanides, additional studies are evidently necessary, because contradictory data have been published[47,48,51].

5. The decomposition of the lanthanide, yttrium, and scandium oxalates *in vacuo* and sometimes in air results in the formation of free carbon due to the disproportionation of CO or the decomposition of carbon–oxygen polymers[2,5,9,14,15,24,42,45,46]. The latter are obtained via the combination of the oxygen-carbon radicals arising after the dissociation of the bonds with the C_2O_4 group. According to various sources, carbon burns in air at a temperature in the range 460–680 °C.

6. In an inert atmosphere the thermal decomposition of the dehydrated oxalate is accompanied by endothermic effects. In air the exothermic effects associated with the oxidation of CO and C are superimposed on them.

7. Recently the majority of investigators have used the following terminology for the intermediates in the decomposition of the oxalates and carbonates; in $Ln_2O(CO_3)_2$—monoxodicarbonate; $Ln_2O_2.CO_3$ dioxomonocarbonate. The composition $Ln_2O_2.CO_3$ (and not $Ln_2O_3.CO_2$) has been confirmed by X-ray diffraction studies[45].

IV. THERMAL DECOMPOSITION OF CARBONATES

Data on the thermal decomposition of lanthanide carbonates represent additional information about the compositions and properties of lanthanide oxide carbonates. The decomposition of lanthanide and yttrium carbonates has been investigated[1,2,18,40,49,57,64–82].

The thermal stability of lanthanide carbonates increases with increasing atomic number of the metal[71]. Thus lanthanum carbonate begins to decompose at 495 °C, while erbium carbonate begins to decompose at 770 °C. In contrast to the oxalates, the decomposition of the carbonates of the light lanthanides[18] takes place only with formation of $Ln_2O_2.CO_3$; compounds of the type $2Ln_2O_3.CO_2$ are not formed. The decomposition of the carbonates of heavy lanthanides and yttrium[73] is accompanied by the formation of $Ln_2O_3.2CO_2$ and $Ln_2O_2.CO_3$. At temperatures of approximately 900 °C and above all the carbonates are converted into the oxides[75].

On the basis of literature data and the results of their own investigations, Kokhanovskii and Pavlyuchenko[82] concluded that the decomposition of lanthanide carbonates proceeds in accordance with the mechanism $Ln_2(CO_3)_3 \rightarrow Ln_2O_2.CO_3 \rightarrow Ln_2O_3$ and is accompanied by the formation of only one intermediate. At the same time, according to their data[82], it is possible to obtain the monoxodicarbonates $Ln_2O(CO_3)_2$. The latter was established from the slight inflections in the TGA and DTA curves. The existence of $Ln_2O(CO_3)_2$ could not be confirmed either by X-ray diffraction or by infrared spectroscopy. The thermal decomposition of dioxomonocarbonates should be an endothermic process. However, bearing in mind the crystallisation of both dioxomonocarbonates and oxides, it is to be expected that the endothermic effects will be significantly distorted by the superposition of the exothermic effects. In this respect the decomposition of yttrium and gadolinium carbonates is extremely characteristic, their thermograms showing only exothermic effects in the region of the decomposition of the dioxomonocarbonates[82].

The data presented on the thermal decomposition of lanthanide carbonates confirm the conclusions reached in the previous Section concerning the thermal stability and composition of and the sign of the thermal effect associated with the intermediates formed on heating anhydrous lanthanide oxalates (carbonates, dioxomonocarbonates). The individuality of $Ln_2O(CO_3)_2$ has not so far been confirmed experimentally.

V. KINETICS OF THE DEHYDRATION AND DECOMPOSITION OF LANTHANIDE OXALATES

There are literature data on the activation energies for the thermal decomposition of lanthanum[9,12,44,83], cerium[9,22], praseodymium[9], neodymium[9], and yttrium[22] oxalates. The enthalpies of the reaction $Ln_2O_3.CO_2 \rightarrow Ln_2O_3 + CO_2$ (where Ln = La, Nd, Sm, Gd, Dy, or Lu) have been calculated from DTA curves[65].

Evidently the kinetics of the dehydration of lanthanide oxalates and of the decomposition of the intermediates formed on heating the oxalates and carbonates have been very little investigated. The number of such studies is small and none

has dealt with the compounds of all the lanthanides. In the main there are data on the oxalates of the first half of the lanthanide group. However, despite the fact that the kinetic data are widely scattered, they permit certain conclusions: (1) the water in the hydrated oxalates is retained less strongly than the oxalato-group. In the range from lanthanum to neodymium the strength of the bond between the water molecules and the lanthanide ion increases[9]. (2) The strength of the bond formed by the carbonato-group in lanthanide dioxomonocarbonates diminishes in the sequence from lanthanum to lutetium[65].

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