Lanthanide oxides: thermochemical approach to hydration

R. ALVERO, A. BERNAL, I. CARRIZOSA, J. A. ODRIOZOLA, J. M. TRILLO
Department of Inorganic Chemistry, Faculty of Pharmacy of Seville, PO Box 874, Seville, Spain

The behaviour toward hydration of a series of Ln_2O_3 has been studied as a function of water pressure and temperature by means of temperature programmed decomposition measurements. Thermochemical calculations have pointed out the structural change associated in going from ytterbium to lutetium in $Ln(OH)_3$ to be responsible for the apparent anomalous behaviour of Lu_2O_3. On this basis generalizations about the expected behaviour along the 4f series have been considered taking into account the simple ionic model for solid lanthanide compounds.

1. Introduction

Early on it was thought that differences on the chemistry of the lanthanides elements only depends on their ionic radii. Along with this idea went the conviction that, within the lanthanide series, any change in properties did not greatly deviate from a smooth variation with atomic number. Recently attention has been paid to bring out chemical reactions of the lanthanide elements in which the obtained sequence along the series does not conform to the traditional belief.

Johnson [1] has established that: "the lanthanide elements behave similarly in reactions in which the 4f electrons are conserved, and very differently in which the number of 4f electrons changes". This principle embraces reactions of the lanthanides of current interest, among these, the preparation of new reduced halides and the high temperature chemistry of the 4f elements are worth of mention.

According to Johnson, when a process involves no changes in the number of f electrons, irregularities in the change in electronic repulsion are small, and the energy variation across the series is relatively smooth, so, complexing reactions are good examples of the traditional belief about lanthanide chemistry. The problem of lanthanide separation involving almost exclusively the chemistry of the tripositive state in solution lend support to systematics like the proposed by Sinha [2], "inclined W theory", based on the orbital moment, L, of isolated cations. Such systematics have been applied recently to catalytic reactions, the activation energies for hydrogenation reactions over Ln_2O_3 as catalysts has been claimed to follow an inclined W along the 4f series [3], or to the O(1s) binding energies for the rare earth sesquioxides [2].

Within the group of reactions involving no changes in the number of 4f electrons is the following:

$$M_2O_{3(c)} + 3H_2O_{(g)} = 2M(OH)_{3(c)} \qquad (1)$$
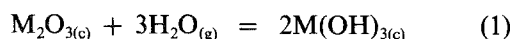
It is clear that the use of rare earth oxides as ceramic materials or as catalysts greatly depends on their capability for undergoing hydration processes. It has been previously reported that Ln_2O_3 undergoes bulk hydration even in the case of the heavier elements [4] depending the hydration extent on the preparation method of the sesquioxide [5, 6]. However, the results obtained for the Lu_2O_3 hydration do not conform with the smooth variation that might be expected according with the absence of changes in the number of 4f electrons along the hydration reaction [7]. This work is an attempt to provide an explanation on the basis of the thermodynamics of the results obtained. In addition, some insights into the implications of the condensed rare earth compounds are considered.

2. Evaluation of the thermodynamic parameters for the hydration reaction

Since thermodynamic data are scarce for $Ln(OH)_3$ an attempt to evaluate such data was performed. The Born–Haber enthalpy cycle for $Ln(OH)_3$ formation is shown in Fig. 1. The sublimation and ionization energy terms were taken from Morss [8]. The common terms are $3\Delta H_f^0(OH_g) - 4RT = 131.1\,\text{kJ mol}^{-1}$. The lattice energy U, Table I, was calculated for each trihydroxide from the equation:

$$U = -69454\,A(n-1)/Rn \qquad \text{kJ mol}^{-1} \quad (2)$$

where A is the Madelung constant, R is the average nearest-neighbour Ln–OH distance and n is the exponent in the repulsive term, $(1/r)^n$, estimated from Pauling's rules [9], in agreement with Morss the repulsive parameter, n, was taken to be equal to nine [8]. Mullica *et al.* [10, 11] have determined by X-ray diffraction the Ln–OH distance in single crystals, an average of such distances was used to determine the lattice energies of the trihydroxides, taking into account the more stable polymorph in our experimental conditions. These values are also shown in Table I. The Madelung constant has been estimated from the values of lattice energies, calculated from thermodynamic cycles, and M–OH of isomorphous hydroxides, cubic $Sc(OH)_3$ and hexagonal $Y(OH)_3$ [12, 13], the obtained figures being shown in Table II.

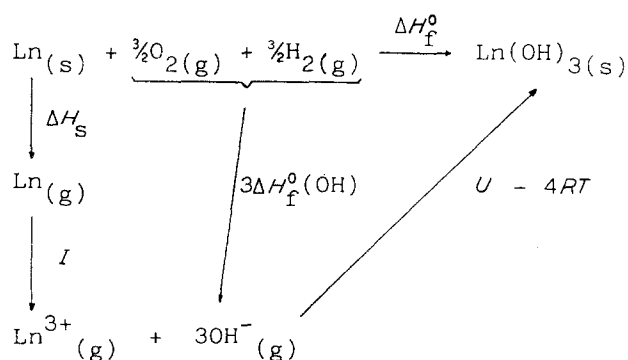*Figure 1* The Born–Haber enthalpy cycle for Ln(OH)₃ formation. I = ionization energy.

From the calculated enthalpies of formation for the trihydroxides, Table I, and the reported ones for cubic sesquioxides [8], an estimation of the enthalpy for the dehydration of the trihydroxides has been carried out, Table III.

It is worth mentioning the break of the sequence for the dehydration enthalpies of the sesquioxides in going from ytterbium to lutetium. The lanthanide trihydroxides show, except in the lutetium case, an hexagonal structure with coordination nine for the cation. The Lu(OH)₃ structure, on the contrary, is isomorphous with the Sc(OH)₃ which present a co-ordination of six for the cation belonging to the cubic system [10, 11]. The structural change along the series is reflected in the M–OH distance, according to Pauling's rules [9] the ionic radius diminishes with the coordination number, influencing the Madelung potential of the lattice that affects the enthalpy of formation of the trihydroxide causing the apparent anomalous behaviour shown in Tables IV and V.

3. Results and discussion

The hydration of the samples was performed in a conventional vacuum system. The vacuum cell was designed in such a way that it could also be used as a temperature programmed decomposition (TPD) reactor. Before the hydration, the Ln₂O₃ samples were activated at temperatures ranging from 823 to 1173 K in order to obtain a clean surface [14]. After the hydration the samples were evacuated at the reaction temperature for half an hour, except when hydrated at

TABLE I Lattice energies, M–OH distances and enthalpy of formation for lanthanide trihydroxides

Element	$-\Delta H_f^0$ (kJ mol^{-1})	$-U$ (kJ mol^{-1})	d (Ln–OH)* (pm)
La	1442	4896	257.6
Pr	1431	4983	253.1
Nd	1436	5021	251.2
Sm	1428	5078	248.4
Eu	1333	5104	247.1
Gd	1410	5121	246.3
Tb	1415	5150	244.9
Dy	1406	5176	243.7
Ho	1412	5201	242.5
Er	1411	5223	241.5
Tm	1391	5240	240.7
Yb	1359	5275	239.1
Lu	1427	5330	224.3

*Data from [11, 12].

TABLE II Estimated Madelung constants for Ln(OH)₃

Structure	A
Hexagonal	20.43
Cubic	19.36

room temperature in which they were evacuated at 330 K in order to avoid the weakly adsorbed water [4]. Hydration was carried out at water pressures ranging from 0 to 3 kPa and temperatures between 298 and 475 K.

Fig. 2 shows the characteristic TPD diagrams for hydrated Ho₂O₃ samples activated at 823 K. The dehydration profiles corresponding to Ln₂O₃ (Ln = Sm, Ho, Yb, Lu) whose hydration has been extensively studied [4–6, 15] are similar in shape. A rather broad peak which has a maximum rate of decomposition at temperatures depending on the nature of the lanthanide cation followed by another broad band at higher temperatures except for samarium in which the later precede the major one is always observed. The temperatures at which the hydrated phase decomposes from the TPD maximum is shown in Table IV. Since the polarizing power of the 4f cation increases in going from samarium to lutetium is worthy of mention, the decomposition temperature of the hydrated phase of the lutetium sesquioxide which according to Stern [16] should be lower than the corresponding to ytterbium.

Assuming the enthalpy (ΔH_r) and the entropy (ΔS_r) of the dehydration reaction do not modify appreciably as a function of the temperature, specially taking into consideration the width of the range considered (300 to 600 K), the reaction will begin when $\Delta G = 0$ and $T = \Delta H_r^0/k\Delta S_r^0$, where k is a constant which is determined by the minimum pressure detectable in our experimental device. Simplifying the evaluation of such a temperature the constancy of ΔS_r^0 along the series has been supposed. The decomposition temperature thus calculated is proportional to the reaction enthalpy estimated from thermochemical cycles. Although the decomposition temperature of the hydrated phase, measured from a TPD run, is not a thermodynamic magnitude, in the case of endothermic reactions the temperature at which the TPD peak reaches a maximum is frequently near to that at which the thermodynamic conditions work. Fig. 3 shows the

TABLE III Enthalpies for the process: $2Ln(OH)_{3(c)} \rightarrow Ln_2O_{3(c)} + 3H_2O_{(g)}$, (kJ mol^{-1}).

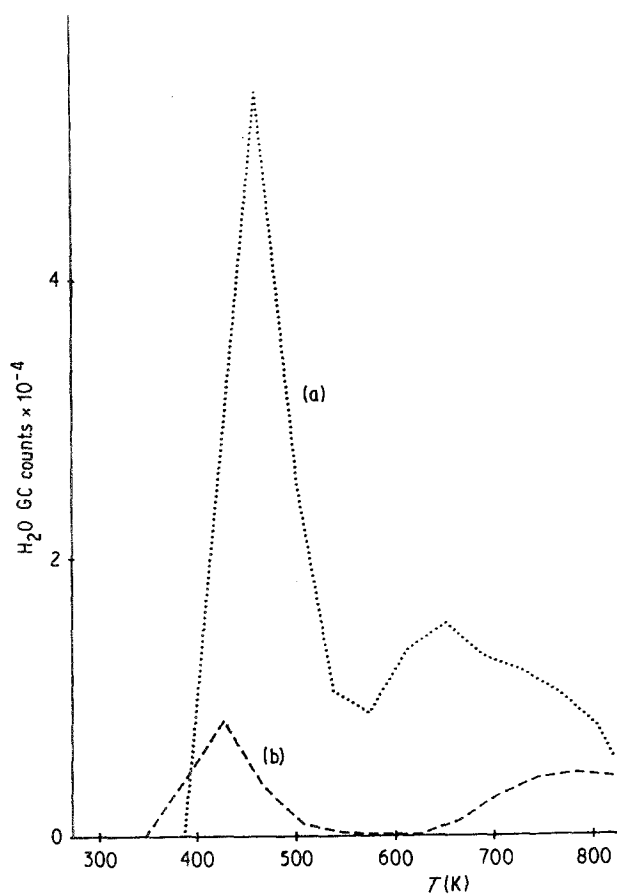| Ln^{3+}	ΔH_r^0
La	360
Pr	309
Nd	335
Sm	303
Eu	278
Gd	268
Tb	240
Dy	224
Ho	218
Er	199
Tm	168
Yb	178
Lu	251

Figure 2 TPD diagrams of Ho_2O_3 previously activated at 823 K and then hydrated at RT for 22 h: (a) 2.0 kPa; (b) 2.5 × 10^{-1} kPa.

relationship found between the decomposition temperature of the hydrated phase, from the TPD run, and the estimated dehydration enthalpies. The apparent contradiction between the observed decomposition temperature for the hydrated phase of lutetium sesquioxide and the polarizing power of the Lu(III) cation is explained on the basis of the above mentioned structural change which allows a variation in the Madelung potential of $Lu(OH)_3$. In such a way, the behaviour of Lu_2O_3 towards the hydration reaction appears more favoured than it could be expected assuming the simplistic terms based on the smooth variation of the ionic radius of isolated cations.

Table V shows the minimum water pressure at

TABLE IV Decomposition temperatures for Ln_2O_3 hydrated phases

Element	$T(K)$
Sm	600
Ho	470
Yb	440
Lu	500

TABLE V Minimum water pressure at which Ln_2O_3 hydration is attainable at room temperature

Element	P (kPa)
Sm	7×10^{-2}
Ho	1.1
Yb	1.1
Lu	7×10^{-2}

TABLE VI Free energies for the dehydration process, and calculated water pressures at which the Ln_2O_3 hydration is not favoured at standard conditions

Element	ΔG_r^0	$\Delta G_{2;350}$	P_{H_2O}
Sm	145	83	2.7×10^{-7}
Ho	60	-2	2.7×10^{-2}
Yb	20	-42	6.4
Lu	93	31	2.7×10^{-4}

which hydration of the sesquioxides is achieved when hydrated at room temperature. Assuming the traditional belief which relates the facility for the hydration to the basic character of the oxide, the similar behaviour of the lutetium oxide to that of samarium is an amazing result. Similarly the reactivity towards the hydration reaction has been measured as a function of the interaction temperature. With 350 K chosen as the temperature at which to carry out the hydration, two different behaviours can be be noticed; at such a temperature the sesquioxides of holmium and ytterbium do not undergo hydration whereas samarium and lutetium sesquioxides do.

In order to explain the differences in pressure and temperature at which the Ln_2O_3 hydration is favoured an estimation for the free energy of the dehydration is needed. Data for the absolute entropy of 4f trihydroxide are scarce, however the term $-T\Delta S_f^0$ for $M(OH)_3$ (M = Ga, Fe, Sc, Pr, Eu) fits well with a mean value of 481.4 kJ mol^{-1} [17]. Assuming a mean value for such a term, 300 kJ mol^{-1} in the case of $C-Ln_2O_3$ [8] it is possible to take the term $T\Delta S_r^0$ for the dehydration reaction to equal 157.5 kJ mol^{-1}, a deviation of 15 kJ mol^{-1} from this mean value could be easily considered for the whole series. This assumption leads to the free energies for the dehydration reaction reported in Table VI. In addition, the pressure at which the equilibrium for the dehydration is reversed is also shown in
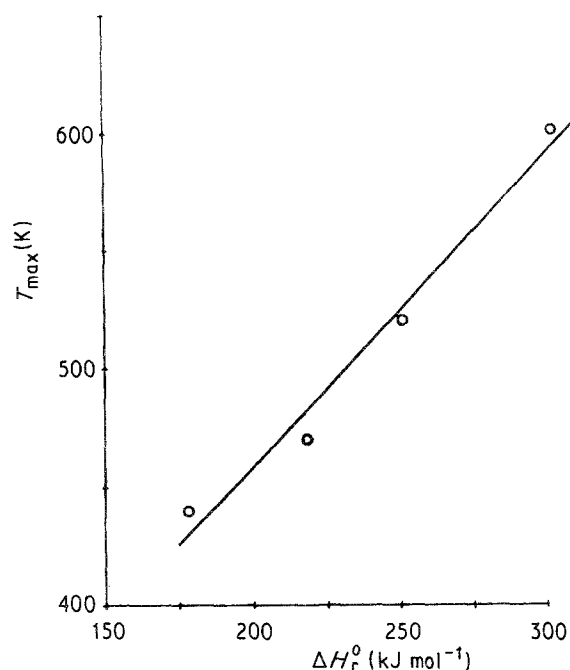

Figure 3 Decomposition temperature of Ln_2O_3 hydrated phases as a function of the calculated enthalpy for the dehydration.
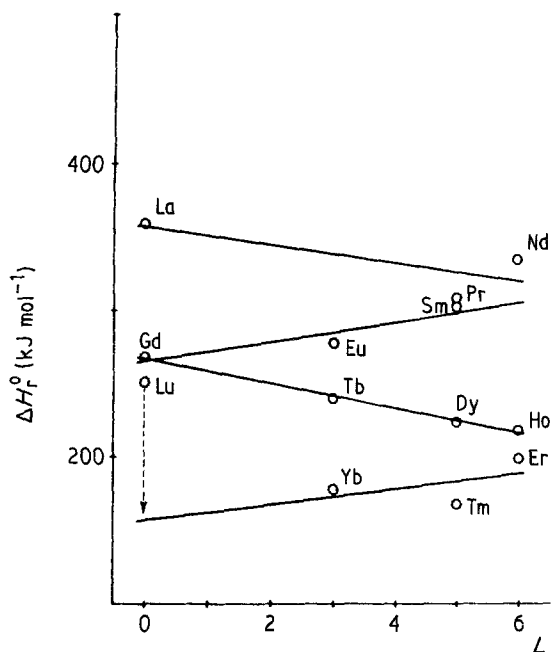
Figure 4 Inclined W plot for the enthalpy of $Ln(OH)_3$ dehydration.

Table VI. The agreement found with the experimental results shown in Table V is better than might be expected on the basis of the oversimplifications performed in the estimation of such values. Moreover, if the previously chosen temperature of reaction, 350 K, and an equilibrium pressure of water, 2.0 kPa, within the usual range employed were considered, the free energy for the dehydration reaction thus calculated would provide a thermodynamic explanation of the behaviour towards the reaction temperature of the studied sesquioxides. The calculated free energies in the specified conditions are also shown in Table VI.

4. Conclusions

The evidence reported in this paper indicates the chemistry of 4f elements is far away from the simplistic treatments based on the diminution of polarizing power. In Fig. 4 is plotted, as an example, the enthalpy of the dehydration reaction as a function of the orbital moment, L, for the lanthanide cation, the so called Sinha's inclined W theory [2]. It is clear that for the isostructural trihydroxides an inclined W representation fits the experimental results although it does not work in the lutetium case.

Taking into consideration the inner character of the 4f shell it is possible to assume the remarkable ionic character of the solid compounds of the lanthanides. In such a way, the coordination number and the structure of the rare earth compounds must obey the radius ratio rules changing along the series. This change invariably leads to a modification of the Madelung potential of the lattice and to an alteration in the thermodynamic magnitudes which govern a chemical process. Then, the affirmation of Johnson [1], "the lanthanide elements behave similarly in reactions in which the 4f electrons are conserved, and very differently in which the number of 4f electrons changes" embraces only reactions in which the structure of the solid compounds along the series remains since some change in the structure of a compound does modify the smooth variation expected.

Acknowledgement

References

1. D. A. JOHNSON, *Advan. Inorg. Chem. Radiochem* **20** (1977) 1.
2. S. P. SINHA, *Struc. Bond.* **30** (1976) 1.
3. S. P. SINHA and F. GOBAL, *Inorg. Chim. Acta* **36** (1979) L415.
4. R. ALVERO, S. BERNAL, J. A. ODRIOZOLA and J. M. TRILLO, *JCS Dalton Trans.* (1984) 87.
5. R. ALVERO, J. A. ODRIOZOLA and J. M. TRILLO, *J. Mater. Sci.* **20** (1985) 1828.
6. R. ALVERO, A. BERNAL, I. CARRIZOSA, A. JUSTO, J. A. ODRIOZOLA and J. M. TRILLO, *J. Less-Common Metals* **112** (1985) 347.
7. R. ALVERO, A. BERNAL, I. CARRIZOSA, J. A. ODRIOZOLA and J. M. TRILLO *ibid.* **110** (1985) 425.
8. L. R. MORSS, *Chem. Rev.* **76** (1976) 827.
9. L. PAULING, "The Nature of the Chemical Bond", 3rd edn. (Cornell University Press, Ithaca, New York, 1960) p. 505.
10. W. O. MILLIGAN, D. F. MULLICA and J. D. OLIVER, *J. Appl. Cryst.* **12** (1979) 411.
11. K. SCHUBERT and A. ZEITZ, *Z. Anorg. Allgem. Chem.* **256** (1948) 226.
12. M. F. C. LADD and W. H. LEE, *Prog. Solid State Chem.* **1** (1964) 37.
13. *Idem, ibid.* **2** (1965) 379.
14. R. ALVERO, S. BERNAL, I. CARRIZOSA, J. A. ODRIOZOLA and J. M. TRILLO, *J. Less-Common Metals* **94** (1983) 139.
15. R. ALVERO, I. CARRIZOSA, J. A. ODRIOZOLA and J. M. TRILLO, *ibid.* **109** (1985) 197.
16. K. H. STERN, *J. Chem. Educ.* **46** (1969) 645.
17. D. D. WAGMAN, W. H. EVANS, V. B. PARKER, R. H. SCHUMM, S. M. BAILEY, I. HALLOW, K. L. CHURNEY and R. L. NUTTALL, "Handbook of Chemistry and Physics", (CRC Press, Boca Raton, Florida, 1983).