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Kinetic study of the coordination compounds $[M(DMA)_3(H_2O)_6](CF_3SO_3)_3$, where $M{=}Ce^{3+}$, Tb^{3+} and Lu^{3+}

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Abstract

The study of the decomposition of coordination compounds by thermogravimetric (TG) and derivative thermogravimetric (DTG) techniques and the determination of kinetic parameters allow us to calculate the reaction order (*n*), activation energy (E_a) and pre-exponential factor (*Z*). The methods employed are those of Coats–Redfern, Zsakó and Sharp. In this work, non isothermal methods were used for reasons of simplicity. © 1998 Elsevier Science S.A.

Keywords: Thermal techniques; Kinetic parameters; Cerium; Terbium; Lutetium

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1. Introduction

When a substance is heated in an inert gas [1] atmosphere an increase of the vibrations of its atoms or ions occurs with modification of crystalline structure, sinterization, melting or sublimation. When the external forces are stronger then the internal ones decomposition may occur giving small particles that become volatile at the decomposition temperature [2].

To follow the progress of the decomposition reaction the concentration is not important, due to the fact that it will remain practically constant.

Using a generic equation to represent the solid state decomposition.

$$aA_{(s)} \xrightarrow{\Delta} bB_{(s)} + cC_{(g)} + \ \ldots$$

The conversion of 'A' into B,C ... is measured through the α parameter, defined according to Eq. (1)

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \tag{1}$$

where m_0, m, m_f and α are the initial mass, the mass that decomposes at a certain temperature or time and the conversion coefficient, respectively. The decomposition speed of 'A' may be expressed as

$$\frac{d\alpha}{dt} = \kappa(1-\alpha)^n \tag{2}$$

where κ represents the specific velocity constant for the reaction under investigation.

Eq. (3), the Arrhenius equation, utilized to calculate the kinetic parameters in isothermal kinetics, gives the pre-exponential factor (*Z*), the activation energy (E_a) and the specific velocity constant (κ):

$$\kappa = Z\,e^{\left(\frac{-E_a}{RT}\right)} \tag{3}$$

For a linear heating, the velocity is given by Eq. (4)

$$\beta = \frac{dT}{dt} \tag{4}$$

Combining Eq. (1)Eq. (2)Eq. (3)Eq. (4) and rearranging in an integral form:

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)} = \frac{Z}{\beta}\int_0^T e^{\frac{-E_a}{RT}}\,dT \tag{5}$$

This form differentiates the various integration methods [3–6] for kinetic calculations utilized in the literature.

The use of the thermal analysis for kinetic studies employing a thermogravimetric balance (TG) is constantly increasing due to recent advances in instrumentation.

In this article, the three kinetic methods described by Coats and Redfern [3], Zsako [4] and Sharp and Wentworth [5] were used to determine the values of E_a, *Z*, and κ

The use of non-isothermal TG curves to calculate the kinetic parameters presents an advantage in relation to the isothermic method, due to the fact that each point in the curve represents an isothermic decomposition and no extra experiments are necessary.

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2. Experimental

The compounds were prepared by reaction of an aqueous suspension of lanthanide basic carbonates, in a small excess, with trifluoromethanesulfonic acid. The solution was filtered and evaporated in a water bath. The products were dried under vacuum, over anhydrous calcium chloride. Two procedures were used: (a) the hydrated trifluoromethanesulfonate was dissolved in a small excess of DMA (*N*,*N*-dimethylacetamide) and the solution left to evaporate under air at room temperature to crystallize; (b) the DMA solution was treated with chloroform to precipitate the compounds. they were dried under vacuum over anhydrous calcium chloride, characterized by CHN microanalytical procedures and complexometric titration of the lanthanides with EDTA, IR spectroscopy, X-ray powder patterns, emission spectra, etc.

The thermogravimetric curves (Fig. 1 Fig. 2) for the cerium, terbium and lutecium trifluoromethanesulfonates in the (III) oxidation state were obtained in a Perkin-Elmer TGA-7 system with a heating rate of 5°C $\min^{-1}$ and 60 $\mathrm{cm}^3\ \min^{-1}$ N_2 flow.

The thermogravimetric results were also treated in order to determine certain variables through mathematical integration methods using non-isothermic data.

The temperature ranges used for the kinetic parameters calculation were 68.62–73.91°C for cerium, 96.01–102.88°C for terbium and 77.47–84.88°C for lutetium.

3. Results and discussion

As already mentioned, the methods used are different in relation to interpretation of Eq. (5). Coats and Redfern utilize the numerical substitution $\mu = E/RT$ and the relation

$$\int_u^\infty e^{-u} u^{-b} \mathrm{d}u \cong u^{1-b}\, e^{-u} \sum_{n=0}^{\infty} \frac{(-1)^n (b)^n}{u^{n+1}} \tag{6}$$

From which we obtain the following equations:

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ZRT^2}{\beta E_\mathrm{a}} \left[1 - \frac{2RT}{E_\mathrm{a}} \right] e^{-E_\mathrm{a}/RT}$$

$$\text{for } n \neq 1 \quad \log \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] \tag{7}$$

$$\text{for } n = 1 \quad \log \left[\frac{-\log(1-\alpha)}{T^2} \right] \tag{8}$$

The plots of Eq. (7) or Eq. (8) (Figs. 3–5) as a function of $1/T$ give the values of the potential energy are the pre-exponential parts. The plots of Figs. 6–8 show the best correlation for the compounds of Ce^{3+}, Tb^{3+} and Lu^{3+}.

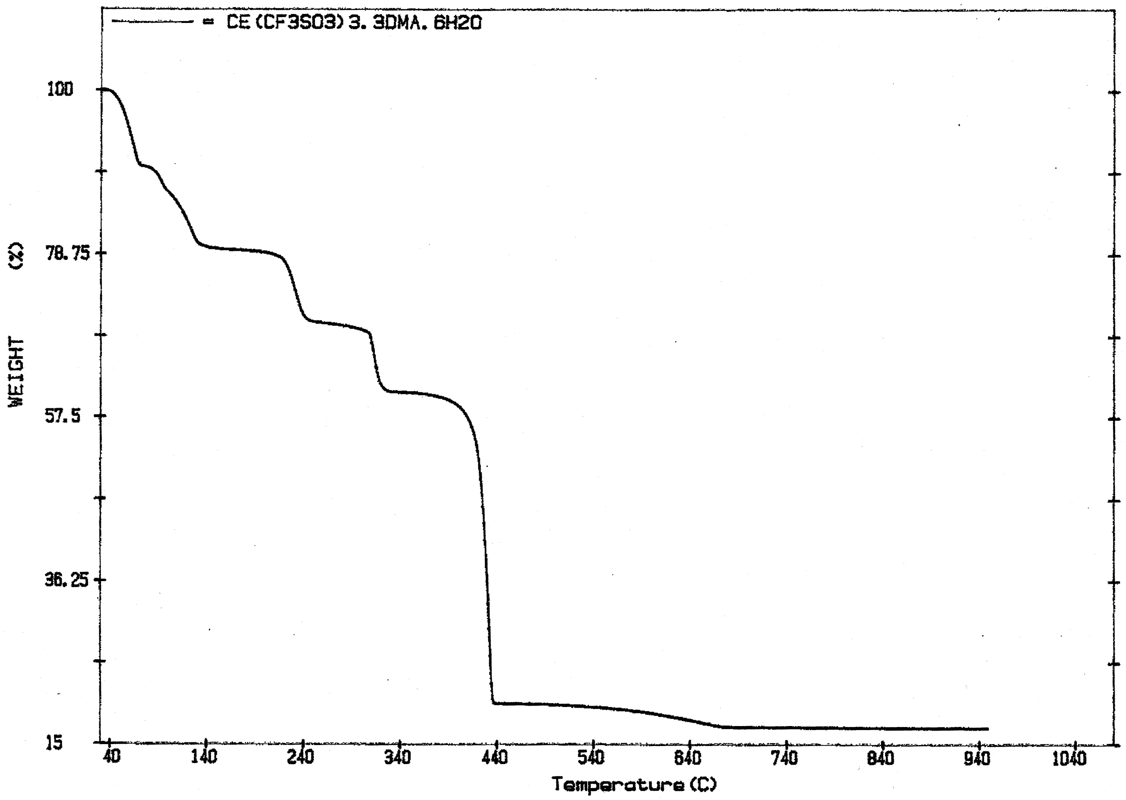

Fig. 1. TG curve for cerium compound.

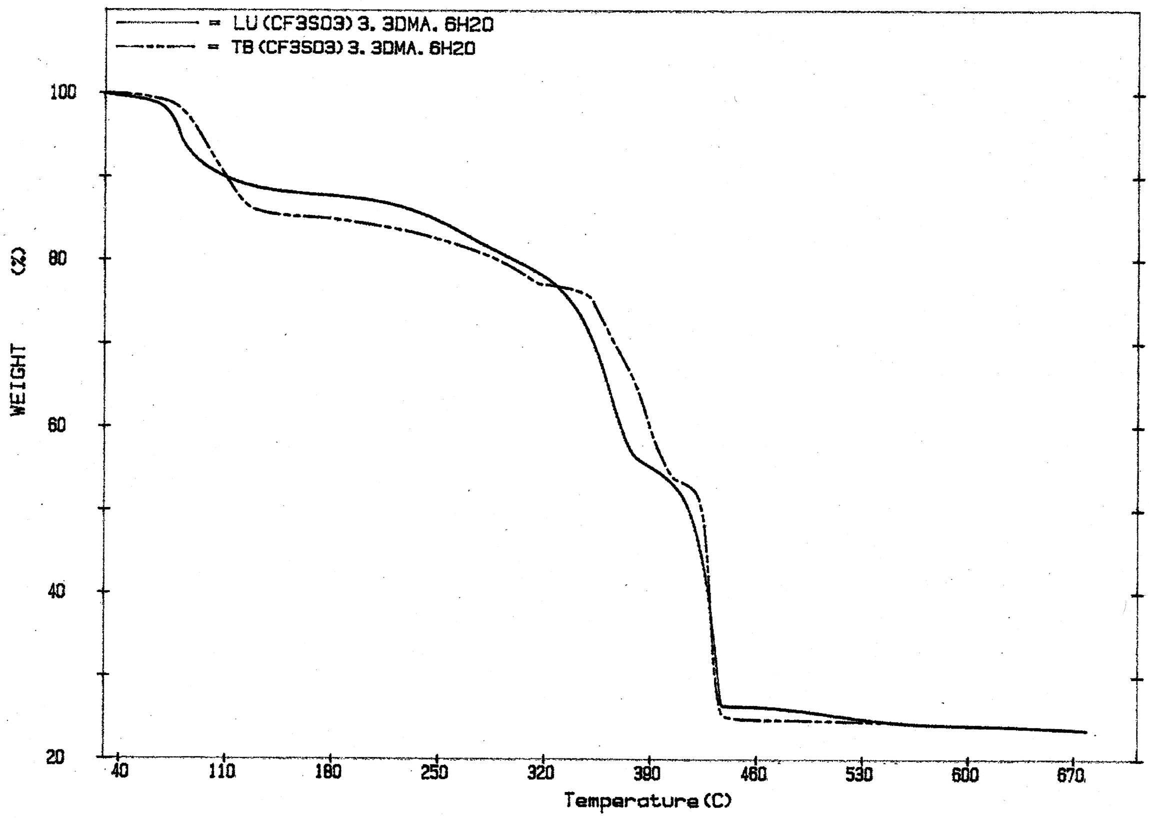

Fig. 2. TG curve for terbium and lutetium compounds.

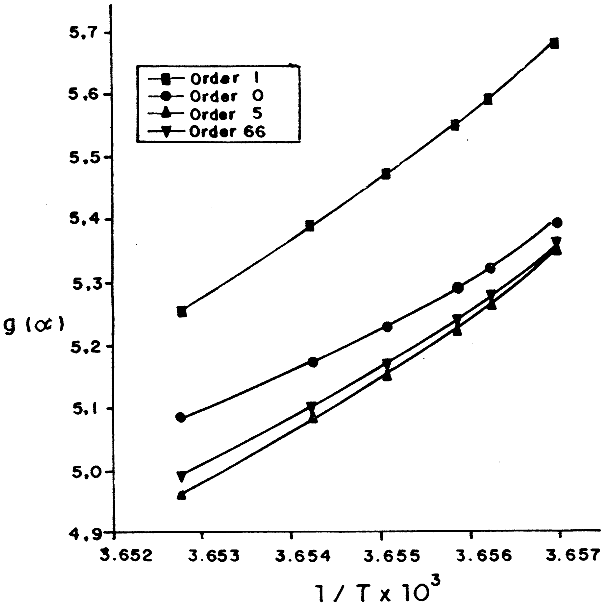

Fig. 3. Plots of results obtained for the Ce^{3+} compound in several orders.

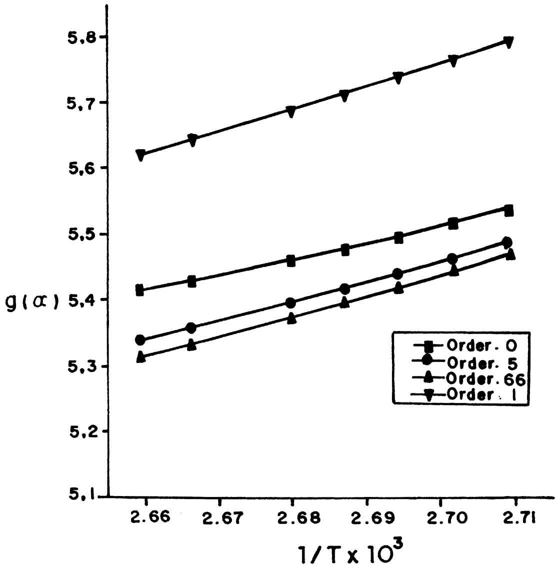

Fig. 4. Plots of results obtained for the Tb^{3+} compound in several orders.

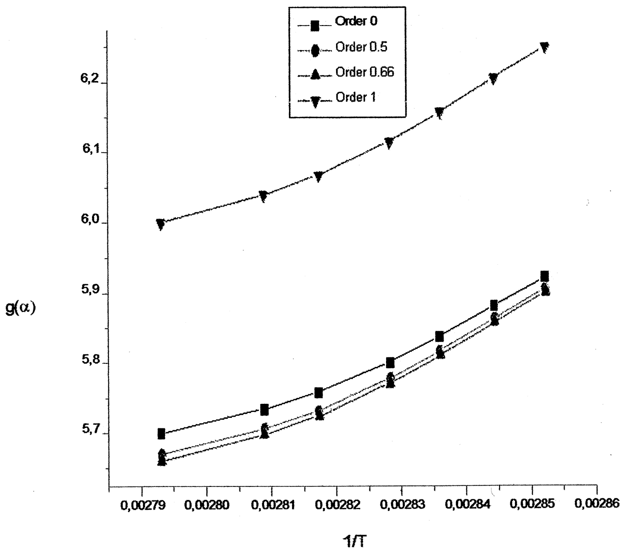

Fig. 5. Plots of results obtained for the Lu^{3+} compound in several orders.

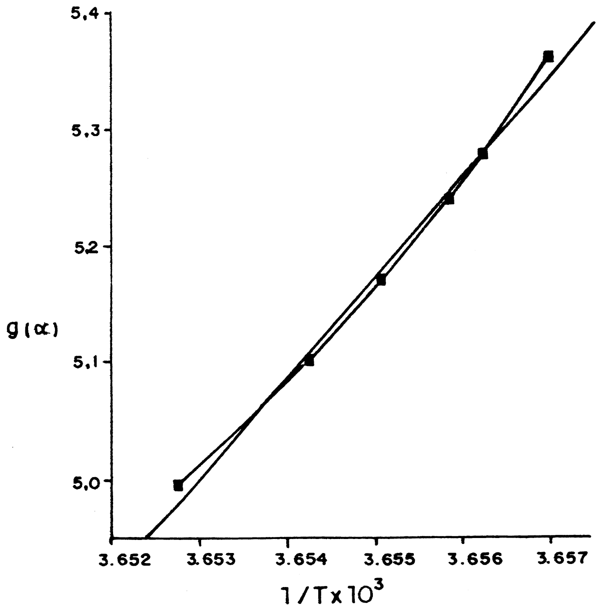

Fig. 6. Plot with the best correlation to the Ce^{3+} compound.

Zsako uses a numerical method in which

$$p(x) = -\int_{\infty}^{x} \frac{e^{-u}}{u^2}\,du = \frac{e^{-x}}{x} - \int_{x}^{\infty} \frac{e^{-u}}{u}\,du, \qquad (9)$$

through the following relation

$$\log \frac{ZE_a}{R\beta} = \log g(\alpha) - \log p(x) = B. \qquad (10)$$

It is possible to observe that the different values obtained in the different methods are coherent (Table 1). The higher activation energy was observed for the cerium compound, probably, as a function of the ionic radius, higher then that

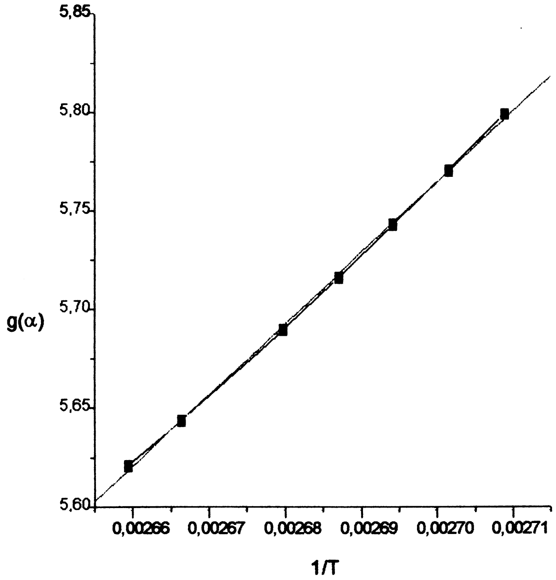

Fig. 7. Plot with the best correlation for the Tb^{3+} compound.

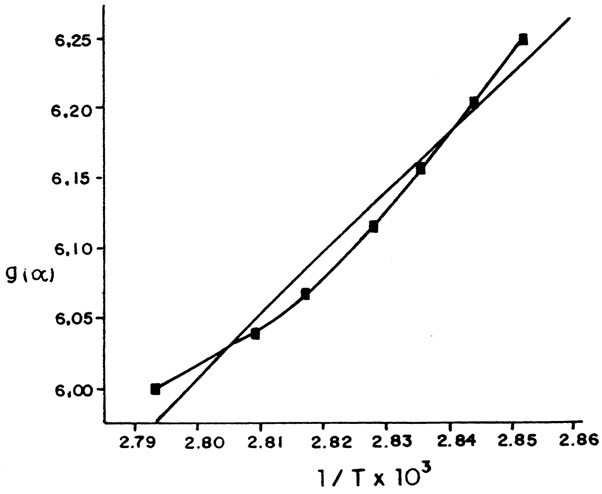

Fig. 8. Plot with the best correlation for the Lu^{3+} compound.

Table 1
Summary of results obtained using the methods [2–5] for the compounds Ce^{3+}, Tb^{3+} and Lu^{3+}

Methods	Compounds	E_a (kJ mol^{-1})	Z (s^{-1})	n
Coats	Ce	99.87	7.38×10^{13}	0
Zsakó	Ce	87.99	7.38×10^{13}	0
Sharp	Ce	93.31	5.46×10^{12}	?
Coats	Tb	57.30	5.82×10^{10}	1
Zsakó	Tb	67.04	9.91×10^{9}	1
Sharp	Tb	48.16	7.87×10^{8}	?
Coats	Lu	77.16	1.70×10^{10}	0
Zsakó	Lu	75.42	1.82×10^{11}	0
Sharp	Lu	90.94	1.84×10^{10}	?

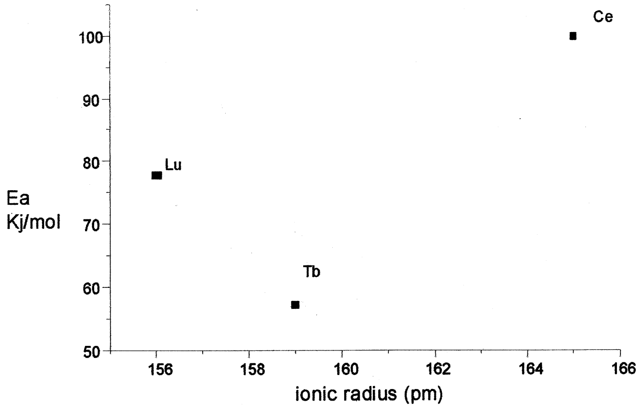

Fig. 9. Plot as a function of lanthanide ionic radius.

of terbium and lutetium. The plots in Fig. 9 show the behavior of the lanthanides as a function of the activation energy and the ionic radius.

4. Conclusions

The Coats–Redfern method was the best for decomposition reaction in the temperature ranges 68.62–73.91, 96.01–102.88 and 77.47–84.88°C for cerium, terbium and lutecium, respectively. These temperature ranges result in the first dehydration phase in an irregular decomposition pattern.

The plot in Fig. 9 indicates that the bonding electrostatic character in the lanthanide complexes is more intense in the cerium complex due to its ionic radius, which increases the complex energy.

Acknowledgements

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