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Dehydration and decomposition kinetics of complexes of some rare earth (La, Nd, Dy and Eu) picrates and 2,2′-dithiobis (pyridine-N-oxide)

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Abstract

The dehydration and decomposition behavior of some rare earth complexes is analyzed under a kinetic point of view. The experimental data were obtained thermogravimetrically and the kinetic parameters are calculated by a non-linear method. The results are similar for La, Nd and Dy but different in the case of Eu. The relative mass loss and its first derivative curves as a function of temperature are compared in order to evaluate the quality of the parameters obtained. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Rare earths; 2,2′-Dithiobis(pyridine-N-oxide); Thermal decomposition; Non-linear method and kinetic parameters; Thermogravimetry

1. Introduction

The rare earth compounds are not well studied in thermal decomposition processes probably due to the fact that the thermogravimetric (TG) curves are frequently quite complex, presenting several peaks and the known parameter obtention methods need curves whose first derivatives are well defined and covering a large temperature range.

2. Experimental

Synthesis and characterization of the compounds are described elsewhere [1] and suggest the formula $Ln(pic)_3 \cdot 1.5dithio \cdot 4H_2O$, where: Ln = La, Nd, Dy and Eu; pic = picrate and dithio = 2,2′-dithiobis (pyridine-N-oxide). Thermogravimetry was performed on a Shimadzu TGA 50 equipment under a heating rate of $0.17\ K\ s^{-1}$ and a nitrogen atmosphere flux of $0.83\ cm^3\ s^{-1}$. All the compounds were heated between 300 and 1170 K.

3. Methodology

The solid decomposition kinetic study is based on the velocity of a chemical reaction. An important contribution is the activated complex theory [2,3] which allows us to include in the Arrhenius equation the high temperature as an exponent when one considers the partition functions of the vibrational, translational and rotational movements of the activated

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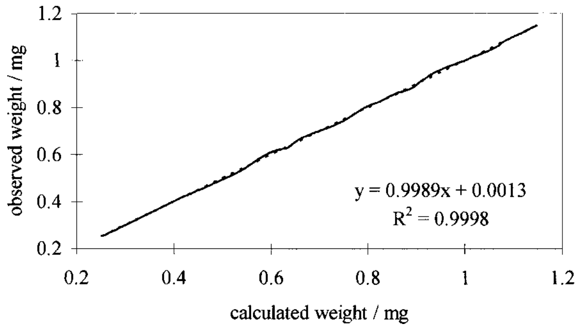

Fig. 1. Observed relative mass (continuous line) vs. calculated (dotted line) for thermal decomposition of the Dy compound with dithio.

complex and of the reagents:

$$\frac{\mathrm{d}m}{\mathrm{d}T}=\frac{k_0}{\beta}\exp\left(-\frac{E_\mathrm{a}}{RT}\right)T^n m^a. \qquad (1)$$

In Eq. (1) m is the sample mass at time t, E_a the activation energy, T the temperature, a the reaction order, k_0 the pre-exponential factor and β is the heating rate.

In order to obtain the kinetic parameters a nonlinear differential method was employed. This method [4] permits work with a larger number of experimental points than the other methods, present better correlation and the DTA curve and that obtained from the parameters do also show a very good correlation, as seen in Fig. 1 for the Dy compound. The method obtains the mass change using Eq. (1) and minimizes the relative difference between observed and calculated mass differences, that is:

$$\sum\left(\frac{\text{observed mass}-\text{calculated mass}}{\text{observed mass}}\right)^2. \qquad (2)$$

For this, an initial value is given to the parameters and the optimum values calculated employing a simplex algorithm [5].

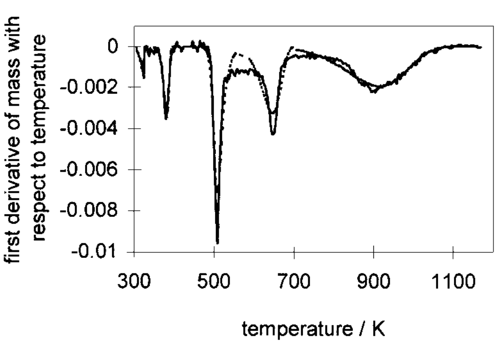

Fig. 2. First derivatives of the observed relative mass (continuous) and calculated (dotted).

4. Results and discussion

All the compounds present four peaks corresponding to the dehydration process albeit some are not completely clear and well defined. Each peak is probably the result of loss of one water molecule. However care is needed since some peaks are tiny and close together except in the case of La (see also Table 1).

Fig. 1 shows that the kinetic parameters are qualitatively good since the mass values obtained are in excellent agreement with the experimental values. It is important to mention that the calculations were done independently for each process.

Fig. 2 shows that the first derivative calculation agrees reasonably well with the experimental results. The decomposition peaks are coincident for all compounds (see also Tables 2–4).

Fig. 3 shows a good correlation and calculated mass values, very close to the experimental ones.

Table 1 includes the kinetic parameters obtained for the La compound dehydration. The method is able to make use of all points including the shortest peaks and more, an excellent correlation.

Table 1
Kinetic parameters of the several dehydration peaks shown by the La compound[a]

Peak	Correlation	E_a (kJ mol^{-1})	k_0	Order	T_i	T_f	nd
1	0.9930	255.3	3.7×10^{10}	1	305	332	27
2	0.9955	307.6	3.7×10^{46}	1	328	346	23
3	0.9984	156.3	1.8×10^{22}	1	343	362	24
4	0.9974	124.7	5.7×10^{16}	1	359	381	28

[a] T_i and T_f indicate initial and final temperatures and nd is the total number of experimental points used.

Table 2
Kinetic data of the first picrate decomposition[a]

Rare earth	Correlation	E_a (kJ mol^{-1})	k_0	T_i	T_f	nd	Order
La	0.9954	284.2	7.0×10^{27}	465	535	86	1
Nd	0.9944	274.6	3.3×10^{26}	469	543	89	1
Eu	0.9978	192.2	1.7×10^{18}	470	542	145	1
Dy	0.9928	259.0	2.8×10^{25}	462	535	890	1

[a] T_i and T_f indicate initial and final temperatures and nd is the total number of experimental points used.

Table 3
Kinetic data of the second decomposition[a]

Rare earth	Correlation	E_a (kJ mol^{-1})	k_0	T_i	T_f	nd	Order
La	0.9992	222.2	7.1×10^{16}	607	668	75	1
Nd	0.9991	191.9	2.0×10^{14}	604	674	85	1
Eu	0.9993	126.7	5.8×10^{8}	600	697	195	1
Dy	0.9985	197.8	5.4×10^{14}	604	674	85	1

[a] T_i and T_f indicate initial and final temperatures and nd is the total number of experimental points used.

Table 4
Kinetic data for the third decomposition[a]

Rare earth	Correlation	E_a (kJ mol^{-1})	k_0	T_i	T_f	nd	Order
La	0.9991	88.9	1280	732	1161	514	1
Nd	0.9993	84.2	800	738	1161	507	1
Eu	0.9984	56.3	12	759	1166	811	1
Dy	0.9993	84.8	840	704	1161	547	1

[a] T_i and T_f indicate initial and final temperatures and nd is the total number of experimental points used.

Table 2 presents data for one dithio loss. The Eu data are quite different from those of La, Nd and Dy. In this case, it is possible that a difference exists in the oxidation number, which may have been caused by the nitrogen atmosphere with an eventual oxygen removal.

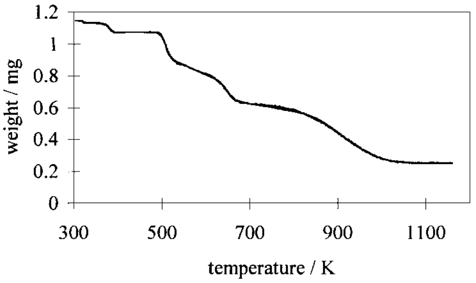

Fig. 3. Observed relative mass (continuous line) and calculated (dotted line) vs. temperature for thermal decomposition of the Dy compound.

Table 3 shows data on a half dithio molecule loss and some picrate decomposition. Eu compound present, again, a distinct behavior, a further indication for the oxidation number change.

Table 4 is related to the rare earth oxides formation with Eu compound data markedly different.

In order to better see the DTG peaks use was made of a binomial filter used five times along the DTG data. The passage of the binomial filter [6] results in a slight peak area modification and for this reaction it was tried to minimize this procedure.

The first decomposition is related to one ligand loss, the exception being the Eu compound which presents 30–40% lower activation energy and a substantially different pre-exponential factor.

The second decomposition is similar for all the compounds, if reaction order, temperature interval and correlation are analyzed as seen in Table 3. In this case there seems to be an influence of the next decomposition step.

The plateau between the third and fourth peaks does not approach zero. May be the influence of the fourth peak reaction is less important than that related to the second peak.

The last peak falls always at the same temperature interval. It is a sharp peak, indicative of a transformation reaction where the reagents and products have similar masses.

There is coherence among the parameters with exception to the Eu compound which coincidentally had a much larger number of experimental points.

5. Conclusions

The kinetic parameters along with different process show a coherence for the La, Nd and Dy compounds and on other hand a different behavior for Eu compound. This can be due to a +2 oxidation number for Eu. The method employed in the parameter calculations is good enough as shown by the correlation in observed and calculated mass loss curves superposition, as well as those for the first derivatives.

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