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LANTHANIDE NITRATE COMPLEXES WITH 2-AZACYCLONONANONE
Thermal and kinetic studies

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Thermal behavior of rare earth nitrate complexes with 2-azacyclononanone (AZA) with $Ln(NO_3)_3 \cdot 3(AZA)$ composition (where *Ln*=Gd, Er and Ho) was analyzed in kinetic point of view. Kinetic parameters were calculated from thermogravimetric data. All obtained results were similar. The first decomposition step was representative to the loss of ligand and the residue was essentially Ln_2O_3. Furthermore, a reaction path was proposed for the thermal decomposition of the $Ln(NO_3)_3 \cdot 3(AZA)$.

Keywords: *2-azacyclononanone, lanthanide(III), nitrates(V)*

Introduction

Rare earth elements have several technological application including glass discolorations, lasers and ceramics [1, 2]. Lactams have similar structures to some biological proteins. Thus, they are interesting ligands to study their reactions with lanthanides(III). Lanthanide complexes with 2-azacyclononanone as ligands have been studied previously [3–6]. Kinetic studies were shown to be useful in the thermal decomposition analyses of complexes formed between rare earth metal(III) salts and several ligands. Up till now kinetic analysis results involving compounds containing nitrates and 2-azacyclononanone (AZA) were not found in the literature [7–10]. In this paper the kinetic parameters obtained from thermogravimetric data of the lanthanide nitrate and 2-azacyclononanone complexes are reported.

Experimental

Synthesis and characterization of complexes by elemental analysis, titration with EDTA, the results of FTIR and X-ray single crystal studies, emission and absorption spectrum of some lanthanide compounds are thoroughly described [3]. The state of the art suggests the $Ln(NO_3)_3 \cdot 3(AZA)$ formula.

Thermogravimetric curves were recorded by Shimadzu TGA-50H at a heating rate of 10 K min^{-1} in a dynamic nitrogen atmosphere (flow rate: 50 cm^3 min^{-1}). The initial sample mass was approximately 2.5 mg in all experiments and it was normalized to 100%. The normalized masses of intermediers are the used parameters in Eq. (1). The investigated temperature range was between 302 and 1150 K. The kinetic parameters were obtained by simulating TG curves using the equations presented in this paper.

Kinetic analysis–theoretical principles

Several methods are used to obtain kinetic parameters from TG curves [6, 7]. In general, it is not trivial to obtain TG curves with full plateau. In this work, it was possible by simulating TG curves using the equations presented herein. An n=1 as reaction order was proposed since any other reaction order would be difficult to be theoretically justified. Vyazovkin [11] studied the difficulties to obtain kinetic parameters with minimum uncertainty.

It is possible to simulate the curves with reaction order, n=2 however, the molar masses of the intermediates should be the same in all cases.

The quality of the theoretical approach to fit the observed curves is visually established. The first and second derivatives of the TG curves are particularly helpful in this aspect. Gathering such parameters is important in order to establish mechanisms, as they provide information on intermediates as well as about a possible reaction path.

A theoretical kinetic study was carried out inserting TG data into the QBASIC program. For each step of the process the following kinetic equation can be applied:

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$$\Delta m_{i,j} = -\frac{k_{O,i}}{\beta}\exp\left(\frac{-E_{ai}}{RT}\right) m_{i,j-1}\cdot\Delta T_j + \frac{M_{i+1}}{M_i}\cdot\Delta m_{i,j-1} \quad (1)$$

where $\Delta m_{i,j}$ represents the mass increase of the i^{th} compound in the j^{th} step, $k_{0,i}$ is the pre-exponential factor, $E_{a,i}$ is the activation energy of the i^{th} compound, M_i represents the molar mass of the compound i, and β is the heating rate.

The initial mass of the first component is the initial sample mass (m_0) is to be analyzed. For the other components, the initial mass is 0 (zero) mg. Using a set of activation energies and pre-exponential factors, it is possible to approximate visually the theoretical mass concerning to the experimental value. The theoretical mass is given by:

$$m_j = \sum_i m_{i,j} \quad (2)$$

where m_j is the total mass at the j^{th} step.

The advantages of determination of the kinetic parameters in such a way are the following:

- It is possible to study the thermogravimetric curves in the whole temperature range even for parallel or consecutive reactions;
- It is possible to predict the amount and the molar mass of the reaction intermediate and
- Using the mechanic proposal it is possible to determine the experimental curve and test the initial hypothesis.

Results and discussion

The analytical results are in good agreement with the composition of $Ln(NO_3)_3{\cdot}3$(AZA), (*Ln*=Gd(III), Er(III) and Ho(III); AZA=2-azacyclononanone) [3]. TG curves were recorded in order to characterise the thermal stability of the complexes and to provide data for the kinetic study. In general, for all the three compounds, the first step of the process occurred at between 302–571 K with the initial decomposition of AZA, resulting gaseous products as $C_8H_{15}NO$ and C_6H_{12}. If thermal decomposition takes place with the evolution of two AZA molecules, the deviation in the molar mass of the intermedier would be higher than the expected one. The second step (between 556–736 K) corresponds to the loss of two molecules of H_2CCONH. The decomposition of nitrates occurred between 632–936 K resulting lanthanide oxides (Ln_2O_3) as a final product at 903–936 K. The obtained thermogravimetric data are summarized in Table 1. The difference between the experimental and theoretical values obtained for Ho_2O_3 were not in good agreement compared to the others. However, the solid end-products of the decomposition around 632 K have the same characteristic than that of the lanthanide oxides have. In this case, the light yellow colour of the final residue indicated the existence of Ho_2O_3.

Figure 1 shows the observed and calculated TG curves for Er(III), Gd(III) and Ho(III) complexes, in arbitrary units (a. u.). Figure 2 shows the first and second derivatives of both calculated and observed TG curves for the three complexes. E_{ai}, k_{0i} and intermediate molar masses were determined by fitting the observed curves.

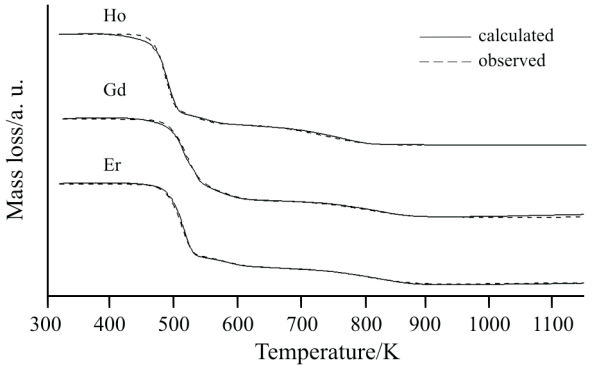

Fig. 1 Experimental and calculated TG curves for Er(III), Gd(III) and Ho(III) complexes

Table 1 Summary of the representative thermogravimetric data of $Ln(NO_3)_3{\cdot}3$(AZA) compounds

Ln	Temperature range/K	Mass loss/%		Attribution
Gd	302–571	56.8	55.0	AZA decomposition
	571–736	6.4	6.2	AZA decomposition
	736–903	12.2	12.1	NO_3 decomposition
	903	24.6	24.5	Gd_2O_3
Er	302–556	54.4	54.5	AZA decomposition
	556–632	6.3	6.4	AZA decomposition
	632–936	14.7	14.4	NO_3 decomposition
	936	25.1	24.6	Er_2O_3
Ho	302–562	54.5	54.7	AZA decomposition
	562–669	6.4	6.4	AZA decomposition
	669–905	12.3	11.2	NO_3 decomposition
	905	26.8	24.4	Ho_2O_3

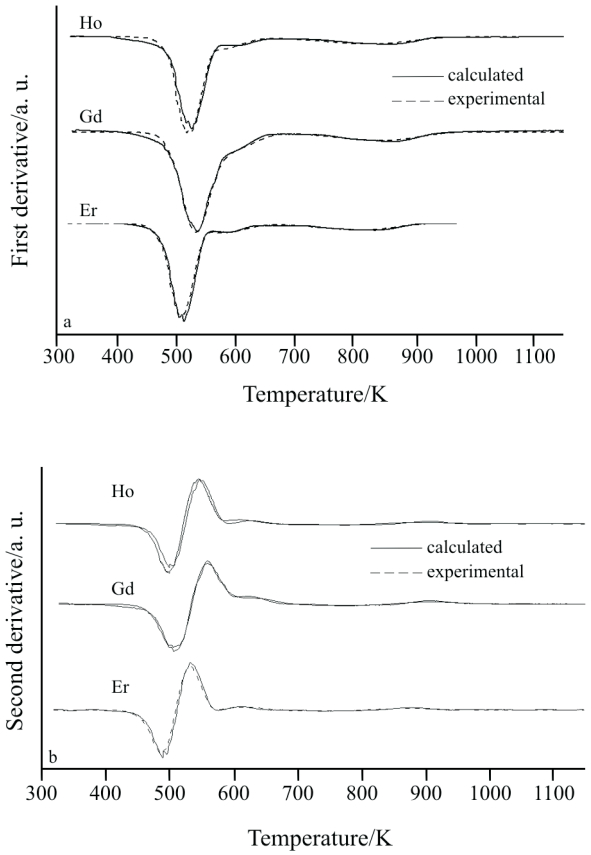

Fig. 2 a – First and b – second derivatives of TG curves, experimental and calculated for Er(III), Gd(III) and Ho(III) compounds

The global process was consistent with the following decomposition reactions:

$$2[Ln(NO_3)_3\cdot(C_8H_{15}NO)_3]\rightarrow 2[Ln(NO_3)_3]\cdot \cdot 2H_2CCONH+4C_8H_{15}NO\uparrow+2C_6H_{12}\uparrow \quad (1)$$

$$[Ln(NO_3)_3]\cdot 2H_2CCONH\rightarrow \rightarrow 2[Ln(NO_3)_3]+2H_2CCONH\uparrow \quad (2)$$

$$2[Ln(NO_3)_3]\rightarrow 2LnO_2NO_3+4NO_2\uparrow \quad (3)$$

$$2LnO_2NO_3\rightarrow Ln_2O_3+2NO_2\uparrow+3/2O_2\uparrow \quad (4)$$

Kinetic parameters (activation energies and pre-exponential factors) from the thermogravimetric data were calculated assuming n=1 as the order of the reaction (Table 2). Mechanisms were proposed to simulate the experimental TG curves. In the first and second derivatives (Fig. 2) one can observe the good agreement between experimental and calculated curves (coincident curves); this is associated with the kinetic Eqs (1) and (2) reflecting a good experimental behavior.

The usual molar mass of the intermediate allows good approximation between observed and calculated curves. The proposed mechanism for thermal degradation of this lanthanide nitrate complexes with 2-azacyclononanone is in a good agreement with the:

Table 2 Kinetic parameters for $Ln(NO_3)_3\cdot 3AZA$ compounds and mass percentage of intermediate products

Metals	Steps	k_O/s^{-1}	E_a/kJ mol^{-1}	Normalized mass/%
Gd	1	$2.5\cdot10^{12}$	147	100
	2	$7.0\cdot10^{2}$	60	55
	3	$4.0\cdot10^{2}$	86	41
	4	$2.0\cdot10^{2}$	75	31
Er	1	$1.0\cdot10^{12}$	141	100
	2	$6.0\cdot10^{2}$	61	52
	3	$0.9\cdot10^{1}$	64	43
	4	$2.0\cdot10^{2}$	49	31
Ho	1	$1.0\cdot10^{14}$	161	100
	2	$1.0\cdot10^{3}$	35	50
	3	$5.5\cdot10^{2}$	58	38
	4	$4.5\cdot10^{1}$	70	30

- molar masses obtained from TG curves and the
- material balance of each mechanism step.

Conclusions

The proposed mechanism for the observed thermal decomposition involves consecutive polymerization reactions of the organic intermediates. The previously described method [8] shows a good agreement between the plotted curves and suggests that each peak correspond to more than one reaction. The first and second derivatives indicated the high quality of the optimization of the experimental and calculated curves and this is associated to the kinetic Eqs (1) and (2) reflecting a good experimental behavior.

The decomposition takes place in four steps with similar activation energies and pre-exponential factors.

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