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LANTHANIDE TRIFLUOROACETATE COMPLEXES WITH 2-AZACYCLONONANONE
Thermal and kinetic studies

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Abstract

$Ln(TFA)_3\cdot 3AZA$ (*Ln*=La, Sm, Er; *TFA*=trifluoroacetate and *AZA*=2-azacyclononanone) compounds were synthesized and characterized by microanalytical procedures, IR spectroscopy, X-ray powder diffraction, and thermal analysis. A kinetic study using La, Sm and Er thermogravimetric curves was carried out aiming to proposing a mechanism for the thermal decomposition of such complexes.

Keywords: 2-azacyclononanone, lanthanide, trifluoroacetate

Introduction

Lanthanide complexes with lactam 2-azacyclononanone (AZA) have been described in literature [1, 2]. AZA is a traditional ligand containing two *cis-trans* isomers that may coexist [3, 4]. The interest in trifluoroacetates comes from the fact that they may act as monodentates, bidentates, or bridges, between two central atoms, either coordinated or not [5].

In this article we describe the characterization of $Ln(TFA)_3\cdot 3AZA$ compounds by microanalytical procedures, infrared absorption spectroscopy, X-ray powder diffraction and thermogravimetric analysis. A kinetic study using thermogravimetric curves obtained for La, Sm and Er was also carried out.

Experimental

The complexes were prepared from the reaction of hydrated lanthanide trifluoroacetates with AZA in ethanol (molar ratio 1:3). Carbon, hydrogen and nitrogen contents were determined using a Perkin Elmer CHN analyser model 240. Thermogravimetric curves were obtained on a Perkin Elmer TGA-7 instrument at a heating rate of 10 K min^{-1} in nitrogen flowing at a rate of 50 $\mathrm{cm}^3\ \mathrm{min}^{-1}$.

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Kinetic theoretical basis

Several methods are used to obtain kinetic parameters regarding 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 here in. Reaction of order one was proposed as any other would be order difficult to be theoretically justified. Vyazovkin and Lesnikovich [8] studied the difficulty to obtain kinetic parameters with minimum uncertainty. It is possible to simulate the curves with reaction of order two, for instance, but the intermediate molecular masses would have to be the same in all cases.

The quality of the theoretical approach to fit the observed curves is visually established and the first and second derivatives of TG curves are particularly helpful in this sense.

Gathering such parameters is important in order to establish mechanisms, as they offer information on intermediates, and a likely reaction path.

A theoretical kinetic study was carried out feeding TG data in the QBasic program. For each step of the process it is possible to apply the following kinetic equation:

$$\Delta m_{\mathrm{i,j}} = -\frac{k_{0,\mathrm{i}}}{\beta}\exp\left(\frac{-E_{\mathrm{ai}}}{RT}\right)m_{\mathrm{i,j}} - 1\Delta T_{\mathrm{j}} + \frac{M_{\mathrm{i+1}}}{M_{\mathrm{i}}}\Delta m_{\mathrm{i,j-1}} \qquad (1)$$

where $\Delta m_{\mathrm{i,j}}$ represents the mass increment of the *i*-th compound at the *j*-th step, $k_{0,\mathrm{i}}$ is the pre-exponential factor, $E_{\mathrm{a,i}}$ is the activation energy of the *i*-th compound, $M_{\mathrm{i,j}}$ represents the molar mass of the compound i, and β is the heating rate.

The initial mass of the first component is the initial mass m_1 of the sample to be analyzed. For the other components the initial mass is null.

Using a set of activation energies and pre-exponential factors, it is possible to visually approximate the theoretical mass to the experimental one. The theoretical mass is given by:

$$m_{\mathrm{j}} = \sum_{\mathrm{i}} m_{\mathrm{i,j}} \qquad (2)$$

where m_{j} is the total mass at the *j*-th step.

The advantages of determing the kinetic parameters this way are:

- it is possible to study the whole temperature range of the thermogravimetric curve even with parallel or consecutive reactions;
- it is possible to predict the quantity and the molar mass of the reaction intermediates and
- using the mechanistic proposal it is possible to determine the experimental curve, and test the initial hypothesis.

Results and discussion

The analytical results are in agreement with $\mathrm{Ln(TFA)_3{\cdot}3AZA}$ (*Ln*=La, Sm, Er; *TFA*=trifluoroacetate and *AZA*=2-azacyclononanone) composition. IR data indicate that the trifluoroacetate counter-ions are bound to the central ion as monodentate, bidentate or even bridges between two lanthanide ions. According to X-ray powder patterns, the lanthanum compound is different from the isomorphous Sm and Er ones.

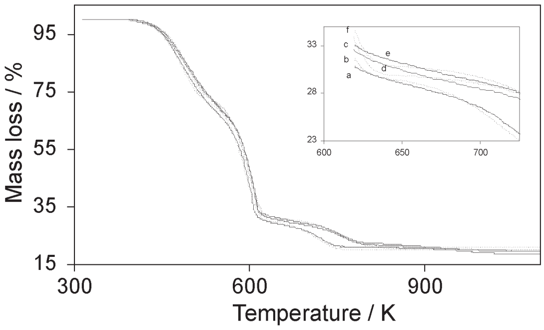

Fig. 1 Thermogravimetric curves experimental and calculated obtained for La, Sm and Er complexes. TG curves experimental (a, d and e) and calculated (b, c and f) by La, Sm and Er compounds respectively

Thermogravimetric curves were recorded to evaluate the thermal stability of the compounds and to assist in the kinetic study. The heating rate and atmosphere were chosen according to preliminary investigations. Figure 1 shows the curves obtained in N_2 atmosphere, at 10 K min^{-1}. They are similar to the curves recorded in air.

Table 1 Summary of thermogravimetric results of $Ln(TFA)_3 \cdot 3AZA$ compounds, in flowing N_2 (50 cm^3 min^{-1}). Heating rate: 10 K min^{-1}

Ln	Temperature range/K	Mass loss/%		Attribution
		theor.	exp.	
La	377– 551	–	33.81	AZA decomposition
	551–668	–	38.19	AZA and TFA decomposition
	668 –1170	–	10.11	TFA decomposition
	1170	18.34	18.20	LaOF
Sm	393–556	–	31.52	AZA decomposition
	556–673	–	38.24	AZA and TFA decomposition
	673–1170	–	10.75	TFA decomposition
	1170	19.51	19.16	SmOF
Er	343– 553	–	32.98	AZA decomposition
	553–669	–	37.92	AZA and TFA decomposition
	669–1170	–	8.59	TFA decomposition
	1170	21.34	21.75	ErOF

The first step of the kinetic process occurred at about 373 K with the decomposition of AZA, producing C_6H_{12}. If thermal decomposition occurred with the evolution of two AZA molecules, the error in the molar mass of the intermediary would be higher than the expected one. The second step, between 553–673 K, corresponded to the loss of H_2CCONH molecules and gaseous products due to the decomposition of TFA. According to Rillings and Roberts [9], it consists in the formation of CO, CO_2, CF_3OF and $(CF_3CO)_2O$. The decomposition continued up to 1273 K, with formation of lanthanide oxyfluorides (LnOF) as final residues. Table 1 summarizes the obtained thermogravimetric data.

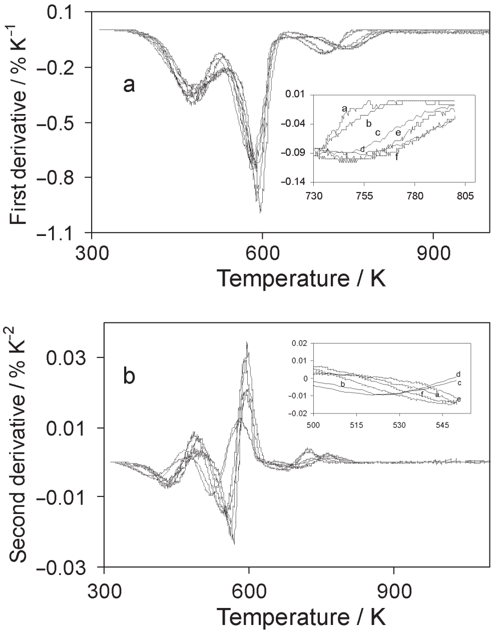

Fig. 2 First (a) and second (b) derivative TG curves experimental (a, d and e) and calculated (b, c and f) by La, Sm and Er compounds respectively

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 fitting the observed curves. The global process was consistent with the following decomposition reactions:

$$Ln(TFA)_3{\cdot}3AZA \rightarrow Ln(TFA)_3{\cdot}3H_2CCONH+3C_6H_{12}$$
$$Ln(TFA)_3{\cdot}3H_2CCONH \rightarrow LnO(OCOCF_3)+(CF_3CO)_2O+3H_2CCONH$$
$$LnO(OCOCF_3) \rightarrow LnO(COF)+OCF_2$$
$$LnO(COF) \rightarrow LnOF+CO$$

The kinetic parameters obtained for each thermal decomposition step are presented in Table 2.

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

Compound	Step	k_0/s^{-1}	E_a/kJ mol^{-1}	m/%	Molar mass calculated	
					a	*b*
La	1	$1.1 \cdot 10^5$	67.7	100	901	901
	2	$3.0 \cdot 10^9$	132.0	72	649	649
	3	$1.5 \cdot 10^6$	116.0	30	268	268
	4	$9.0 \cdot 10^7$	134.0	22	202	202
	5	$2.0 \cdot 10^1$	450.0	20	180	174
Sm	1	$1.1 \cdot 10^5$	69.0	100	912	912
	2	$3.0 \cdot 10^9$	133.2	72	660	660
	3	$3.0 \cdot 10^5$	113.5	31	279	279
	4	$9.0 \cdot 10^7$	135.0	23	213	213
	5	$2.0 \cdot 10^1$	450.0	21	191	185
Er	1	$1.1 \cdot 10^5$	68.7	100	929	929
	2	$3.0 \cdot 10^9$	133.3	73	677	677
	3	$1.9 \cdot 10^5$	110.0	31	288	296
	4	$9.0 \cdot 10^7$	140.0	25	230	230
	5	$2.0 \cdot 10^1$	450.0	22	202	202

a – molar mass obtained by simulation and *b* – molar mass calculated adding atomic masses

Conclusions

The proposed mechanism for the observed thermal decomposition consists of consecutive polymerization reactions of the organic intermediates. The method previously introduced [10] showed a good agreement with 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 mass curves. The decomposition occurs in five steps with similar activation energies and pre-exponential factors.

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