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Kinetic study of the thermal decomposition of the compound of terbium(III) trifluoromethanesulfonate and hexamethylphosphoramide (HMPA) employing both Zsakó's and nonlinear methods

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Abstract

Terbium trifluoromethanesulfonate compound with hexamethylphosphoramide was synthesized and characterized. Thermogravimetric data with three heating rates were used to obtain kinetic parameters such as activation energy (E_a), reaction order (n) and preexponential factor (k_0). The results obtained by two different methods, Zsakó's and a nonlinear one, are compared.

Keywords: Rare earth elements; Thermal decomposition; Trifluoromethanesulfonate; Kinetic parameters; Zsakó's and nonlinear methods

1. Introduction

The coordination chemistry of rare earths underwent an enormous progress during the last decade. These studies are generally based on the determination of factors which have an influence on the formation of the complex species, on stoichiometry coordination number, ion–ligand interaction nature, etc. [1]. The trifluoromethanesulfonate anion presents a low coordination capacity and thermal stability [2].

Hexamethylphosphoramide (HMPA) was initially used as a solvent, catalyst and organic reaction environment. It is a colorless, water soluble liquid, miscible with polar or nonpolar organic solvents. HMPA has a larger basic character than DMF and dimethyl sulfoxide (DMSO) [3], having also a high ‘‘donation number’’ [4].

There are few references in the literature on kinetic approaches about rare earth complexes' thermal decomposition [5,6] in spite of some work on ligands loss without kinetic parameters determination.

This paper studies the synthesis and characterization of terbium trifluoromethanesulfonate with HMPA and the acquisition of kinetic parameters of the thermal decomposition process through nonisothermal thermogravimetric (TG) data, and first three ligands leaving process employing two different methods.

2. Experimental

The compound was prepared by dissolving the hydrated trifluoromethanesulfonate in absolute ethanol and acetone and treatment with HMPA (molar ratio 1:6). The solution was mixed, left to react on a water-bath and later at room temperature for precipitation.

Terbium ion was determined by complexometric titration with EDTA [7]. Analysis of carbon, hydrogen and nitrogen was performed by usual microanalytical procedures. Fourier transform infrared spectra were recorded on a Perkin-Elmer 16 PC spectrophotometer using KBr plates.

TG curves with heating rates 5, 10, 15 K min^{-1} under 50 ml min^{-1} nitrogen were obtained in a TGA-50H Shimadzu System.

Zsakó's [8] and nonlinear [9] methods were used in order to obtain kinetic parameters of the thermal decomposition reactions in nonisothermal processes from TG data.

Temperature ranges for the kinetic parameters of the

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first weight loss (two ligands leaving) and the second are, respectively, 300–489 K and 453–587 K.

3. Theory

Zsakó's method is one of the most frequently used to obtain kinetic parameters of thermal decomposition reactions in nonisothermal processes from TG data.

To begin, a kinetic equation:

$$\frac{\mathrm{d}w}{\mathrm{d}t} = -k_0 \exp\left(\frac{-E_\mathrm{a}}{RT}\right) w^n \tag{1}$$

where w is the compound's sample weight at time t, k_0 and E_a are preexponential factor and activation energy, respectively, T is temperature and n is reaction order. In a linear program t and T are related by:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \beta \tag{2}$$

where β is the heating rate.

Eq. (1) becomes:

$$\frac{\mathrm{d}w}{\mathrm{d}T} = \frac{-k_0}{\beta} \exp\left(\frac{-E_\mathrm{a}}{RT}\right) w^n \tag{3}$$

which, under integration, becomes:

$$f(w) = \int_{w_0}^{w'} \frac{\mathrm{d}w}{w^n} = \frac{-k_0}{\beta} \int_{T_0}^{T'} \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \mathrm{d}T = g(T) \tag{4}$$

It is not really necessary to do $T_0 = 0$ K, but it is usual. Integration of the right side of the Eq. (4), (called temperature integral) was numerically obtained by a Gauss quadrature method with 48 points collected from T_0 as the temperature onset for each studied process.

By applying logarithms on both sides of Eq. (4), the optimized value of E_a can be found when the slope is unity and preexponential factor achieved through linear coefficient.

The nonlinear method used in this work takes the weight increase for ith point, Δw_i, of Eq. (1), and relates it to the calculated weight of the ith point, w_i:

$$w_{i+1} = w_i + \Delta w_i \tag{5}$$

The objective function, F, to be minimized is:

$$F = \sum_{i=1}^{N} \left[1 - \frac{w_{i,\mathrm{calc}}}{w_{i,\mathrm{obs}}} \right]^2 \tag{6}$$

where calc and obs are indices which represent calculated and observed weights. N is data's number.

An algorithm of Simplex's [10] type was used to minimize F. It is necessary, for nonlinear methods to introduce germen values for E_a, n and k_0, as input.

For reasons of comparison, a correlation was made of log $f(w)$ versus log $g(T)$ for Zsakó's method and calculated weight versus observed weight for the nonlinear method.

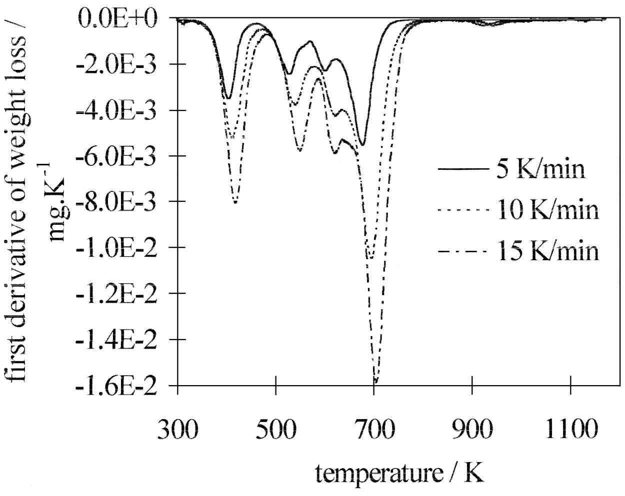

Fig. 1. First derivatives of thermogravimetric curves for $Tb(CF_3SO_3)_3 \cdot$ 6HMPA. Thermal decomposition at three different heating rates.

4. Results and discussion

The analytical results for Ln, C, H and N confirm the general formula $Tb(CF_3SO_3)_3 \cdot 6(HMPA)$. The TG curves, in Fig. 2, were obtained at three different heating rates. In both Figs. 1 and 2, it is seen that the weights drop slowly but linearly with temperature after 1000 K. TG curves indicate that the compounds are anhydrous. The final residue is TbF_3. The presence of fluoride was proved by the glass corrosion test with concentrated H_2SO_4 [11].

The integral methods present results easier to understand when compared to parameters obtained by differential

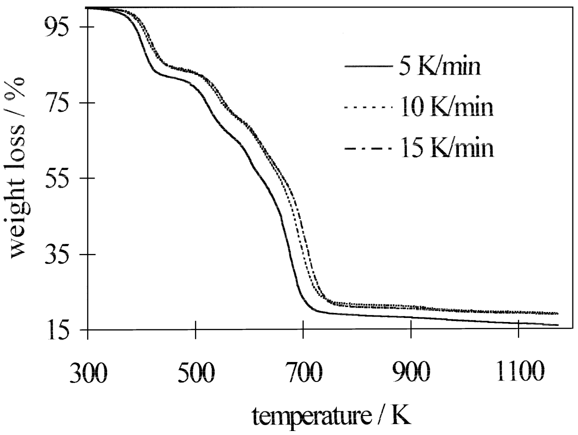

Fig. 2. Thermogravimetric curves of $Tb(CF_3SO_3)_3 \cdot 6HMPA$. Thermal decomposition at three different heating rates.

Table 1
Kinetic parameters for the first thermal decomposition of Tb's compound by Zsakó's and nonlinear methods: n_p is the number of points used and r is the correlation

Method	β (K min^{-1})	E_a (kJ mol^{-1})	k_0 (min^{-1})	T_i (K)	T_f (K)	n_p	r
Zsakó	5	52.5	$2.1 \cdot 10^3$	327	459	160	0.9902
	10	64.2	$1.0 \cdot 10^5$	336	461	155	0.9925
	15	57.8	$1.5 \cdot 10^4$	336	475	186	0.9916
Nonlinear	5	64.8	$6.1 \cdot 10^8$	300	463	196	0.9990
	10	73.2	$4.7 \cdot 10^9$	349	461	140	0.9990
	15	62.7	$1.3 \cdot 10^8$	322	489	226	0.9980

methods in the case of kinetic parameters of nonisothermal thermal decomposition processes due to low dispersion. A possible explanation is that the data obtained with robust instrumentation, computer managed, can show noise. Derivatives of these data increase the noise and, the data plot results in a pronounced dispersion.

The integral methods damp off these noises. Of the integral methods, Zsakó's is the best known since it is not necessary to do any approximation to calculate the temperature integral. The results presented in Tables 1 and 2 were acquired using onset temperatures as the ones presented in the T_i column. All reaction orders were unit and errors in E_a less than 0.1 kJ mol^{-1}.

The correlations presented by the nonlinear method are closer to unit than those obtained from Zsakó's method. The number of points used in the parameters calculation by nonlinear methods was the same or more than those used for Zsakó's method. For both methods the activation energies are comparable for each decomposition and the same is true for the preexponential factor. The weight loss first derivative is easier to calculate for a nonlinear method than for Zsakó's and this is a very important factor of choice in an Arrhenius equation type calculation.

The derivative of weight with respect to temperature is represented in Fig. 1 for the first and second decompositions by two sealed peaks. They shift to higher temperatures with the heating rates increase.

5. Conclusion

The comparison between the nonlinear method developed by our group and Zsakó's is not made with the intention to be a substitute of an already well known method but to show that it can be used with the same reliability and also to show that in the present case as also in other situations [9] better dispersions and correlations are obtained.

Concerning the kinetic aspects of the ligand decomposition, it can be observed that in both cases activation energies are quite similar. The reaction order (always 1) well characterizes the complex decomposition, beginning with HMPA ligands loss and not the salt.

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Table 2
Kinetic parameters for the second thermal decomposition of Tb's compound by Zsakó's and nonlinear methods: n_p is the number of points used and r is the correlation

Method	β (K min^{-1})	E_a (kJ mol^{-1})	k_0 (min^{-1})	T_i (K)	T_f (K)	n_p	r
Zsakó	5	88.1	$1.4 \cdot 10^5$	453	572	143	0.9952
	10	91.2	$3.6 \cdot 10^5$	472	571	120	0.9981
	15	87.8	$1.6 \cdot 10^5$	478	587	146	0.9985
Nonlinear	5	86.1	$6.1 \cdot 10^8$	453	573	143	0.9990
	10	111.6	$1.6 \cdot 10^{11}$	472	571	120	0.9998
	15	103.4	$1.4 \cdot 10^{10}$	478	587	146	0.9998

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