Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 805-810

KINETIC STUDY OF THERMAL DECOMPOSITION OF THE DMIT COMPLEX OF COBALT

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Abstract

In this work, a cobalt complex with dmit (1,3-dithiol-2-thione-4,5-dithiolate) as ligand was prepared and its thermal stability was studied by thermogravimetric analysis and kinetics by means of the Zsakó method and a non-linear method. For both methods, numerical binomial and polynomial filters were used, where points in the central interval were utilized.

Keywords: cobalt, dmit ligand, kinetics, non-linear method, Zsakó method

Introduction

Many types of material, including coordination compounds, polymers, etc., have been studied by non-isothermal thermogravimetric analysis. This technique has an advantage over constant-temperature measurements: in the latter case, part of the sample may undergo changes while the sample is being heated to the desired temperature [1].

In order to follow the thermal decompositions of solids, it is much more interesting to present the kinetic rate equation as a function of mass than in concentration terms.

With a generic equation to represent the solid-state decomposition:

$$aA(s) \rightarrow bB(s) + cC(s) + \ldots$$

the conversion of A into B, C,... is measured through the parameter α, defined as

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

where m_o, m and m_f are the initial mass, the mass that decomposes at a certain temperature or time, and the final mass, respectively, and α is the conversion degree. The rate of decomposition of A may be expressed as

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1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

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

where k is the specific velocity constant for the reaction under investigation.

The constant k is related to the temperature (T), activation energy (E) and pre-exponential factor (A) through the Arrhenius equation:

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{3}$$

The hypothesis that Eqs (2) and (3) hold for the reactions under study was reinforced from the correlations found between the relative (calculated) mass and the observed one, in the case of the non-linear method.

For linear heating, the rate is given by

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

Equations (1)–(4) can be combined and rearranged into an integral form.

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)} = \frac{A}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right)dT \tag{5}$$

The Zsakó [2] method was used, a numerical method in which the temperature integral is resolved by a 48-point Gauss quadrature. Zsakó's method correlates the logarithms of the two sides of Eq. (5) and looks for the activation energy at the point where the slope of the straight line remains at unit. In this sense, the method of Zsakó tries to find the optimum activation energy, using the best correlation as a criterion. The non-linear method [3, 4] was also applied for comparison reasons, as in this method the mass increment may be obtained from

$$dm = -\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)m^n dT \tag{6}$$

The minimized function (F) was used:

$$F = \sum_{i=1}^{N}\left[1 - \frac{m_{calc}}{m_{obs}}\right]^2 \tag{7}$$

Experimental

The ligand dmit (1,3-dithiol-2-dithione-4,5-dithiolate), produced by the removal of two protons from H_2dmit (4,5-dimercapto-1,3-dithiolate-2-thione), was prepared by Steimecke *et al.* [5].

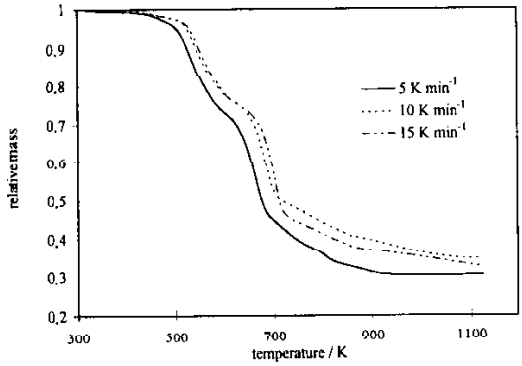

Fig. 1 Thermogravimetric curves for thermal decomposition of the Co complex at different heating rates

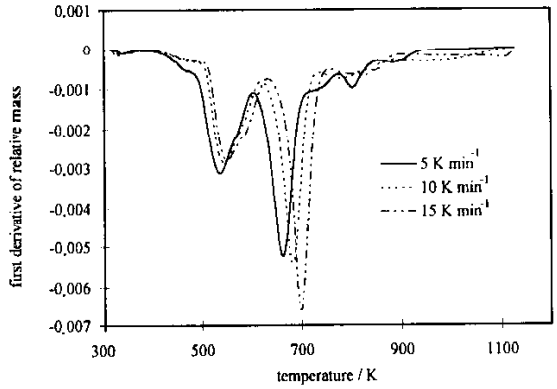

Fig. 2 First derivatives of the thermogravimetric curves of the Co complex at different heating rates

The cobalt complex was prepared by two routes: the method of Steimecke *et al.* [5] and Barreto's [6] method. In the latter case, one stage is eliminated (recovery of the ligand from 4,5-bis[dithiobenzoil]-1,3-dithio-2-thione with sodium methoxide).

After preparation, the complex was characterized by CHN microanalysis on a Perkin-Elmer model 240 elemental analyser. The metal ion concentration was determined by titration with EDTA. Infrared spectra were recorded on a MIDAC spectrophotometer, using KBr plates. Thermogravimetric curves were obtained at 5, 10 and 15 K min^{-1}, under a N_2 flow of 50 ml min^{-1}, on a Shimadzu TG 50H thermobalance.

For the kinetic study, the Zsakó and non-linear methods were used through Eqs (1)–(5) and (6)–(7), respectively. For both methods, a numerical filter was used, i.e. a polynomial approximation where points in the central interval were utilized.

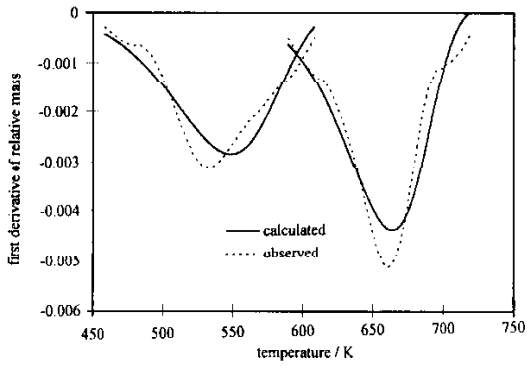

Fig. 3 First derivative of relative mass as a function of temperature for a heating rate of 5 K min^{-1} in thermogravimetric measurements on the Co complex

Results and discussion

The thermogravimetric curves obtained at 5 and 10 K min^{-1} are similar and reveal constant mass after 1070 K (Fig. 1). In the curve at 15 K min^{-1}, the mass is still not constant at 1070 K. Figure 2 depicts the first derivative of the relative mass, while Fig. 3 shows the first derivative of the relative mass for the theoretical values and the experimental ones at a rate of 5 K min^{-1}.

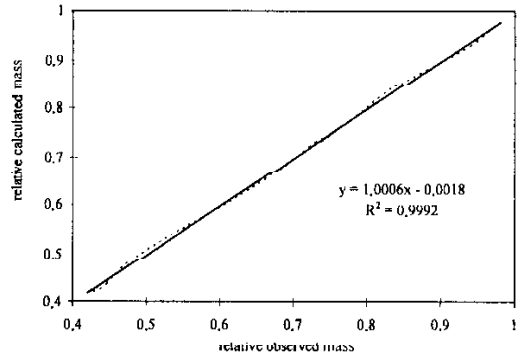

Fig. 4 Relative calculated mass *vs.* relative observed mass for thermal decomposition of the Co complex at 5 K min^{-1}

From Fig. 4, two important facts can be observed: a) there is a correlation between the observed and calculated relative masses, and this correlation is very close to one; b) the slope of the straight line is also close to one, indicating that the calculated values are similar to the experimental values.

Table 1 Kinetic parameters for the first thermal decomposition of the Co complex by the Zsakó method

β/K min^{-1}	E/kJ mol^{-1}	A	Order	T_i/K	T_f/K	Np	Correlation
5	76.1	$8.5 \cdot 10^{1}$	1.0	445	599	184	0.9799
10	95.5	$1.1 \cdot 10^{4}$	1.4	456	616	319	0.9844
15	77.3	$1.6 \cdot 10^{2}$	1.1	454	628	233	0.9918

Table 2 Kinetic parameters for the second thermal decomposition of the Co complex by the Zsakó method

β/K min^{-1}	E/kJ mol^{-1}	A	Order	T_i/K	T_f/K	Np	Correlation
5	218.8	$1.9 \cdot 10^{12}$	2	599	722	149	0.9860
10	236.7	$2.9 \cdot 10^{13}$	1.7	615	734	239	0.9889
15	241.7	$3.5 \cdot 10^{13}$	1.9	628	768	187	0.9892

Tables 1 and 2 show the kinetic parameters for the first and second thermal decomposition stages with the Zsakó method, where A is the pre-exponential factor. T_i and T_f are the initial and final temperatures, and Np is the point number for the obtained parameters.

Table 3 Kinetic parameters for the first thermal decomposition of the Co complex by the non-linear method

β/K min^{-1}	E/kJ mol^{-1}	A	Order	T_i/K	T_f/K	Np	Correlation
5	64.5	$2.9 \cdot 10^{3}$	1	459	611	30	0.9978
10	68.0	$8.7 \cdot 10^{3}$	1	488	628	281	0.9955
15	63.1	$3.6 \cdot 10^{3}$	1	504	640	271	0.9969

Table 4 Kinetic parameters for the second thermal decomposition of the Co complex by the non-linear method

β/K min^{-1}	E/kJ mol^{-1}	A	Order	T_i/K	T_f/K	Np	Correlation
5	122.0	$1.1 \cdot 10^{7}$	1	590	721	261	0.9977
10	156.4	$6.8 \cdot 10^{9}$	1	598	728	261	0.9977
15	189.7	$1.8 \cdot 10^{12}$	1	614	739	271	0.9978

Tables 3 and 4 present the kinetic parameters for the first and second thermal decomposition stages with the non-linear method. In fact, with this method, the reaction order is 1 for the two decomposition stages. The activation energies are coherent for both methods, but the better correlation is noted for the non-linear method.

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The authors gratefully acknowledge grants from FINEP and CAPES. F.M.M.B. acknowledges a DCR fellowship from CNPq.

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