



Thermal decomposition kinetics of nickel(II) and cobalt(II) azo barbituric acid complexes

Xiaoyi Li^a, Yiqun Wu^{a,b,*}, Donghong Gu^a, Fuxi Gan^a

^a Key Laboratory of Material Science and Technology for High Power Lasers, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China

^b Key Lab of Functional Inorganic Material Chemistry (Heilongjiang University), Ministry of Education, Haerbin 150080, China

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ABSTRACT

Thermal decomposition kinetics of ML_2 ($M = Ni(II)$ and $Co(II)$; $L = 5-(2-(1,5\text{-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)hydrazono)-1,3\text{-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione}$) complexes were investigated by thermogravimetric analysis (TGA). The first decomposition process of the NiL_2 and CoL_2 complexes occurs in the temperature range of 320–350 °C. Kinetics parameters corresponding to this step, such as activation energy, E_a , and apparent pre-exponential factor, $\ln A_{app}$, were calculated from the thermogravimetric data at the heating rates of 5, 10, 15 and 20 $K\ min^{-1}$ by differential (Friedman's equation) and integral (Flynn–Wall–Ozawa's equation) methods. The results show that the activation energy evidently depends on the extent of conversion. As far as their activation energy is concerned, NiL_2 complex shows a higher thermal stability than the CoL_2 complex.

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1. Introduction

Metal complex dyes have been widely used in many fields, for example, in medical applications as hypnotic and local anaesthetic drugs [1–3], in high-technological frontier applications as key functional materials, in nonlinear optical elements [4], in printing system [5] and in high-density memory storage systems (CD-R, DVD-R, HD DVD-R and BD-R) [6–10]. In recent years, these metal complex dyes used as high-density storage media, especially as blue-ray disc-recordable (BD-R) medium, have attracted a great deal of interest due to their blue-violet absorption, high solubility in organic solvents, good film-forming properties, thermal stability, good optical properties and so on [9–14]. The notable features, especially the thermal property, of the metal(II) complex dyes are very important for their uses as blue-ray disc-recordable media, but no detailed studies on their thermal decomposition kinetics have been reported so far. It is well known that recordable optical storage is based on the irreversible local thermal decomposition or deformation (pit formation) of the organic dye (recording layer) induced by the modulated laser [15]. The recording characteristics strongly depend on the decomposition or deformation. Hence, the thermal decomposition property of the dyes is important for

design and synthesis of a better optical recording medium. In this paper, we report the thermal decomposition kinetics of nickel(II) and cobalt(II) complexes containing barbituric acid derivatives as novel ligands. Kinetic parameters such as activation energy, E , and apparent pre-exponential factor, $\ln A_{app}$, were calculated using both the Friedman [16] and Flynn–Wall–Ozawa (FWO) [17,18] methods.

2. Experimental

2.1. Materials

The ligand and the corresponding nickel(II) and cobalt(II) complexes were synthesized by diazotization, coupling and metalization. Their structures were investigated by elemental analyses, 1H NMR, ESI-MS, FT-IR spectra and UV–vis absorption spectra [19], and are shown in Fig. 1.

2.2. Instrument and methods

Thermal properties of the nickel(II) and cobalt(II) complexes were measured on a TA instrument, the STA 449C Simultaneous DSC/TGA Analyzer, at a heating rate of 10 $K\ min^{-1}$ from 50 to 700 °C in a dynamic nitrogen atmosphere with the flow rate of 50 $ml\ min^{-1}$, using 4–5 mg of powdered samples. On the other hand, thermogravimetric measurements were carried out for the kinetic analysis at different heating rates (5, 10, 15 and 20 $K\ min^{-1}$) from room temperature to 800 °C under a 20 $ml\ min^{-1}$ stream of nitrogen, using about 20 mg samples. Kinetic parameters

* Corresponding author at: Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, No. 390, Qinghe Road, Jiading District, Shanghai 201800, PR China. Tel.: +86 21 69918087; fax: +86 21 69918562.

E-mail addresses: xyli@siom.ac.cn (X. Li), yqwu@siom.ac.cn (Y. Wu).

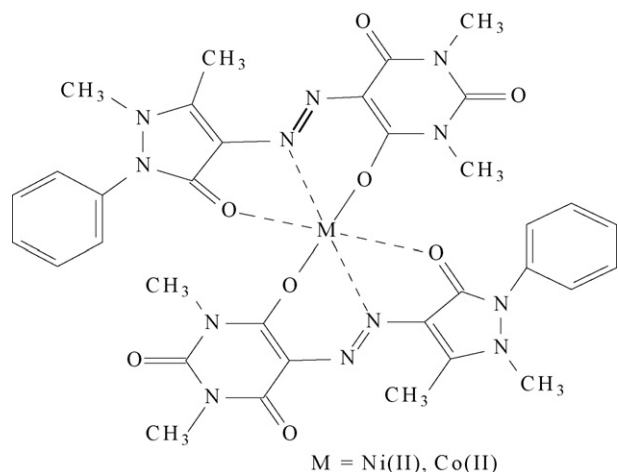


Fig. 1. Structure of the nickel(II) and cobalt(II) complexes.

were obtained from the TG data using both the Friedman and Flynn–Wall–Ozawa methods.

2.3. Theoretical analysis

The application of dynamic TG methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during solid-state degradation. Kinetics of solid-state reactions is usually described by the following equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where $d\alpha/dt$ is the rate of conversion and α is the fraction decomposed defined as $\alpha = (m_0 - m_t)/(m_0 - m_f)$, where m_t represents the mass of the sample at arbitrary time t (or temperature T), whereas m_0 and m_f are the masses of the sample at the beginning and at the end of the process, respectively, $f(\alpha)$ is the differential conversion function and $k(T)$ is the specific rate constant, whose temperature dependence is commonly described by the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where E is the activation energy, A the pre-exponential factor, R the gas constant and T is the absolute temperature. Moreover, taking into account that under non-isothermal condition the heating rate $\beta = dT/dt$, where t is the time, by combining Eqs. (1) and (2), it results

$$\frac{d\alpha}{dt} \equiv \beta \frac{d\alpha}{dT} = Af(\alpha) \exp\left(-\frac{E}{RT}\right) \quad (3)$$

Most of the methods that describe the kinetics of reactions in solids use Eq. (3) as well as several approximation of its integral form

$$g(\alpha) = \left(\frac{A}{\beta}\right) \int_0^\alpha \exp\left(-\frac{E}{RT}\right) dT \quad (4)$$

where

$$g(\alpha) = \int_0^\alpha (f(\alpha))^{-1} d\alpha \quad (5)$$

is the integral form of the model function that does not depend on the heating rate used.

2.3.1. Model-free methods

Model-free method allows the activation energy to be determined as a function of the extent of conversion or temperature without making any assumptions about the reaction model [20].

Therefore, in order to establish if such dependence on α exists or not, the kinetic procedure adopted in this work was first based on two multi-heating rate methods, differential method (Friedman equation) as well as integral method (Ozawa–Flynn–Wall equation), at different fixed heating rates without choosing a certain model function. The basic data (β , α , T) taken from the TG curves are used in the equation below.

Ozawa–Flynn–Wall equation [17,18]:

$$\ln(\beta)_\alpha = \ln\left[\frac{A_\alpha E_\alpha}{R}\right] - \ln g(\alpha) - 5.3305 - 1.052\left(\frac{E_\alpha}{R}\right)\left(\frac{1}{T_\alpha}\right) \quad (6)$$

Once the Doyle's approximation [21,22]: $\ln p(x) = -5.3305 - 1.052x$, where $x = E_\alpha/(RT_\alpha)$ and $20 \leq x \leq 60$, is verified to be valid over the entire range of α , then at any selected value of α , from the slope of the related regression straight line derived by the $\ln(\beta)_\alpha$ versus $1/T_\alpha$ plot, the corresponding E_α value is derived as a function of α .

Friedman equation [16]:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \quad (7)$$

It can be seen from Eqs. (6) and (7) that the graphs $\ln \beta$ versus $1/T$ and $\ln(d\alpha/dt)$ versus $1/T$ both show straight lines with slopes $m(1) = -1.052E/R$ and $m(2) = -E/R$. The slopes of these straight lines are directly proportional to the reaction activation energy (E).

3. Results and discussion

3.1. Thermal decompositions of NiL₂ and CoL₂ complexes

Fig. 2 presents the recorded TG/DTG and DSC curves for NiL₂ and CoL₂ complexes in nitrogen atmosphere. The thermal analysis data of NiL₂ and CoL₂ complexes are summarized in Table 1. From Fig. 2

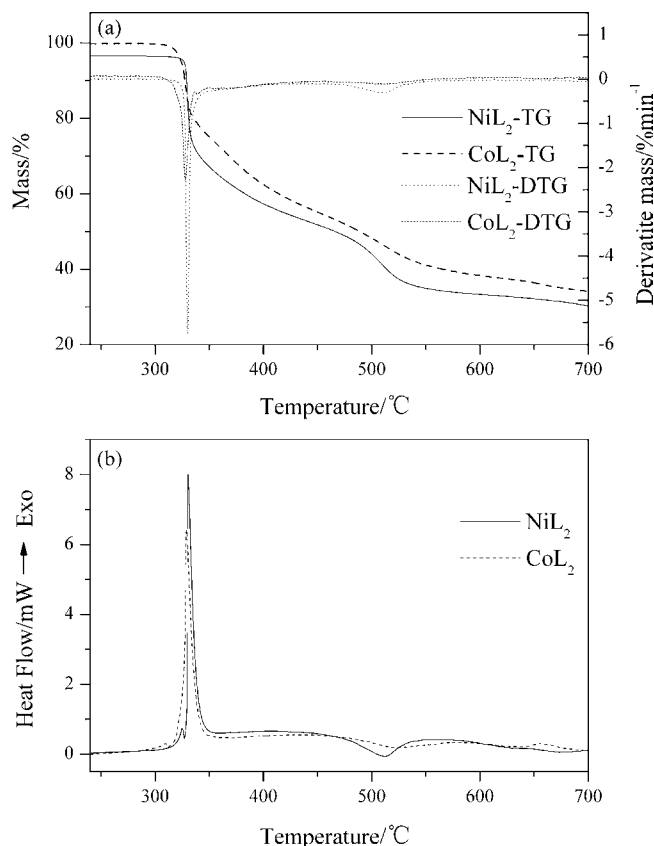


Fig. 2. (a) TG/DTG curves of the NiL₂ and CoL₂ complexes and their DSC curves (b) at the heating rate of 10 K min⁻¹.

Table 1Thermal analysis data of the NiL₂ and CoL₂ complexes.

Complexes	Stage	Temperature range (°C)	DTG peak (°C)	DSC peak (°C)	Mass loss (%)
NiL ₂	I	327.1–338.5	330.0	330.2	25.42
	II	338.5–700	510.7	512.2	30.89
CoL ₂	I	315.8–341.6	328.5	329.0	22.37
	II	341.6–700	518.2	524.9	43.52

and Table 1, it can be seen that the TG curves of NiL₂ and CoL₂ complexes show no any mass loss up to 300 °C, indicating the absence of water molecule and any other adsorptive solvent molecules in the coordination sphere. As the temperature increases, the TG/DTG curves of NiL₂ and CoL₂ complexes exhibit a sharp mass loss at the temperature of about 328.5–330.0 °C, which are accompanied by a sharp exothermic peak in the DSC curves. The correlations between the different decomposition steps of NiL₂ and CoL₂ complexes and the corresponding mass losses are discussed in terms of the proposed formulae of NiL₂ and CoL₂ complexes.

From the TG curve of the NiL₂ complex, it can be seen that decomposition starts at 327.1 °C and shows almost a continuous weight loss in the temperature range of 327.1–700 °C. Based on the percentage of mass losses and the DTG curve, two-step decomposition is proposed for this complex, which is similar to the decomposition pattern reported previously in the literature [11]. According to literature the azo bonds in the azo metal complexes breakdown when the temperature is higher than 280 °C resulting in the exothermic peaks [23]. The first decomposition step with an estimated mass loss of 25.42% within the temperature range 327.1–338.5 °C may be attributed to the loss of C₁₁H₁₃N₃O molecule (diazo moiety of the ligand) (calcd. 25.49%). The DTG peak corresponding to this stage is at 330.0 °C and the recorded DSC curve reveals a sharp exothermic peak at 330.2 °C. The second step of decomposition occurs after the rapid mass loss with an estimated mass loss of 30.89%, which may correspond to the degradation of the residual ligand molecules. The small and broad DTG peak corresponding to this stage is at 510.7 °C. The simultaneously recorded DSC curve also reveals a weak and broad endothermic peak at 512.2 °C. In the case of the CoL₂ complex, similar to the NiL₂ complex, the first step occurs within the temperature range of 315.8–341.6 °C with an estimated mass loss of 22.37%, which may also be attributed to the loss of diazo moiety of the ligand (calcd. 25.48%). The DTG peak corresponding to this stage is at 328.5 °C. The DSC curve shows an exothermic peak at 329.0 °C. When further heating up to 700 °C, a gradual decomposition occurs. This may be due to decomposition of the residual ligand molecules with an estimated mass loss of 43.52%. A broad peak at 518.2 °C and a small endothermic peak at 524.9 °C in the DTG and DSC curves, respectively were observed.

The above TG and DTG data show that the decomposition pattern of NiL₂ and CoL₂ complexes is similar. Both complexes underwent a two-step decomposition. The first decomposition process occurs in the temperature range of 320–350 °C, with steep thermal decomposition and high mass loss rate. These properties are important to a recording material. Suzuki et al. have reported the relation between the performance of disc and the thermal property of dye used for recording [24]. They think that the steep thermal decomposition makes the mark edge clear and reduces mark jitter. As we all know, the optical recording process (pit formation) owing to the decomposition of the complex is thought to occur as follows: when the complex is struck by a pulse of modulated laser, it absorbed the laser radiation and electronically excited, then the absorbed laser radiation is converted into heat. The complex is thermally stable up to its decomposition point and would be destroyed by the laser with an intensity above its decomposition threshold. Therefore, decomposition of the complex causes formation of the

recorded pits and at the same time generates and releases gas [25]. Based upon the above analysis, it becomes very necessary to understand the thermal decomposition kinetics of the NiL₂ and CoL₂ complexes. In the following, experimental results on the kinetics of the first decomposition process of the NiL₂ and CoL₂ complexes will be presented.

3.2. Non-isothermal kinetics of NiL₂ and CoL₂ complexes

The mass loss versus temperature curves of the thermal decomposition of NiL₂ and CoL₂ complexes were obtained from room temperature to 800 °C at the heating rates of 5, 10, 15 and 20 K min⁻¹, respectively, and under nitrogen atmosphere. For both complexes, delay in decomposition and shifts of the curves toward the higher temperature with increasing heating rate are observed. These shifts can be attributed to the variations in the rate of heat transfer with the change in the heating rate and the short exposure time to a particular temperature at the higher heating rates, as well as the effect of kinetics of decomposition [26]. Fig. 3 shows examples of experimental TG curves for the NiL₂ and CoL₂ complexes at the heating rate of 10 K min⁻¹.

The α -T and $d\alpha/dT$ curves at different heating rates for the first decomposition step of NiL₂ and CoL₂ complexes are gained from the TG data. Figs. 4 and 5 show the α -T and $d\alpha/dT$ curves at the heating rate of 10 K min⁻¹, respectively. Using the data, plots of $\ln \beta$ versus $1/T$ (FWO's equation) and $\ln(d\alpha/dT)$ versus $1/T$ (Friedman's equation) are obtained. From the slopes values ($-1.052E/R$ or $-E/R$), a number of activation energies are obtained, depending on the extent of conversion.

In order to evaluate the pre-exponential factor ($\ln A$), a prevalent approach is to assume a particular reaction model (e.g., first-order reaction), and to solve Eq. (3) or Eq. (4) by force-fitting the kinetic equation to the experimental data. However, Vyazovkin and Wight [27] revealed that force-fitting to a first order reaction model can lead to unreliable value of $\ln A$ for two reasons. First, this model-fitting method produces only one activation energy value for the

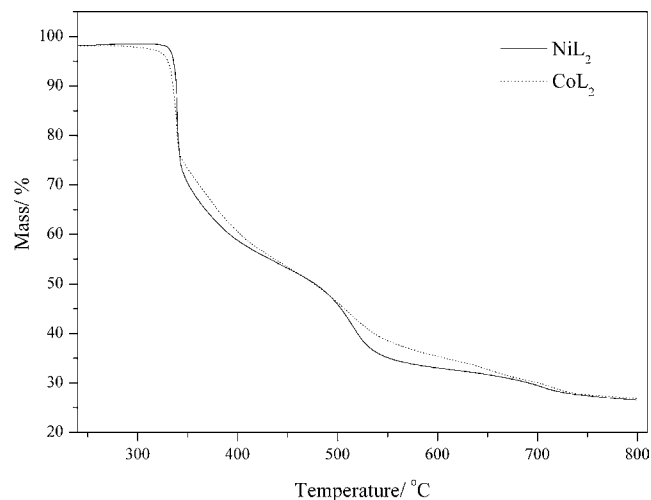


Fig. 3. TG curves of the NiL₂ and CoL₂ complexes at the heating rate of 10 K min⁻¹.

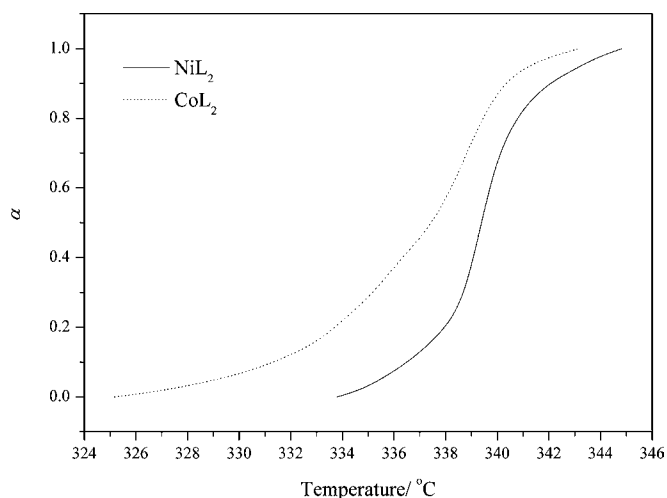


Fig. 4. Degree of conversion (α) as a function of temperature (T) in the first steps of the NiL_2 and CoL_2 complexes at the heating rate of 10 K min^{-1} .

reaction, but E_α may actually vary with the extent of conversion during the course of the reaction, which is generally observed especially in multi-step processes. In this case, the model-fitting method cannot be used to extract the information. Second, unless the reaction model can be determined by some independent means, it is often difficult to select among the different model functions on the basis of the best fits to the experimental data. Vyazovkin and Lesnikovich [28] have also revealed that incorrect identification of the reaction model results in errors in the values obtained for the pre-exponential factor.

In order to avoid questionable values of pre-exponential factor in this work the intercept in Y axis ($\ln[A_\alpha E_\alpha / Rg(\alpha)] - 5.3305$ and $\ln[Af(\alpha)]$) from plots of Ozawa–Flynn–Wall equation and Friedman equation are denoted as apparent pre-exponential factor ($\ln A_{\text{app}}$).

Fig. 6 shows the dependences of both the activation energy and apparent pre-exponential factor on the extent of conversion of the NiL_2 complex for the process being considered using FWO equation and Friedman equation. From Fig. 6, it can be found that the values of the activation energy demonstrate a noticeable variation with the extent of conversion (α), which is an evidence of the complex decomposition mechanism. From the conversion dependence of the activation energy using FWO equation, it can be seen that at the beginning of the dependence curve in the

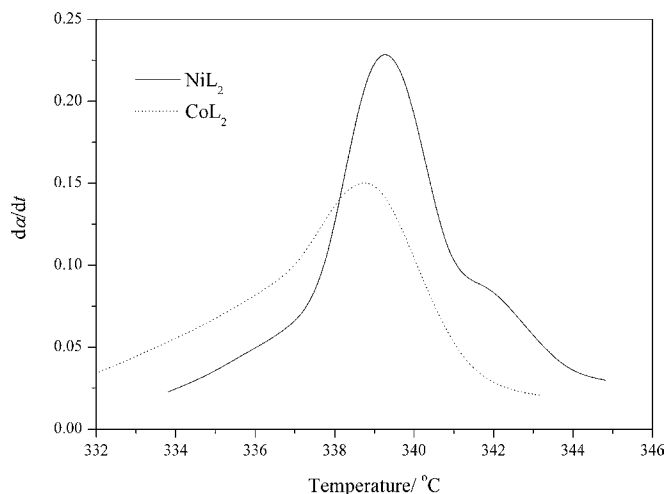


Fig. 5. Reaction rate curves of the NiL_2 and CoL_2 complexes at the heating rate of 10 K min^{-1} .

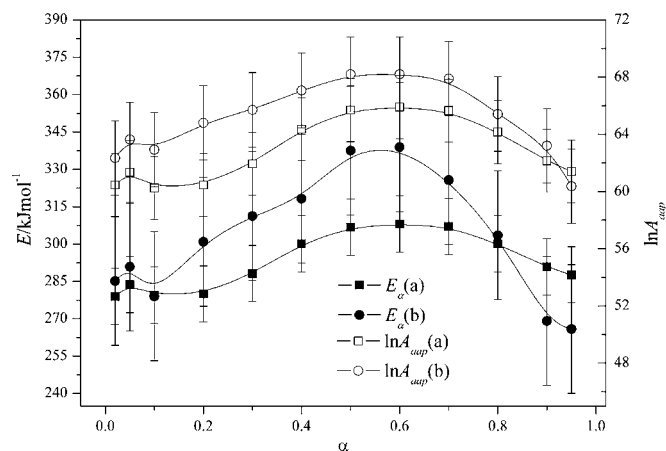


Fig. 6. Dependence of E_α and $\ln A_{\text{app}}$ on extent of conversion for decomposition of NiL_2 : E_α (a) and $\ln A_{\text{app}}$ (a) by FWO method and E_α (b) and $\ln A_{\text{app}}$ (b) by Friedman method.

conversion range 0.05–0.10, activation energy decreases from 283.7 to $279.5 \text{ kJ mol}^{-1}$. This behavior is an indication of a reversible reaction, such as $\text{solid} \leftrightarrow \text{solid} + \text{gas}$, which is found for many solid-state reactions [29]. With increasing extent of conversion to 0.60, activation energy increases to $308.1 \text{ kJ mol}^{-1}$. An increasing dependence of E_α on α is found for competing or consecutive reactions. Such processes occur frequently in solids, which decompose following a $\text{solid} \rightarrow \text{solid} + \text{gas}$ reaction [20]. After $\alpha = 0.60$, E_α decreases. The shape of decrease E_α on α may correspond to change in the mechanism from a kinetic to a diffusion regime [30]. In the case of using Friedman equation, the shape of the dependence of activation energy on the extent of conversion is almost similar to that obtained using FWO equation, but the activation energy is higher.

Fig. 7 shows the dependences of both the activation energy and apparent pre-exponential factor on the extent of conversion of the CoL_2 complex using FWO equation and Friedman equation. Similar to the NiL_2 complex, from the conversion dependence of the activation energy using FWO equation, it also can be seen that the CoL_2 complex also shows a decreasing dependence of E_α on α in the conversion range of 0.05–0.10 with the maximum value of $245.2 \text{ kJ mol}^{-1}$. As mentioned above, this behavior is found in reversible reactions, such as $\text{solid} \leftrightarrow \text{solid} + \text{gas}$ [29]. An increasing dependence of E_α on α is found with a maximum value of E_α , $287.0 \text{ kJ mol}^{-1}$, at $\alpha = 0.60$. This process may be also related to competing reactions or due to consecutive reactions [20]. The final

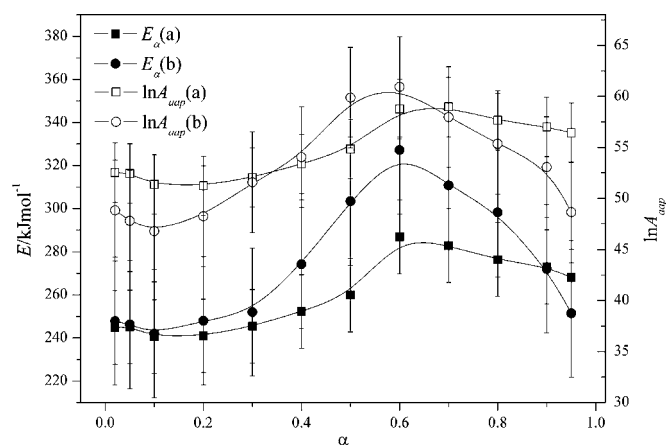


Fig. 7. Dependence of E_α and $\ln A_{\text{app}}$ on extent of conversion for decomposition of CoL_2 : E_α (a) and $\ln A_{\text{app}}$ (a) by FWO method and E_α (b) and $\ln A_{\text{app}}$ (b) by Friedman method.

decomposition stage occurs with a decreasing dependence of E_{α} on α . The shape of dependence of E_{α} on α may correspond to the change in the mechanism from a kinetic to a diffusion regime [30].

For NiL_2 and CoL_2 complexes, variation in the values of activation energy can be observed. The explanation for the variation of activation energy as a function of the extent of the conversion or reaction progress has been a controversial subject for many years. Galwey [31] reported several proposed explanations for the variation of E_{α} with the extent of conversion.

From Figs. 6 and 7, it is shown that the values of E_{α} and $\ln A_{\text{app}}$ calculated by different methods are comparable, indicating that the kinetic parameters thus obtained are reasonable. However, some values of activation energy, calculated by the FWO method, are lower than those obtained by the Friedman method. This is because the Friedman method is very sensitive to experimental noise, and so tends to be numerically unsound when employing instantaneous rate values. However, when E_{α} varies with the extent of conversion (α), the FWO method introduces some systematic error in estimating E_{α} . This error does not appear in the differential method of Friedman [32–34]. For this reason, integral and differential methods tend to produce somewhat different dependencies of E_{α} on α .

From Figs. 6 and 7, it also can be found that the NiL_2 complex demonstrates evidently higher activation energy than the CoL_2 complex. Hence, one can say that the NiL_2 complex possesses higher thermal stability than the CoL_2 complex. This can be discussed in terms of effect of coordination atoms of the ligand on d-orbital of the central ion. According to crystal field theory [35], the repulsion between negative charges of the ligand and d-orbital electron cloud of the central ion leads to the splitting of d-orbital energy level, which makes d-electron rearrange and system energy decrease, then produces extra crystal field stabilization energy (CFSE). Generally, the larger the CFSE is, the higher the stability of the complex is. Because the larger ionic size of Co(II) than Ni(II) results in a higher splitting energy, while the CFSE of CoL_2 is lower than that of NiL_2 , the NiL_2 complex has a higher stability than the CoL_2 complex.

4. Conclusions

Thermal decomposition kinetics of ML_2 ($\text{M}=\text{Ni(II)}$ and Co(II) ; $\text{L}=5-(2-(1,5\text{-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)hydrazono)-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione}$) were investigated by thermogravimetric analysis. The TG analysis shows that NiL_2 and CoL_2 complexes are thermally stable up to 300°C and the first decomposition process of NiL_2 and CoL_2 complexes occurs in the temperature range of $320\text{--}350^\circ\text{C}$. Kinetics parameters, such as activation energy, E_{α} , and apparent pre-exponential factor, $\ln A_{\text{app}}$, have been calculated from the thermogravimetric data at heating rates of 5, 10, 15 and 20Kmin^{-1} by differential (Friedman's equation) and integral (Flynn–Wall–Ozawa's equation) methods. The NiL_2 complex is more stable than the CoL_2 complex in terms of activation energy. From the dependence of E_{α} on extent of conversion it may be concluded that the decomposition reactions are typical multi-step

reactions. The thermal decomposition properties and decomposition kinetics of NiL_2 and CoL_2 complexes are very helpful to the design and synthesis of better optical recording media, and also provide a reference to investigation of metal complexes used in other high-technological frontier applications as key functional materials.

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