Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thermochimica Acta 443 (2006) 217–224

thermochimica acta

www.elsevier.com/locate/tca

# The decomposition kinetics of $[Et_4N]_2[M(dmit)_2]$ (M = Ni, Pd) in a nitrogen atmosphere using thermogravimetry

Antonio Gerson Bernardo da Cruz, James L. Wardell, Ana Maria Rocco *

*Grupo de Materiais Condutores e Energia, Instituto de Química, Universidade Federal do Rio de Janeiro Cidade Universitária,*
*Centro de Tecnologia, Bloco A, 21945-970 Rio de Janeiro, RJ, Brasil*

Received 25 October 2005; received in revised form 14 January 2006; accepted 24 January 2006
Available online 6 March 2006

## Abstract

Thermal properties and thermal decompositions of $[NEt_4]_2[M(dmit)_2]$ (M = Ni(II), Pd(II), dmit = 1,3-dithiole-2-thione-4,5-dithiolate) have been studied by thermogravimetry (TG). The TG analysis has shown that the complexes are thermally stable up to 460 K and the decomposition of the complexes occurs in three consecutive stages up to 873 K. A thermal stability scale for $[M(dmit)_2]^{n-}$ anions was based on the thermal properties. Kinetics parameters, such as activation energy, $E_a$, and kinetic apparent pre-exponential factor, $\ln A_{app}$, have been calculated from the thermogravimetric data at heating rates of 10, 15, 20 and 25 K/min involving differential (Friedman's equation) and integral (Flynn-Wall-Ozawa's equation) methods.

*Keywords:* Thermal kinetics; bis(1,3-Dithiole-2-thione-4,5-dithiolato); Dmit; Nickel(II) and palladium(II) complexes; Activation energy; Thermal decomposition

## 1. Introduction

Compounds containing the heterocyclic dianion 1,3-dithiole-2-thione-4,5-dithiolato, $[C_3S_5]^{2-}$, $[dmit]^{2-}$, have been the subject of a substantial amount of research. The extensive research has been facilitated by the efficient synthesis of $[dmit]^{2-}$ by alkali metal reduction of carbon disulfide, see Scheme 1 [1,2]. The interest in this anion is primarily as a precursor to electronic and photonic materials [3]. The coordination complexes of $[dmit]^{2-}$, especially those of nickel and palladium, have been particularly well studied. Various papers have been published on salts of $[M(dmit)_2]^{n-}$ (M = Ni and Pd and $0 < n < 2$). The interest is due to the discovery that certain salts of $[M(dmit)_2]^{n-}$ (M = Ni, Pd), have metallic-like conductivity. At least, eight $[M(dmit)_2]^{n-}$ salts (M = Ni, Pd) are found to be superconductors [4].

While the organic and coordination chemistries and crystal structure of dmit-containing compounds have been examined extensively [5–8], thermal behaviour and thermal properties of these compounds are rare in literature. Among the very few reports on the thermal behavior of dmit complexes are those on Co, Cd and Zn dmit complexes [9,10]. There clearly remains much to investigate in the area of thermal properties of dmit compounds. In materials science, thermal properties have crucial importance.

To complete the characterization of these compounds we have investigated the thermal properties and the thermal decomposition kinetics of $[Et_4N]_2[M(dmit)_2]$ complexes (M = Ni, Pd). Kinetic parameters such as activation energy, $E_a$, and apparent pre-exponential factor, $\ln A_{app}$, have been calculated using both the Friedman [11] and Flynn-Wall-Ozawa (FWO) [12,13] methods. We now report our results.

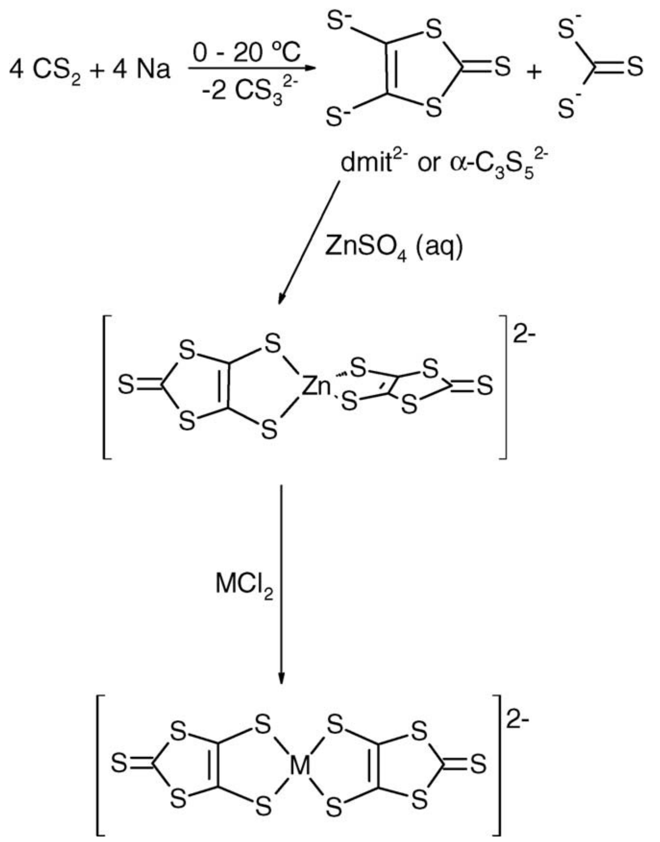
## 2. Kinetic studies

The Arrhenius parameters, $\ln A$, $E_a$, together with the reaction model are sometimes called the kinetic triplet. The correlation of kinetic parameters with the apparent kinetic model does not allow a correct analysis to be obtained from only one experimental TG–DTG curve [14]. This problem can be solved, however, if a multiple-scan method is employed.

---

* Corresponding author. Tel.: +55 212 562 7250; fax: +55 212 562 7559.
*E-mail address:* amrocco@iq.ufrj.br (A.M. Rocco).

0040-6031/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2006.01.027



Scheme 1. Simplified synthetic pathway for $[M(dmit)_2]^2$ complexes.

### 2.1. Calculation of the activation energy

For kinetic analysis, model-free isoconversional methods play an important role. These methods are based on the isoconversional principle that states that the reaction rate at a constant extent of conversion is only a function of the temperature [15].

$$\frac{d\ln(d\alpha/dt)_\alpha}{dT^{-1}} = -\frac{E_a}{R} \tag{1}$$

Henceforth, the subscript $\alpha$ will indicate the values related to a given extent of conversion. By rearranging Eq. (1), one can arrive at Eq. (2)

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta\frac{d\alpha}{dT}\right) = \ln[A(f(\alpha))] - \frac{E_a}{RT} \tag{2}$$

where $f(\alpha)$ is a function called reaction model (RO) which describes the dependence of the reaction rate on the extent of reaction, $T$ is the temperature, $E_a$ and $\ln A$ are the Arrhenius parameters (activation energy and pre-exponential factor, respectively) and $R$ is the molar gas constant (8.314 J/K mol).

The Eq. (2) is the basis of the differential isoconversional method of Friedman [11]. By ploting $\ln(d\alpha/dt)$ against $1/T$, one directly obtains $-E_a/R$ for a given value of $\alpha$.

Use of Eq. (1) in its integral form and the linear Doyle's approximation ($\ln p(x) = -1.052x - 5.331$) [16,17] ($p(x) \approx \exp(-x)/[x(x+2)]$) allows one to arrive at Eq. (3)

$$\ln(\beta) = \ln\left[\frac{AE_a}{Rg(\alpha)}\right] - 5.331 - 1.052\frac{E_a}{RT} \tag{3}$$

where $\beta$ is the heating rate, $g(\alpha)$ is a function called reaction model. The Eq. (3) is the basis of the integral isoconversional methods of Flynn and Wall [12] and Ozawa (FWO) [13]. For a given value of $\alpha$, the plots of $\ln\beta$ versus $1/T$, shows straight lines whose slopes give $-E_a/R$ values.

In order to avoid questionable values of pre-exponential factor in this work the intercept in $Y$ axis $n$ ($\ln[A(f(\alpha))]$ and $\ln[AE_a/Rg(\alpha)]-5.331$) from plots of Friedman and Flynn-Wall-Ozawa are denoted as apparent pre-exponential factor ($\ln A_{app}$).

The Friedman method and the FWO method are both "model free" methods based on multiple heating rate experiments, where a kinetic model is not required to calculate the activation energy.

## 3. Experimental

### 3.1. Preparation of solid $[Et_4N]_2[M(dmit)_2]$ complexes

$[Et_4N]_2[Zn(dmit)_2]$ was synthesized according to a literature procedure [1]. To a red solution $[Et_4N]_2[Zn(dmit)_2]$ (1 mmol) in MeOH (30 ml) was added an aqueous solution of $NiCl_2 \cdot 6H_2O$ (1 mmol in 10 ml) or $PdCl_2$ (1 mmol in 10 ml). The reaction mixture was stirred for 24 h at room temperature, the dark green $[Et_4N]_2[Ni(dmit)_2]$ or brown $[Et_4N]_2[Pd(dmit)_2]$ precipitate was collected by filtration and recrystallized from MeOH. Yield: 86% (Ni); 78% (Pd).

### 3.2. Characterization

#### 3.2.1. IR and UV–vis spectroscopy

Fourier transform infrared spectra (FTIR) of the solid samples in CsI pellets were recorded using a Nicolet 760 Magna-IR spectrometer, in the region 4000–400 $cm^{-1}$. UV–vis spectra in $CH_3CN$ solution were obtained using an HP845a diode array spectrophotometer.

#### 3.2.2. Thermal analysis (TGA)

Thermogravimetric analysis (TGA) curves were obtained using a TGA 50H Shimadzu Instrument in a dynamic atmosphere of nitrogen (50 $cm^3$/min) at different heating rates (10, 15, 20 and 25 K/min) from room temperature to 873 K, with 10 mg samples. The TG–DTG data were used to obtain kinetic parameters using both the Friedman and Flynn-Wall-Ozawa method.

## 4. Results and discussion

### 4.1. Absorption (UV–vis) and vibrational spectroscopy (FTIR)

The UV–vis spectra of the complexes showed absorption bands at 226, 262, 314, 402 and 586 nm ($[Et_4N]_2$ $[Ni(dmit)_2]$) and 220, 278, 316, 438 ($[Et_4N]_2$ $[Pd(dmit)_2]$) ascribed to $\pi$–$\pi^*$ intraligand transitions of the $dmit^{2-}$. The bands in the region at 430–590 nm correspond to characteristic bands as also observed

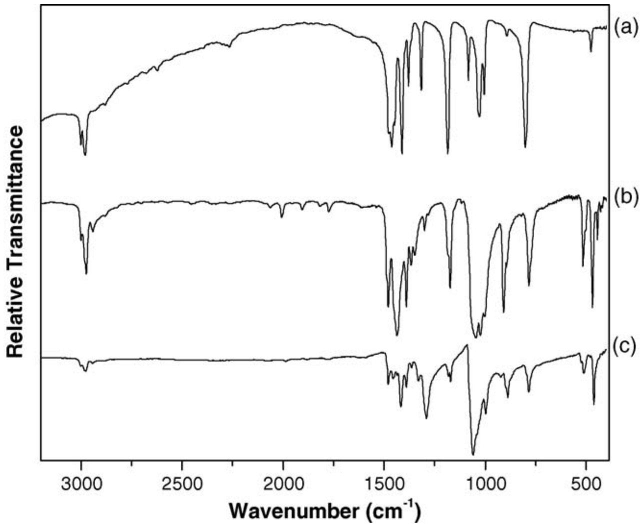


Fig. 1. Infrared vibrational spectrum for (a) $Et_4NBr$ (b) $[Et_4N]_2$ [Ni(dmit)$_2$] and (c) $[Et_4N]_2$ [Pd(dmit)$_2$].

for [Na$_2$(dmit)] and [Zn(dmit)$_2$]$^{2-}$ [18]. The band at 314 [Ni complex]/316 nm [Pd complex] can be assigned to the d–p interaction due to interaction between the d orbitals (metal ion) with the p orbitals of the dmit moieties [19,20].

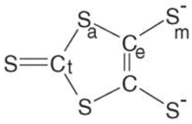
Fig. 1 shows the infrared spectra of $[Et_4N]_2$ [M(dmit)$_2$] as well as that of $Et_4NBr$. Each of the square planar [M(dmit)$_2$]$^{2-}$ (M = Ni or Pd) dianions possess a $D_{2h}$ structural symmetry, and has 45 vibrational modes. These modes may be classified as Raman active ($8_{Ag} + 7B_{1g} + 4B_{2g} + 2B_{3g}$), silent ($3_{Au}$), and infrared active ($5B_{1u} + 8B_{2u} + 8B_{3u}$). The $B_{3u}$ are out-of-plane vibrations and the $B_{1u}$ and $B_{2u}$ are in-plane vibrational modes. The band at ≈1028 cm$^{-1}$ is assigned to the C=C displacement out of plane. The band at ≈1059 cm$^{-1}$ is assigned to S–C–S + C=S stretch and the band at ≈1454 cm$^{-1}$ is assigned to C=C stretch [21–24].

The bands at 3000 and 2979 cm$^{-1}$ and the low intensity bands at 1500 and 1100 cm$^{-1}$, 785 and 419 cm$^{-1}$ are assigned to the tetraethylammonium cation. Table 1 lists the most important bands and assignments for both complexes.

Table 1
Assignments for the vibrational frequencies in the [M(dmit)$_2$]$^{2-}$ dianion

| Wavenumbers (cm$^{-1}$) | Mode description assignment |
|---|---|
| 1444 | $\nu$(C=C) |
| 1419 | $\nu$(C=C) |
| 1053 | $\nu$(C=S) |
| 1034 | $\nu$(C=S) |
| 1001 | $\nu$(Ce-S$_m$) |
| 895 | $\nu(C_e–S_m) + \nu(C_e–Sa)$ |
| 523 | $\nu(C{=}S) + \nu(Ct–S)$ |
| 463/453 | $\omega(SC_tS) + \nu(C_e–S_m) + \nu(C_e–S_a)$ |
| 441 | $\omega(SC_tS)$ |

$\nu$: (strefcmng mode), $\omega$: (wagging mode),



.

### 4.2. Thermogravimetric analysis (TGA)

Both complexes were studied by thermogravimetric analysis from room temperature to 873 K in a nitrogen atmosphere. The temperatures ranges of the decomposition stages, DTG$_{(max)}$ and weight loss data for the $[Et_4N]_2$[M(dmit)$_2$] (M = Ni, Pd) and $Et_4NBr$ are listed in Table 2.

The TG–DTG curves at the heating rate of 10 K/min for the $[Et_4N]_2$ [M(dmit)$_2$] (M = Ni, Pd) and $Et_4NBr$ are shown in Fig. 2(a)–(c). The decompositions of the $[Et_4N]_2$ [M(dmit)$_2$] complexes occur in three stages without formation of thermally stable intermediates, while the decomposition of $Et_4NBr$ occurs is a single stage reaction.

#### 4.2.1. $[Et_4N]_2$ [Ni(dmit)$_2$]

From the TG–DTG curve in Fig. 2(a), it can be seen that $[Et_4N]_2$ [Ni(dmit)$_2$] is thermally stable up to 440 K, but then decomposes in three stages. The first stage, between 440 and 491 K, brings a 10.15% mass loss. The second one occurs in the temperature range of 491–540 K and is associated with a 26.11% mass loss. The third stage occurs in the temperature range of 540–663 K, with a 22.20% mass loss. Mass loss was still being observed up to 873 K.

#### 4.2.2. $[Et_4N]_2$ [Pd(dmit)$_2$]

The TG–DTG curve of $[Et_4N]_2$ [Pd(dmit)$_2$], see Fig. 2(b), indicates that the complex is thermally stable up to 463 K. The decomposition, as does that of $[Et_4N]_2$ [Ni(dmit)$_2$] occurs in three distinct stages: in the temperature ranges 463–520, 520–571 and 571–680 K the weight losses are 12.23, 11.08 and 7.48%, respectively. As with $[Et_4N]_2$ [Ni(dmit)$_2$], mass loss was still being observed up to 873 K.

#### 4.2.3. General considerations on the thermolysis

Initially it was considered that the first decomposition stage was related to the decomposition of the cation and loss of lower-mass and volatile fragments. Indeed, the thermal analysis of the $Et_4NBr$ shows only one decomposition step in the range of 453–873 K as can be seen in Fig. 2(c). The decomposition of $Et_4NBr$ starts at about 453 K, which is similar to the temperatures observed for the complexes. However, the mass losses found for $[Et_4N]_2$ [M(dmit)$_2$], are not in agreement with the value calculated for the loss of the cation.

The thermal decomposition products of dmit and dithiolene compounds have not been reported previously in the literature. We can only make assumptions about the products formed during the decomposition of $[Et_4N]_2$ [M(dmit)$_2$]. However, metal, e.g., Mn(II), Fe(II), Ni(II), Cu(II) and Zn(II), complexes with the ligand cyanodithiolformate, which have some structural similarities with dithiolene complexes, have been studied by Prasad [25]. This study provides a guide to the products obtained from the dmit compounds. The first mass loss may correspond to the loss of two CS fragments from the dmit ring. The second and third decomposition stages may correspond to the loss of $CS_2$. The coefficient of the products may change from a complex to other due to metal-ligand bonding force and/or ionic size ($r$).

Table 2
Stages, temperatures ranges, $DTG_{(max)}$ and weight loss data for the $[Et_4N]_2[\mathbf{M}(dmit)_2]$ ($\mathbf{M}$ = Ni, Pd) and for the $Et_4NBr$ salt

| Complexes | Stage | Temperature range (K) | $DTG_{(max)}$ (K) | Mass loss (%) |
|---|---|---|---|---|
| $[Et_4N]_2[Ni(dmit)_2]$ | I | 440–491 | 473.2 | 10.15 |
| | II | 491–540 | 513.7 | 26.11 |
| | III | 540–663 | 575.0 | 22.20 |
| $[Et_4N]_2[Pd(dmit)2]$ | I | 463–520 | 513.0 | 12.23 |
| | II | 520–571 | 537.2 | 11.08 |
| | III | 571–680 | 580.3 | 7.48 |
| $Et_4NBr$ | I | 453–873 | 609.2 | 99.97 |

Different coefficients and products were observed for the compounds of cyanodithiolformate [25].

Even if the observed mass losses were in agreement with specific calculated values, the TGA technique, being involved with just mass loss, cannot provide any structural information of the decomposition products.

Melo et al. observed a similar multiple-step thermal decomposition for an unspecified dmit based cobalt complex [9]. They observed three decomposition stages at 400–570, 570–710 and 710–850 K. These values are lower than those obtained in our study. Incredibly Melo et al. did not specify which cobalt-dmit complex they were studying. Some of us have investigated the thermal stabilities of $[Q][Bi(dmit)_2]$ complexes (Q = tetraalkylammonium and dimethylpyridinium). Interestingly here too, a three stage decomposition process for the $[Et_4N][Bi(dmit)_2]$ complex [26] was observed. In this case, the ranges found, 443–518, 518–603 and 603–663 K, are close to those found for the Ni and Pd complexes. By considering the temperatures for the onset of decompositions for dmit-complexes, a thermal stability scale can be established as $[Et_4N]_2[Pd(dmit)_2] > [Et_4N][Bi(dmit)_2] > [Et_4N]_2[Ni(dmit)_2] > [Q]_x[Co(dmit)_y]$, where Q = cation, $x$ and $y$ are integers.

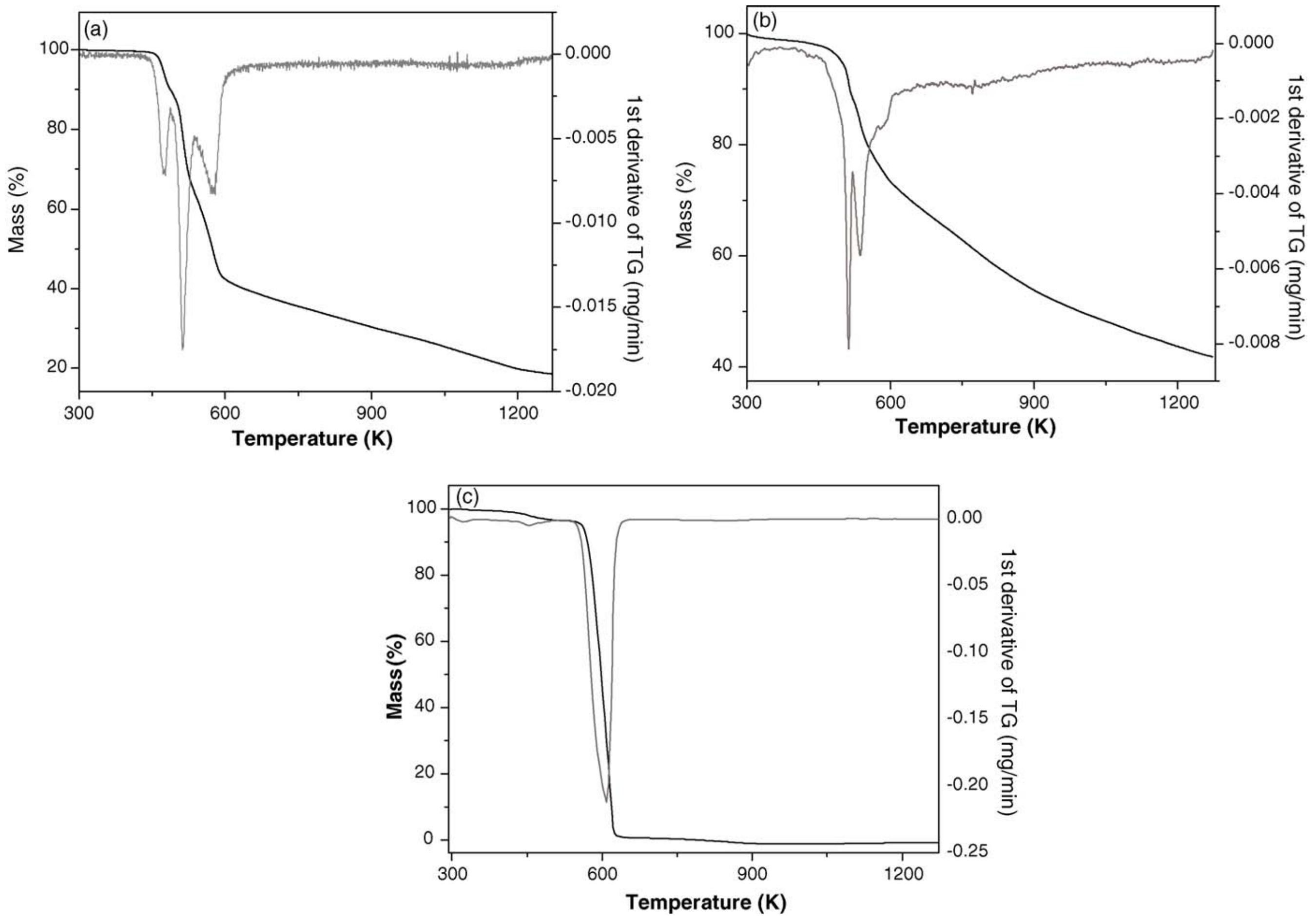


Fig. 2. TG–DTG curves for (a) $[Et_4N]_2$ $[Ni(dmit)_2]$, (b) $[Et_4N]_2$ $[Pd(dmit)_2]$ and (c) $Et_4NBr$ at a heating rate of 10 °C/min.

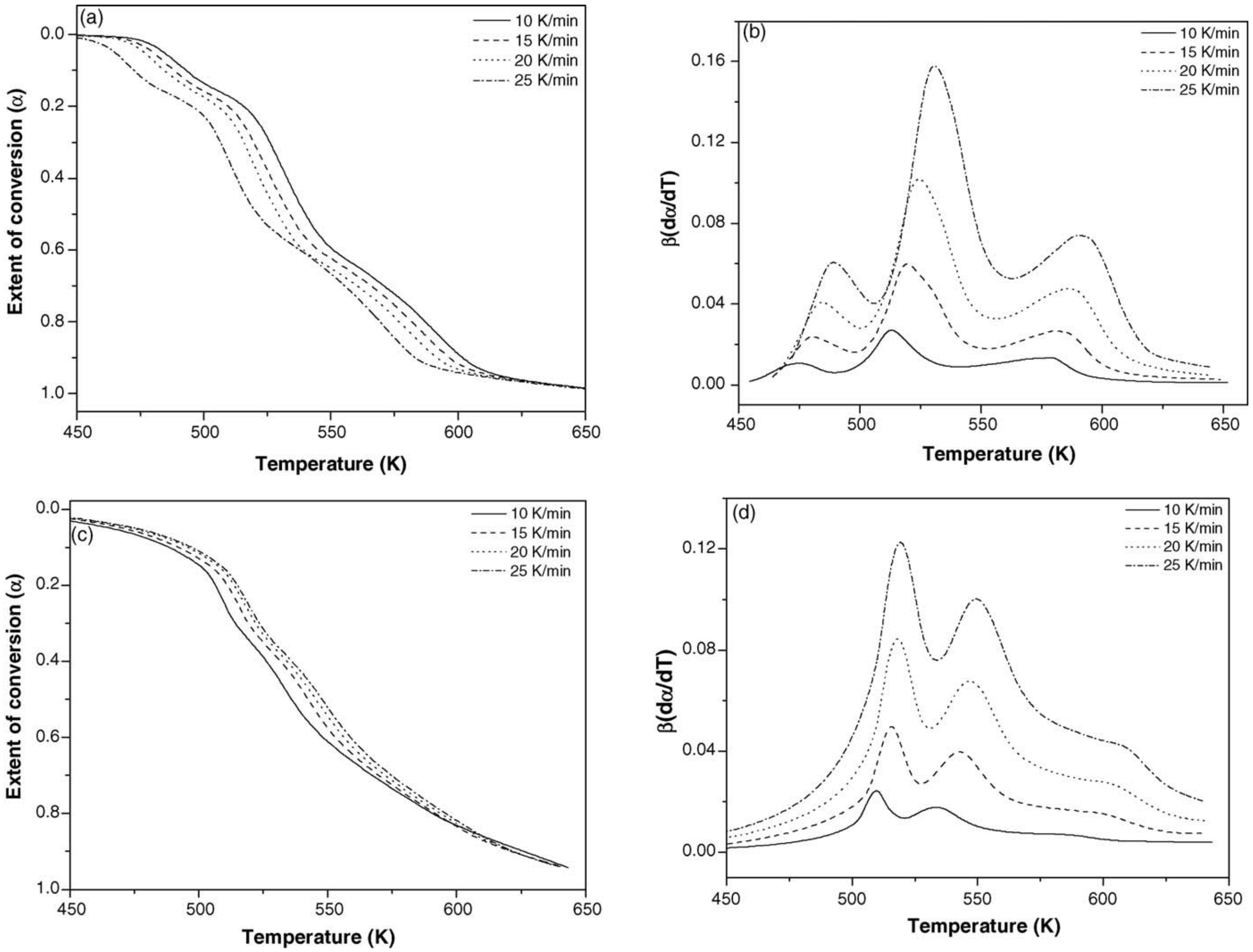


Fig. 3. (a) $\alpha$–$T$ curves for $[Et_4N]_2$ $[Ni(dmit)_2]$ at different heating rates. (b) Reaction rate curves for $[Et_4N]_2$ $[Ni(dmit)_2]$ at different heating rates. (c) $\alpha$–$T$ curves for $[Et_4N]_2$ $[Pd(dmit)_2]$ at different heating rates. (d) Reaction rate for $[Et_4N]_2$ $[Pd(dmit)_2]$ at different heating rates.

### 4.3. Evaluation of kinetics parameters

The $\alpha-T$ and $d\alpha/dt-T$ plots obtained for the $[Et_4N]_2$ $[M(dmit)_2]$ (M = Ni, Pd) complexes at different heating rates are shown in Fig. 3(a)–(d). Using these data, plots of $\ln(d\alpha/dt)$ versus $1/T$ (Friedman's equation) [11] and of $\ln\beta$ versus $1/T$ (FWO's equation) [12,13] are obtained. From the slopes values ($E_a/R$), a number of activation energies are obtained, with all depending on the extent of conversion.

In order to estimate the pre-exponential factor, $\ln A$, some authors assume the thermal decomposition to be a series of successive first-order. With the reaction order $n$ as unity, the intercept in $Y$ axis is $\ln A$.

It should be emphasized that by this method the pre-exponential factor can be evaluated. However, the force-fitting to a first order reaction model cannot lead to reliable values of $\ln A$. Vyazovkin and Kesnikovich [27] have clearly shown that incorrect identification of the reaction model leads to errors in the values obtained for the pre-exponential factor. Vyazovkin also showed that as they cannot be estimated independently of $E_a$, being subjected to a linear relationship between the activation energies ($E_a$) and the logarithm of the pre-exponential factors ($\ln A$) denoted as compensation effect [28]. A model independent estimate of pre-exponential factor can only be obtained though the use of an artificial isokinetic relationship (IKR) [28].

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

In Fig. 4(a) and (b) are shown the dependences of both the activation energy and apparent pre-exponential factor on the extent of conversion of the Ni complex. From the graphs, approximately four $E_a$ maximum values can be detected, indicating that the thermal decomposition of the Ni complex occurs in more than three steps.

The first stage of the decomposition occurs in one step with a decrease in the dependence of $E_a$ on $\alpha$, in the range of 100–130 kJ/mol. This behavior is an indication of a reversible reaction, such as solid ↔ solid + gas, which is found for many solid-state reactions [28]. In the second step, we see more than one $E_a$ maximum. We can suppose that the second stage of the thermal decomposition occurs in 2–3 steps with a maximum

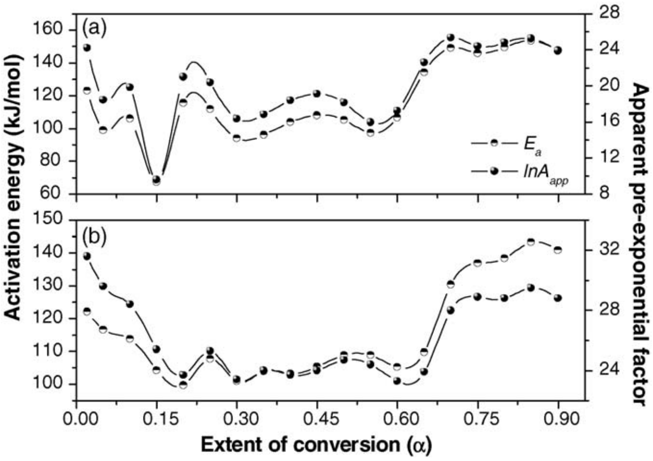


Fig. 4. Dependence of the $E_a$ and $\ln A_{app}$ on extent of conversion for decomposition of $[Et_4N]_2$ $[Ni(dmit)_2]$ (a) using Friedman method and (b) using FWO method.

value of $E_a$ in the range of 100–115 kJ/mol. Increasing dependence of $E_a$ on $\alpha$ is found in competing or consecutive reactions. Such processes also occur frequently in solids, which decompose according to a solid → solid + gas reaction, and which are related to processes proceeding with a change from a kinetic to a diffusion regime [29]. Increasing dependence of $E_a$ on $\alpha$ is also found for the third stage, which occurs in a single step with $E_a$ maximum values in the range of 130–150 kJ/mol. In this latter stage, we observe quasi-constant $E_a$ values, which suggest an independence of $E_a$ on the extent of decomposition. The increasing dependence on $E_a$ has been related previously to competing reactions or due to consecutive reactions [26,28].

In Fig. 5(a) and (b) are shown the dependences of both the activation energy and apparent pre-exponential factor on the extent of decomposition of the Pd complex. Similarly to the Ni complex, the Pd complex also shows a decreasing dependence of $E_a$ on $\alpha$ in the first decomposition stage with maximum values in the range of 200–340 kJ/mol. As mentioned above, this behavior is found in reversible reactions such as solid ↔ solid + gas [28]. The second decomposition stage occurs in 1–2 steps with a maximum value of $E_a$ in the range of 220–350 kJ/mol, with increasing dependence of $E_a$ on $\alpha$. The third decomposition stage occurs with an increasing dependence of $E_a$ on $\alpha$ and appears to involve 2–3 steps with a maximum value of $E_a$ in the range of 300–500 kJ/mol. As mentioned above, the increasing dependence of $E_a$ on $\alpha$ may be related to competing reactions or due to consecutive reactions [26,28].

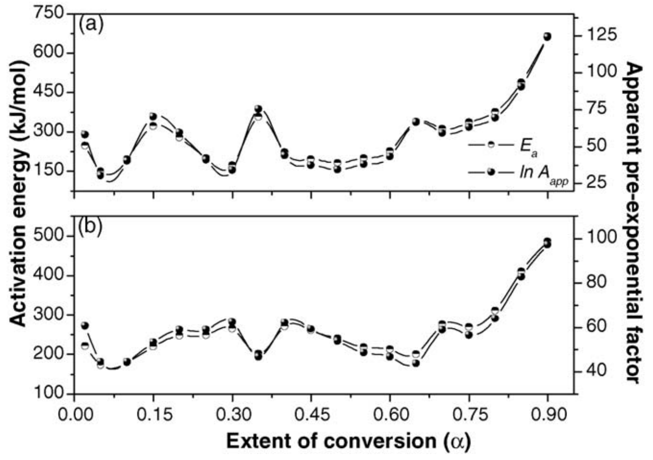


Fig. 5. Dependence of the $E_a$ and $\ln A_{app}$ on extent of conversion for decomposition of $[Et_4N]_2$ $[Pd(dmit)_2]$ (a) using Friedman method and (b) using FWO method.

For both complexes, a variation in the values of the activation energy can be observed, see Figs. 4 and 5. Vyazovkin [28] has shown this behavior in homogeneous phases. 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, with several proposed explanations for the variation of $E_a$ with the extent of the conversion, see the review by Galwey [30].

A variation in activation energy can be observed for both elementary and complex reactions. An elementary reaction can show variable activation energy during its progress, as a result of product formation and the consequent heterogeneous nature of the residual solid sample. Such changes lead to systematic changes in the reaction kinetics. Solid-state reactivity of an elementary reaction could also be affected by experimental variables that can change at a reaction interface.

The reaction is called a complex reaction if two or more elementary steps, each having unique activation energies, control the rate of product formation. In such a reaction, a change in the activation energy would be observed as the extent of conversion increase. This change will depend on the contribution of each elementary step, which gives an “effective” activation energy that varies with the extent of the conversion. Kinetic complexities are not limited to multiple chemical steps. They may also include physical processes having different activation energies. The experimental activation energies and pre-exponential factors are listed in Table 3.

A comparison of the dependence of $E_a$ on $\alpha$ for the complexes shows that the $E_a-\alpha$ dependences sometimes show a drastic drop in the $E_a$ values. This usually occurs at the point of transition from one mass loss step to another, when the reaction rate shows a marked decrease.

The first decomposition stage shows a decrease of the activation energy for $[Et_4N]_2[M(dmit)_2]$ (M = Ni, Pd) using both methods. At the beginning of the second stage as shown by both methods, the activation energy increases for both complexes, with higher values for the Pd complex.

At the end of the third decomposition stage for each complex, the process evidently accelerates with more than 40% weight loss occurring in the temperature range of 540–680 K. For both complexes, the highest decomposition rates were reached at the end of the third step, with some changes in the activation energy.

On the basis of these results, the proposed stability scale is confirmed and the second step (Pd) and third step (Ni) show higher $E_a$ values and represent the rate-determining steps.

Some values of the activation energy, calculated by the FWO method, are lower than those obtained by the Friedman method.

Table 3
Activation energies "$E_a$" and apparent pre-exponential factor "$\ln A_{app}$" of $[Et_4N]_2[Ni(dmit)_2]$ and $[Et_4N]_2[Pd(dmit)_2]$ using Friedman and FWO methods

| α | $TEA_2$ Ni-$dmit_2$ | | | | $TEA_2$ Pd-$dmit_2$ | | | |
|---|---|---|---|---|---|---|---|---|
| | Friedman method | | FWO method | | Friedman method | | FWO method | |
| | $E_a$ (kJ/mol) | $\ln A_{app}$ | $E_a$ (kJ/mol) | $\ln A_{app}$ | $E_a$ (kJ/mol) | $\ln A_{app}$ | $E_a$ (kJ/mol) | $\ln A_{app}$ |
| 0.02 | 123.0 | 24.2 | 122.2 | 31.6 | 247.9 | 58.2 | 221.6 | 60.7 |
| 0.05 | 98.9 | 18.5 | 116.7 | 29.6 | 149.9 | 30.3 | 173.2 | 44.5 |
| 0.10 | 106.1 | 19.8 | 113.8 | 28.4 | 194.4 | 40.3 | 179.7 | 44.4 |
| 0.15 | 67.3 | 9.6 | 104.3 | 25.4 | 322.7 | 70.3 | 220.1 | 53.2 |
| 0.20 | 115.7 | 21.0 | 99.7 | 23.7 | 277.7 | 59.4 | 247.1 | 59.0 |
| 0.25 | 111.9 | 20.4 | 107.8 | 25.3 | 200.1 | 41.1 | 249.2 | 59.0 |
| 0.30 | 94.1 | 16.4 | 100.9 | 23.4 | 172.3 | 34.2 | 265.4 | 62.4 |
| 0.35 | 96.1 | 16.8 | 104.0 | 24.0 | 356.6 | 75.3 | 201.7 | 46.8 |
| 0.40 | 103.9 | 18.4 | 103.3 | 23.7 | 222.3 | 44.0 | 271.2 | 62.1 |
| 0.45 | 108.0 | 19.1 | 105.4 | 24.0 | 194.4 | 37.5 | 261.7 | 59.3 |
| 0.50 | 105.3 | 18.2 | 108.9 | 24.7 | 181.5 | 34.3 | 240.2 | 53.9 |
| 0.55 | 97.3 | 15.9 | 108.8 | 24.4 | 200.4 | 38.1 | 218.4 | 48.6 |
| 0.60 | 106.7 | 17.3 | 105.2 | 23.3 | 226.8 | 43.1 | 212.6 | 46.8 |
| 0.65 | 134.4 | 22.6 | 109.8 | 23.9 | 339.1 | 66.2 | 201.0 | 43.6 |
| 0.70 | 149.2 | 25.3 | 130.4 | 28.0 | 311.1 | 58.9 | 276.3 | 59.0 |
| 0.75 | 146.0 | 24.4 | 137.0 | 28.9 | 336.3 | 62.9 | 270.1 | 56.6 |
| 0.80 | 149.6 | 24.8 | 138.4 | 28.8 | 375.55 | 69.5 | 311.1 | 64.0 |
| 0.85 | 153.6 | 25.3 | 143.3 | 29.5 | 488.9 | 90.4 | 411.4 | 82.9 |
| 0.90 | 147.7 | 23.9 | 140.9 | 28.8 | 664.9 | 124.1 | 486.6 | 97.2 |

TEA = tetraeihylammonium; $\ln A_{app}$ = the intercept in $Y$ axis.

This is due to the Friedman method being very sensitive to experimental noise, and so tends to be numerically unsound when employing instantaneous rate values. However the FWO method produces a systematic error in $E_a$ when it varies with. This error does not arise in the Friedman method [15].

As a summary, the thermal decomposition of the complexes shows that for both complexes the second stage is the rate-determining step and from the $E_a/\alpha$ graphs the first decomposition step contains an initial reversible step such as solid ↔ solid + gas and other irreversible steps.

## 5. Conclusion

In this paper, the thermal properties and thermal decomposition of $[Et_4N]_2[M(dmit)_2]$ complexes (M = Ni or Pd; dmit = 1,3-dithiole-2-one-4,5-dithiolate) have been studied by thermogravimetry (TG). The TG analysis has shown that the complexes are thermally stable up to 440 K and their decomposition occurs in three consecutive stages up to 873 K. Kinetic parameters such as activation energies, $E_a$, and kinetic apparent pre-exponential factor, $\ln A_{app}$, have been determined from the thermogravimetric data using heating rates 10, 15, 20 and 25 K/min involving differential (Friedman's equation) and Integral (Flynn-Wall-Ozawa's equation) methods. The Pd complex, $[Et_4N]_2[Pd(dmit)_2]$ is slightly more stable than the Ni analogue. From the dependence of $E_a$ on extent of conversion it may be concluded that the reactions under consideration are typical complex muti-step reactions. The $E_a-\alpha$ dependence values are in agreement with the stability scale found for the dmit complexes.

## Acknowledgements

Authors thank Capes and CNPq for fellowships, and FAPERJ for financial support (proc. No. E-26/170.700/2004). To N. M. Comerlato and G. B. Ferreira for supplying the $[NEt_4]_2[Zn(dmit)_2]$ complex. To Janaína Lopes Leitinho and Laboratório de Análises Térmicas Ivo Giolito (DQOI-UFC) for the Thermogravimetric Analysis.

## References

[1] G. Steimecke, H.–J. Sieler, R. Kirmse, E. Hoyer, Phosporous Sulfur 7 (1979) 49.
[2] L. Yu, D. Zhu, Phosporous Sulfur 116 (1996) 225.
[3] I. Malfant, N. Cordente, P.G. Lacroix, C. Lepetit, Chem. Mater. 10 (1998) 4079.
[4] P. Cassoux, L. Valade, H. Kobayashi, R.A. Clark, A.E. Underhill, Coord. Chem. Rev. 110 (1991) 115.
[5] P. Cassoux, L. Valade, in: W.D. Bruce, D. O'Hare (Eds.), Inorganic Materials, Wiley, New York, 1992.
[6] H. Tajima, M. Inokachi, A. Kobayashi, A. Sato, T. Naito, H. Kobayashi, H. Kuroda, Synth. Met. 85 (1997) 1585.
[7] A.E. Underhill, B. Girmay, J.D. Kilburn, Synth. Met. 55–57 (1993) 1920.
[8] C.S. Winter, S.N. Cliver, R.T. Manning, J.D. Rush, C.A.S. Hill, A.E. Underhill, J. Mater. Chem. 2 (1992) 443.
[9] D.M.A. Melo, F.M.M. Borges, F.J.S. Lima, H. Scatena Jr., L.B. Zinner, V.J. Fernandes, W.S.C. Souza, Z.R. Silva, J. Therm. Anal. Calorim. 56 (1999) 805.
[10] Z.R. Lu, Y.C. Ding, Y. Xu, J. Dai, Chin. J. Inorg. Chem. 19 (2003) 920.
[11] H.L. Friedman, J. Polym. Sci., Part C 6 (1963) 183.
[12] J.H. Flynn, L.A. Wall, J. Polym. Sci., Part B. 4 (1966) 323.
[13] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.
[14] S. Vyazovkin, C.A. Wight, Thermochim. Acta 340/341 (1999) 53.
[15] S. Vyazovkin, J. Comput. Chem. 22 (2001) 178.

[16] C.D. Doyle, J. Appl. Polym. Sci. 5 (1961) 68.
[17] C.D. Doyle, J. Appl. Polym. Sci. 6 (1962) 258.
[18] G. Matsubayachi, K. Takahashi, T. Tanaka, J. Chem. Soc., Dalton Trans. (1990) 535.
[19] S.G. Liu, P.J. Wu, Y.F. Li, D.B. Zhu, Phosphorus Sulfur 90 (1994) 219.
[20] J. Zhai, T.-X. Wei, C.-H. Huang, H. Cao, J. Mater. Chem. 10 (2000) 625.
[21] A.M. Rocco, R.P. Pereira, J.A.P. Bonapace, N.M. Comerlato, J.L. Wardell, B.F. Milne, S.M.S.V. Wardell, Inorg. Chim. Acta 357 (2004) 1047.
[22] G. Liu, Q. Fang, W. Xu, H. Chen, C. Wang, Spectrochim. Acta, Part A. 60 (2004) 541.
[23] L. Valade, J.-P. Legros, P. Cassoux, Mol. Cryst. Liq. Cryst. 140 (1986) 335.
[24] A.E. Pullen, K.A. Abboud, J.R. Reynolds, Phys. Rev. B. 53 (1996) 10557.
[25] R. Prasad, A. Kumar, Thermochim. Acta 383 (2002) 59.
[26] A.M. Rocco, J.L. Wardell, N.M. Comerlato, R.P. Pereira, (Unpublished results).
[27] S. Vyazovkin, A.I. Lesnikovich, Thermochim. Acta 182 (1991) 133.
[28] S. Vyazovkin, Int. Rev. Phys. Chem. 19 (2000) 45.
[29] S. Vyazovkin, C.A. Wight, Annu. Rev. Phys. Chem. 48 (1997) 125.
[30] A.K. Galwey, Thermochim. Acta. 413 (2004) 139.