*Journal of Thermal Analysis, Vol. 37 (1991) 791-801*

# THERMAL DECOMPOSITION KINETICS OF THIOPHENE-2-CARBOXALDEHYDE THIOSEMICARBAZONE COMPLEXES OF NICKEL(II) AND PALLADIUM(II)

*K. K. Aravindakshan* and K. Muraleedharan*

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALICUT, KERALA 673 635, INDIA

(Received January 20, 1991)

The thermal analysis of Ni(II) and Pd(II) complexes with thiophene–2–carboxaldehyde thiosemicarbazone have been studied using TG technique. Their decompositions are subjected to critical evaluation using the equations of Coats–Redfern, Horowitz–Metzger and modified Horowitz–Metzger and the kinetic parameters (non–isothermal method) have been evaluated for each step of decomposition by the method of weighted least-squares.

During the course of our studies on metal complexes with technologically important sulphur ligands, we have reported the synthesis, magnetic, spectral and thermal studies of a number of thiosemicarbazone [1, 2] and dithiocarbamate [3–5] complexes. Our literature survey revealed that there appears to be no report on the detailed kinetic study on the thermal decomposition of thiosemicarbazone complexes. Here we report the thermogravimetric analysis and kinetics of thermal decomposition of complexes of two typical transition metal ions, Ni(II) and Pd(II) with an 'off-beat' thiosemicarbazone, i.e., thiophene-2-carboxaldehyde thiosemicarbazone ($C_6H_7N_3S_2$).

---

* To whom all correspondene should be addressed

*John Wiley & Sons, Limited, Chichester*
*Akadémiai Kiadó, Budapest*

## Experimental

Thiophene–2–carboxaldehyde thiosemicarbazone (LH) was synthesized by refluxing recrystallised thiosemicarbazide and thiophene–2–carboxaldehyde (1:1 ratio) in ethanol for 2 h. The brownish yellow solid that obtained on cooling was recrystallised from ethanol. For the preparation of the Ni(II) complex a hot aqueous solution of nickel chloride was added, dropwise, to a refluxing methanolic solution of the ligand containing sodium acetate (1.0 g) until the metal to ligand ratio reached 1:2. The reaction mixture was maintained at refluxing temperature for 1 h. The dark green solid that separated was filtered after cooling the reaction mixture and washed with water and then with methanol and dried over P4O10. The Pd(II) complex was also prepared in the same manner, but using an acidic solution ($pH$ = 4) of PdCl2 [6]. The complexes of general formula M(L)2, where $M$ = Ni(II) or Pd(II) and $L$ = monoanion of the ligand, LH, were characterized [6] by elemental analyses using standard procedures [7], molar conductance and magnetic measurements and by electronic and IR spectral studies.

### *Apparatus*

The thermogravimetric measurements were carried out on a DuPont 990 thermal analyser system with a 951 thermobalance. Following are the operational characteristics: heating rate, 10 deg min$^{-1}$; sample size, 2 to 6 mg; atmosphere, static air; crucible, platinum. The numerical analysis of the thermogravimetric data were realized using a program written in Microsoft BASIC for an IBM computer using DOS 4.00.

The mass loss data obtained from TG were compared with those obtained from independent pyrolysis experiments, in which the samples were heated for 2 h in silica crucibles upto ≈850 K.

### *Theoretical*

The rate of a reaction of a substrate under non-isothermal conditions is generally expressed by the relation [8]

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

where $\alpha$ represents the fraction of the reactant transformed at time $t$, $f(\alpha)$ is the conversion function dependent on the mechanism of reaction and $k(T)$ is the rate constant, dependent on the temperature. In the study of chemical reactions the temperature dependent function, $k(T)$ is of the Arrhenius type [9,10] and can be considered as the rate constant $k$

$$k = Ae^{-E/RT} \tag{2}$$

where $A$ is the pre-exponential factor, $E$ is the activation energy and $R$ is the gas constant.

Combining Eqs (1) and (2), we obtain

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{q} e^{-E/RT} dT \tag{3}$$

where $q$ is the linear heating rate, $dT/dt$. Equation (3) on integration and taking logarithm yields

$$\ln g(\alpha) = \ln(AE/qR) + \ln p(x) \tag{4}$$

where

$$p(x) = \int_x^\infty \frac{e^{-x}}{x^2} dx \qquad \text{and} \qquad x = E/RT$$

This is the basic form of the equation used for analysing non-isothermal data. This equation can be readily applied for the analysis of a non-isothermal TG trace to obtain values of the kinetic parameters once the form of the function, $p(x)$ is established.

It is well known [11] that the $p(x)$ function can not be expressed in a closed form, although there exists several approximations. Most of them utilize Eq. (3) in three different approaches, viz. integral, differential and approximation. The most accurate among them are the integral methods [8,12].

The integral methods are simpler as they do not involve the determination of rates, eventhough they are complicated by the integration of the rate constant. Coats and Redfern [13] used the approximation for the $p(x)$ function as $\exp(-x)\,[(1/x)-(2/x^2)]$ and obtained

$$\ln[g(\alpha)/T^2] = \ln\frac{AR}{qE}\left[1-\frac{2RT}{E}\right]-\frac{E}{RT} \tag{5}$$

The first term in the right-hand side of the above equation is a slowly changing function of the temperature and may be considered as being constant in a narrow temperature range [8].Hence a plot of ln $[g(\alpha)/T^2]$ *vs.* $1/T$ gives a straight line for the correct model relation, $g(\alpha)$.

Differential methods are based on the use of the dependence of the instantaneous reaction rates on the temperature. Many differential methods assume the existence of a single reaction order, $n$ as an empirical constant. The most widely used method is the difference-differential method, first introduced by Freeman and Carroll [14]

$$\frac{\Delta\ln(\mathrm{d}W/\mathrm{d}t)}{\Delta\ln W_r}=\frac{-E/R[\Delta(1/T)]}{\Delta\ln W_r}+n \tag{6}$$

where $W$ is the total loss in weight upto time $t$, $W_r = W_f - W$, $W_f$ is the weight–loss at the completion of the reaction and $\mathrm{d}W/\mathrm{d}t = (\mathrm{d}W/\mathrm{d}T)q$.

Horowitz and Metzger [15] simplified the exponential integral by defining a characteristic temperature deviation, $\theta$ such that $T = T_s + \theta$, where $T_s$ is the DTG peak temperature. Using this definition for $\theta$ in Eq. (3), these authors derived the following equations:

$$\ln[1-(1-\alpha)^{1-n}]=\frac{-E\theta}{RT_s^2}+\ln(1-n)$$

$$(\text{for } n \neq 1) \tag{7}$$

and

$$\ln[-\ln(1-\alpha)]=\frac{-E\theta}{RT_s^2}+C$$

$$(\text{for } n = 1) \tag{8}$$

where $C$ is a constant.

Dharwadkar and Karkhanavala [16] studied the effect of sample size and heating rate on the values of activation energy for the dehydration of calcium oxalate monohydrate of uniform particle size using the method suggested by Horowitz and Metzger and observed large variations in the values of activation energy. Therefore, these authors suitably modified the Horowitz–Metzger equation so as to yield values of activation energy which are independent of the variation in sample size and heating rate. For first order kinetics the modified equation is

$$\ln[-\ln(1-\alpha)] = \frac{E}{RT_i^2} \cdot \frac{100}{(T_f - T_i)}\theta + C \tag{9}$$

where $T_i$ is the temperature of inception of the reaction $T_f$ is the temperature of completion of reaction and $C$ is a constant.

The form of representation of Eqs (5-9) seems to suggest application of least-squares method (LSM) to the relationship $y = mx + b$. The least–squares analysis is based on the observation that, often, random experimental errors closely follow a Gaussian distribution. This assumption fails when $y$ contains a logarithmic function, because using the logarithmic function tends to compress the high values while expanding the low values. This defect can be remedied by using a weighted LSM. Several authors [17–19] have reported that the best fit of their experimental and calculated data was obtained using a weighted LSM. The weights used most often are the inverse of the deviation of the dependent variable [20]. It has been shown [17] that the deviation, $S_\alpha^2$ of the variable $\alpha$ is proportional to $1 + \alpha^2$. Multiplication of the deviation by a constant value does not influence the results of calculation [17, 21]. Thus, for weights calculation one can use $S_\alpha^2 = 1+\alpha^2$. When transforming $\alpha$ into $y$ one should also correspondingly transform $S_\alpha^2$ into $S_y^2$. The deviation of $y$ is calculated from the transformed formula

$$S_y^2 = S_\alpha^2 \cdot \left[\frac{\partial y}{\partial \alpha}\right]^2 \tag{10}$$

and the following is used as weight ($w$) for the weighted least–squares fit:

$$w = 1/S_y^2 \tag{11}$$

## Results

The instrumental TG and DTG traces are shown in Figs 1 and 2. The TG curves were studied in greater detail. The instrumental thermogravimetric traces were redrawn as the fraction decomposed ($\alpha$) *vs.* temperature ($T$) curves to obtain the primary $\alpha$–$T$ data. It has been found that both complexes decompose in two stages. The decomposition reactions of these complexes were subjected to non-isothermal kinetic studies. The kinetic

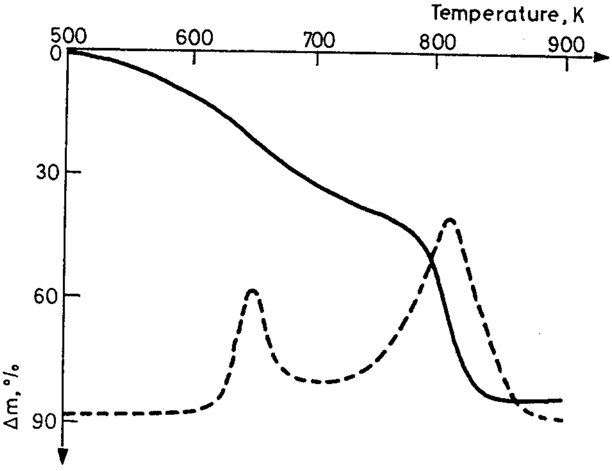

Fig. 1 TG (——) and DTG (- - -) curves of Ni(L)2

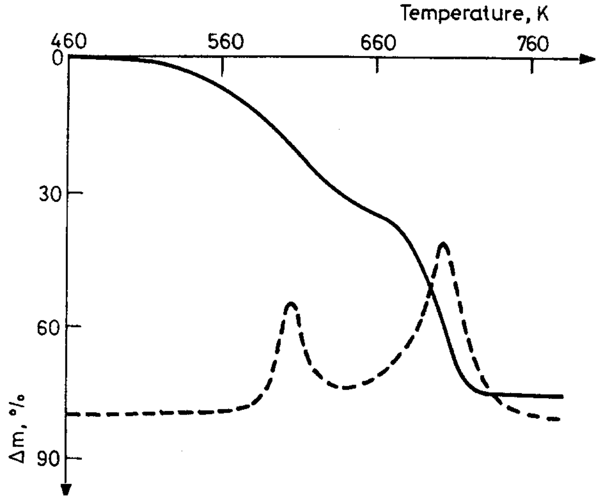

Fig. 2 TG (——) and DTG (- - -) curves of Pd(L)2

parameters such as $n$, $E$, $A$ and entropy of activation ($\Delta S$) were evaluated using weighted LSM.

Freeman–Carroll equation [14] has been used for the determination of the order of reaction. But its applicability is found to be extremely poor as observed from the scattered plot. Several authors [22, 23] have made similar observations. Therefore, the method of Horowitz and Metzger [15] was applied and the order was determined by constructing a 'master curve', as reported in earlier work [24]. We also computed the values of correlation coefficient ($r$) using the weighted LSM, for the equations suggested by Coats and Redfern [13] (with $n = 0$, 1/2, 2/3 and 1) and found a maximum value for the equation with $n = 1$.

Accordingly the kinetic parameters for both the stages of decomposition of these complexes have been computed using the integral method of Coats and Redfern [13], the approximation method of Horowitz and Metzger [15] and the modified method of Horowitz and Metzger [16]. In all cases the weighted least–squares plots were drawn discarding the first few points (upto $\alpha = 0.10$) since they did not fall on the line and hence their inclusion would have resulted in poor correlation. This is as expected since several authors [25, 26] have reported that the decomposition of solids do not obey first-order kinetics in the initial stages.

## Discussion

The weights used for each function [$g(\alpha)$] are given in Table 1. The TG and DTG results are summarized in Table 2. The values of kinetic parameters and correlation coefficients are given in Table 3.

**Table 1** Functions and weights used

| Function, $g(\alpha)$ | | Weights ($w$) used |
|---|---|---|
| $\frac{1-(1-\alpha)^{(1-n)}}{T^2(1-n)}$, | n = 0 | $\frac{\alpha^2}{1+\alpha^2}$ |
| $\frac{1-(1-\alpha)^{(1-n)}}{T^2(1-n)}$, | n = 1/2 | $\frac{\{2(1-\alpha)^{1/2}[1-(1-\alpha)^{1/2}]\}^2}{1+\alpha^2}$ |
| $\frac{1-(1-\alpha)^{(1-n)}}{T^2(1-n)}$, | n = 2/3 | $\frac{\{3(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]\}^2}{1+\alpha^2}$ |
| $\frac{-\ln(1-\alpha)}{T^2}$ | | $\frac{[(1-\alpha)\ln(1-\alpha)]^2}{1+\alpha^2}$ |
| $-\ln(1-\alpha)$ | | $\frac{[(1-\alpha)\ln(1-\alpha)]^2}{1+\alpha^2}$ |

**Table 2** Thermal decomposition data

| Complex | Stability range in TG from ambient to K | Decomposition temperature range in TG, K | Peak temperature in DTG, K | Loss of mass, % | | |
|---|---|---|---|---|---|---|
| | | | | From TG | Theoretical | From independent pyrolysis |
| $Ni(L)_2$ | 520 | 520–740<br>740–850 | 656<br>809 | 82.50 | 82.51 | 82.35 |
| $Pd(L)_2$ | 520 | 520–650<br>650–750 | 605<br>703 | 74.66 | 74.23 | 74.00 |

Table 3 Kinetic data

| Equations | Complex | Decomposition stage | $E$, J·mol$^{-1}$ | $A$, s$^{-1}$ | $\Delta S$, J·K$^{-1}$·mol$^{-1}$ | $r$ |
|---|---|---|---|---|---|---|
| Coats–Redfern | $Ni(L)_2$ | First | $5.395\cdot10^{4}$ | $2.944\cdot10^{3}$ | $-1.851\cdot10^{2}$ | 0.9999 |
| | | Second | $3.644\cdot10^{5}$ | $2.193\cdot10^{23}$ | $1.936\cdot10^{2}$ | 0.9995 |
| | $Pd(L)_2$ | First | $8.521\cdot10^{4}$ | $6.318\cdot10^{6}$ | $-1.206\cdot10^{2}$ | 0.9997 |
| | | Second | $2.469\cdot10^{5}$ | $1.277\cdot10^{18}$ | $9.458\cdot10^{1}$ | 0.9992 |
| Horowitz–Metzger | $Ni(L)_2$ | First | $6.687\cdot10^{4}$ | $3.948\cdot10^{4}$ | $-1.635\cdot10^{2}$ | 0.9982 |
| | | Second | $3.808\cdot10^{5}$ | $2.727\cdot10^{24}$ | $2.146\cdot10^{2}$ | 0.9995 |
| | $Pd(L)_2$ | First | $9.735\cdot10^{4}$ | $1.780\cdot10^{8}$ | $-9.285\cdot10^{1}$ | 0.9989 |
| | | Second | $2.612\cdot10^{5}$ | $1.617\cdot10^{19}$ | $1.157\cdot10^{2}$ | 0.9991 |
| Modified Horowitz–Metzger | $Ni(L)_2$ | First | $5.042\cdot10^{4}$ | $1.458\cdot10^{3}$ | $-1.909\cdot10^{2}$ | 0.9982 |
| | | Second | $3.505\cdot10^{5}$ | $2.762\cdot10^{22}$ | $1.764\cdot10^{2}$ | 0.9995 |
| | $Pd(L)_2$ | First | $9.350\cdot10^{4}$ | $3.628\cdot10^{7}$ | $-1.061\cdot10^{2}$ | 0.9989 |
| | | Second | $2.233\cdot10^{5}$ | $2.113\cdot10^{16}$ | $6.048\cdot10^{1}$ | 0.9991 |

## *Thermal behaviour*

The decomposition of both the complexes are two staged processes. $Ni(L)_2$ is stable upto 520 K. The initial decomposition takes place between 520 and 740 K. It is represented by the DTG peak at 656 K. Its main decomposition takes place between 740 and 850 K and is represented by the DTG peak at 809 K. The decomposition of $Pd(L)_2$ also starts at 520 K. Its first decomposition step is represented by the DTG peak at 605 K. Its main and final decomposition is between 650 and 750 K and is represented by the DTG peak at 703 K.

The observations from the thermogravimetric studies and independent pyrolysis experiments agree favourably (Table 2). The final stable solid decomposition products were analysed to be oxides of general formula MO, where $M$ = Ni(II) or Pd(II).

## *Decomposition kinetics*

The analysis of data using Horowitz–Metzger equation showed that the overall orders for both stages of decomposition of the two complexes are near unity. We also computed the values of $r$ using weighted LSM for the equations suggested by Coats and Redfern [13] (with $n$ = 0, 1/2, 2/3, 1) and got a maximum value for the equation with $n$ = 1. Based on this value of reaction order the kinetic parameters were evaluated using the above mentioned three equations for each stage of decomposition of the two complexes by weighted LSM and are listed in Table 3. Satisfactory values of $r$ ($r \approx 1$) in all cases indicate good agreement with experimental data. The values of kinetic parameters obtained from Coats–Redfern, Horowitz–Metzger and modified Horowitz–Metzger equations are comparable and in good agreement.

For the first stage of the decomposition the entropy of activation varies from $-92.85$ to $-190.9$ $JK^{-1}\cdot mol^{-1}$. The negative values indicate that the activated complex has a more ordered structure than the reactants and that the reactions are slower than normal [27,28]. It is observed that the values of $E$ and $A$ for the first stage of decomposition are higher for the Pd(II) complex. The rate of decomposition of the second stage is higher than that of the first stage. The $\Delta S$ values vary from 60.48 to 214.6 $JK^{-1}\cdot mol^{-1}$. Contrary to the first stage of decomposition, here the $E$ and $A$ values are higher for the Ni(II) complex.

* * *

We thank Prof. C. G. R. Nair, Head of the Department of Chemistry, University of Kerala and Dr. M. P. Kannan, Department of Chemistry, University of Calicut for some helpful discussions.

## References

1 K. K. Aravindakshan and C. G. R. Nair, Ind. J. Chem., 20A (1981) 684.
2 K. K. Aravindakshan, Ind. J. Chem., 26A (1987) 241.
3 K. K. Aravindakshan, Ind. J. Chem., 25A (1986) 292.
4 K. K. Aravindakshan and K. Muraleedharan, J. Thermal Anal., (communicated).
5 K. K. Aravindakshan and K. Muraleedharan, Thermochim. Acta, 140 (1989) 325.
6 C. G. R. Nair and K. K. Aravindakshan, J. Inst. Chemists (India), 53 (1981) 295.
7 A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, ELBS and Longman, London, 1978.
8 J. Sestak, V. Satava and W. W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
9 K. Krishnan, K. N. Ninan and P. M. Madhusudanan, Thermochim. Acta, 125 (1988) 111.
10 R. K. Agrawal, J. Thermal Anal., 32 (1987) 149.
11 J. H. Flynn and L. A. Wall, J. Res. NBS, 70A (1966) 487.
12 J. Sestak, Talanta, 13 (1966) 567.
13 A. W. Coats and J. P. Redfern, Nature (London), 201 (1964) 68.
14 E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
15 H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
16 S. R. Dharwadkar and M. D. Karkhanavala, Thermal Analysis, Vol. II,Proc. 2nd ICTA, Worcester, MA, 1968, Academic Press, New York 1969, p. 1049.
17 C. Rozycki and M. Meciejewski, Thermochim. Acta, 96 (1985) 91.
18 K. Muraleedharan and M. P. Kannan, React. Kinet. Catal. Lett., 39(2) (1989) 339.
19 T. Gangadevi, K. Muraleedharan and M. P. Kannan, Thermochim. Acta, 144 (1989) 109.
20 D. E. Sands, J. Chem. Educ., 51 (1974) 473.
21 W. E. Wentworth, J. Chem. Educ., 42 (1965) 96, 162.
22 R. L. Bohon in H. G. McAdie (Ed.), Proc. 1st Toronto Symposium on Thermal Analysis, Chemical Institute of Canada, Toronto 1959, p. 63.
23 R. L. Reed, L. Weber and B. S. Gottfried, Ind. Engng. Chem., Fundls., 4 (1965) 38.
24 P. M. Madhusudanan, P. N. K. Nambisan and C. G. R. Nair, Thermochim. Acta, 9 (1974) 149.
25 A. W. Coats and J. P. Redfern, J. Polymer Sci., Part 3(B) (1965) 917.
26 P. W. M. Jacobs and F. C. Tompkins in W. E. Garner (Ed.), Chemistry of the Solid State, Butterworths Scientific Publication, London 1955, p. 188.
27 A. A. Frost and R. G. Pearson, Kinetics and Mechanism, John Wiley and Sons, New York, 1961.
28 V. Indira and G. Parameswaran, J. Thermal Anal., 32 (1987) 1151.

**Zusammenfassung** — Mittels TG wurde die Thermoanalyse der Komplexe aus Ni(II) und Pd(II) mit Thiophen-2-carboxaldehyd-thiosemicarbazon untersucht. Ihre Zersetzung wurde mittels der Gleichungen von Coats-Redfern, Horowitz-Metzger und einer modifizierten Horowitz-Metzger-Gleichung einer kritischen Auswertung unterzogen. Die kinetischen Parameter (nichtisotherme Methode) wurden für jeden Zersetzungsschritt mittels der Methode gewichteter Quadratsummen geschätzt.