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THERMAL DECOMPOSITION KINETICS OF FLUORENONE THIOSEMICARBAZONE COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

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Thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves of PdL_2 and $Pt(LH)_2Cl_2$ (LH = fluorenone thiosemicarbazone) in air are studied. Mass loss considerations at the main decomposition stages indicate conversion of the Pd(II) and Pt(II) complexes to PdO and metallic platinum respectively. Mathematical analysis of TG data shows that first order kinetics are applicable in all cases. Kinetic parameters (energy and entropy of activation and preexponential factor) are reported.

INTRODUCTION

Transition metal complexes of Schiff bases have important technical applications. Wendlandt[1-5] and Hill[6,7] studied the thermal properties of metal chelates with different types of complexing ligands. Studies on thermal decomposition and kinetics of metal chelates have been done by a few workers[8,9]. In continuation of our work[10-14] on thermal decomposition kinetics of metal chelates, we report in this paper the thermoanalytical data of two complexes—platinum(II) and palladium(II) complexes of fluorenone thiosemicarbazone (FTSC). Interpretation and mathematical analysis of those data and evaluation of order of reaction and the energy and entropy of activation, based on the integral method using the Coats-Redfern equation[15] and the approximation method using the Horowitz-Metzger equation[16] are given. Zsako's modified Doyle method[17] is also used for finding out the parameters.

EXPERIMENTAL

The metal complexes of fluorenone thiosemicarbazone ($C_{14}H_{11}N_3S$) were prepared by refluxing 1M methanolic solution of the metal chloride and the ligand in 1 : 2 molar ratio for 2 hrs, cooled and the coloured solids separated were filtered, washed with methanol and dried in a desiccator. The structure of Pd(II) and Pt(II) chelates was found to be $[PdL_2)]$ and $[Pt(LH)_2Cl_2]$ respectively, where LH = $C_{14}H_{11}N_3S$. The purity of the samples was checked by i.r. spectra and elemental analysis for the metal, sulphur and chlorine.

Treatment of data

The instrumental TG curves were redrawn as mass vs. temperature (TG) curves and also as the rate of loss of mass vs. temperature (DTG) curves. The instrumental DTA curves were used as such. Typical TG, DTG and DTA curves

are presented in Figs. 1–4 and the decomposition temperature ranges in DTG and DTA for the metal chelates are presented in Table 1.

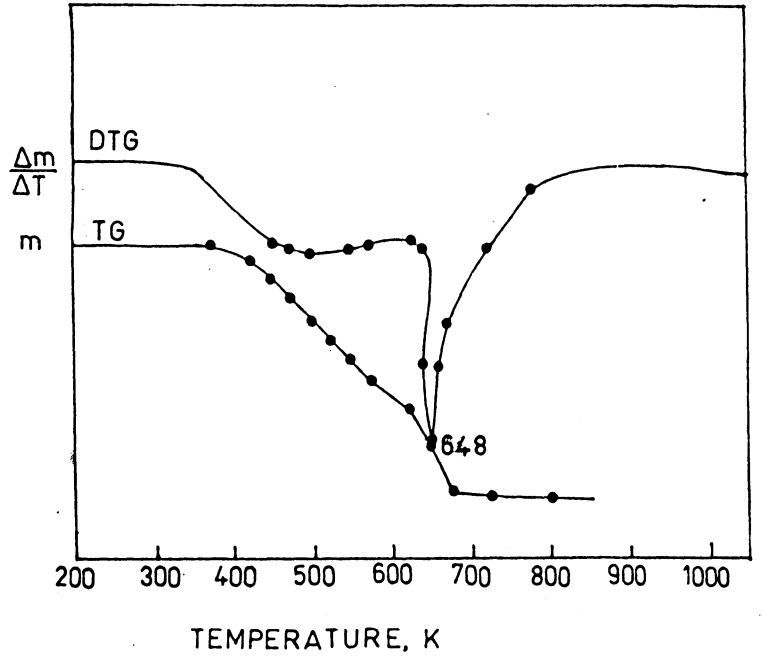

Fig. 1 TG and DTG traces of PdL_2

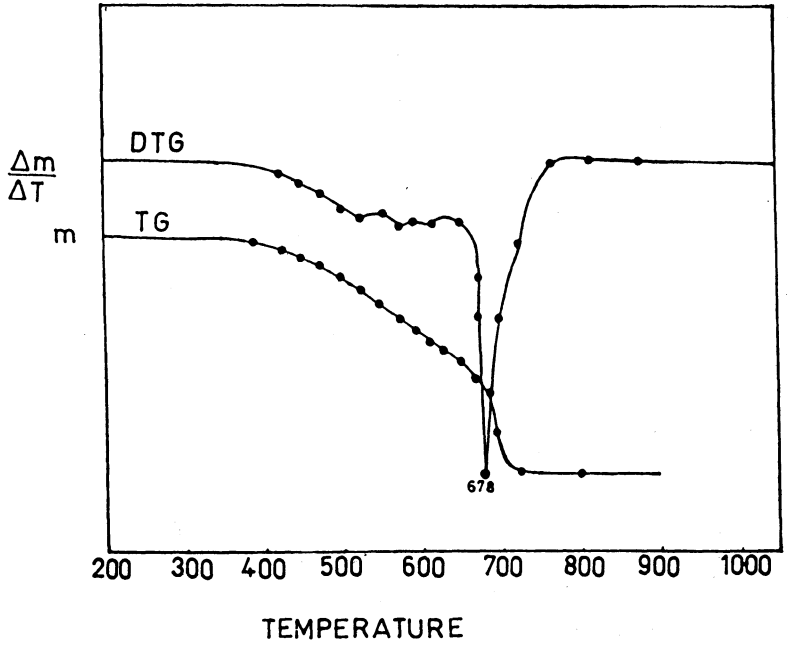

Fig. 2 TG and DTG Traces of $(PtLH)_2Cl_2$

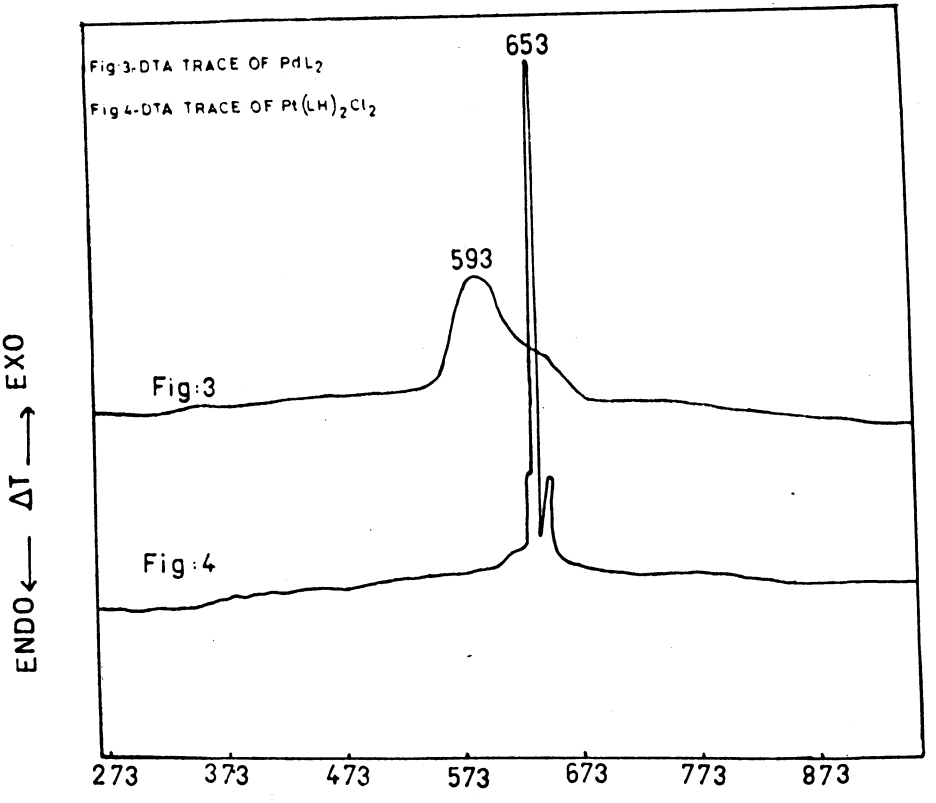

Fig. 3 DTA Trace of PdL_2 Fig. 4 DTA Trace of $Pt(LH)_2Cl_2$

TABLE 1
THERMAL DECOMPOSITION DATA

Substance	Peak Temperature in DTG, K	Temperature ranges in DTG, K	Peak Temperature in DTA, K	Temperature range in DTA, K	Loss of mass %		
					From TG	Theoretical	From independent pyrolysis
[PdL2]	648s	400–750	593(exo)	553–713	20.00	20.03	20.71
[Pt(LH)2Cl2]	678s	450–750	653(exo)	573–663	26.30	25.25	25.85

The TG curves were studied in greater detail. The curves for the two chelates exhibited a characteristic, well defined and non-overlapping decomposition pattern. The mass loss considerations and X-ray diffraction data indicated the products to be metallic Pt and PdO. The relevant portion of the TG curve was redrawn on an expanded scale. Three different methods were used to evaluate kinetic data from these TG traces.

Integral Method Using the Coats-Redfern Equation[15]

Coats-Redfern equation, which is a typical integral method can be represented as

$$\int_0^{\infty} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\phi}\int_0^{T} \exp(-E^*/RT)dT \qquad (1)$$

where α = fraction of the compound decomposed at time t, ϕ, rate of heating in deg. min^{-1}, A = frequency factor and E = activation energy.

The LHS of Eq. (1) has two different solutions, namely

$$1-(1-\alpha)^{1-n}/(1-n) \qquad \text{for } n \neq 1 \text{ and} \qquad (2)$$

$$-\log(1-\alpha) \qquad \text{for } n = 1 \qquad (3)$$

In both cases, the RHS of equation (1) has the solution

$$\frac{ART^2}{\phi E^*}\frac{(1-2RT)}{E^*}\exp(-E^*/RT) \qquad (4)$$

Equations (5) and (6) are obtained after taking logarithms

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\left[\frac{AR}{\phi E^*}\left(1-\frac{(2RT)}{E^*}\right)-\frac{E^*}{2.303\,RT}\right] \qquad (5)$$

for $n \neq 1$ and

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\left[\frac{AR}{\phi E^*}\left(1-\frac{(2RT)}{E^*}\right)-\frac{E^*}{2.303\,RT}\right] \qquad (6)$$

for $n = 1$

In ordinary thermal decomposition reactions, $\log\left[\frac{AR}{\phi E^*}\left(1-\frac{(2RT)}{E^*}\right)\right]$ is practically constant and plots of

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \quad \text{vs.} \quad 1/T \text{ for } n \neq 1 \qquad (7)$$

and

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] \quad \text{vs} \quad 1/T \text{ for } n = 1 \qquad (8)$$

respectively result in a straight line with a slope of $-E^*/2.303R$ for the correctly chosen value of n. The reaction order can easily be estimated by observing the lines drawn by using $n = 0.5$ and 0.67 in eqn. (7) and $n = 1$ in eqn. (8). The application of eqn. (7) and (8) to our data on the platinum(II) and palladium(II) chelates revealed that a better straight line results in eqn. (8) and hence the order of the reaction is unity for both complexes.

For a first order process the Coats-Redfern equation may be written in the form

$$\log\left[\ln\frac{w_\alpha}{w_\alpha - w}\right] = \log\left[\frac{AR}{\phi E^*}\left(1-\frac{(2RT)}{E^*}\right)-\frac{E^*}{2.303\,RT}\right] \qquad (9)$$

Since $1 - \frac{2RT}{E^*} = 1$, a plot of LHS of Eq. (9) against $1/T$ was drawn (Figs. 5 and 6). E^* was calculated from the slope and A was found out from the intercept. ΔS^* was obtained from the equation

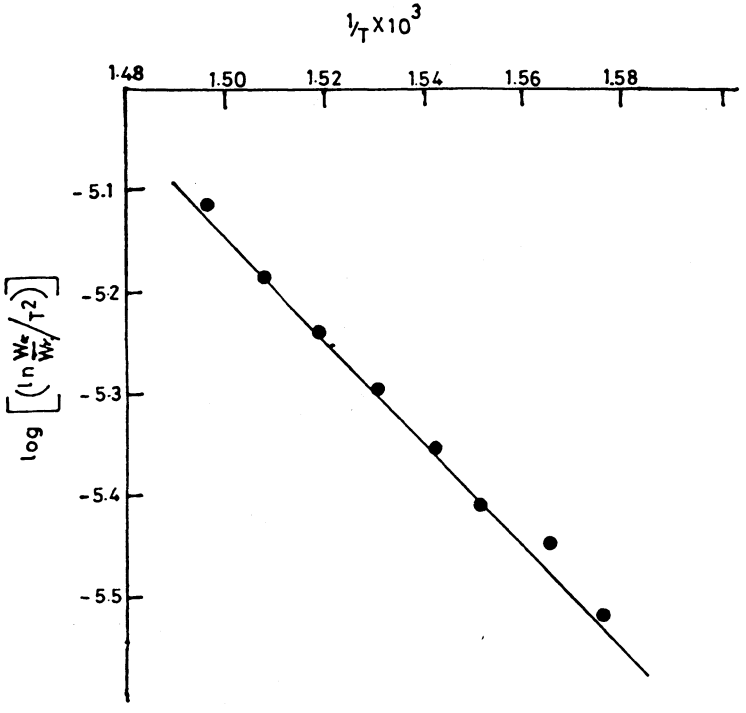

Fig. 5. Coats redfern plot for PdL_2.

$$A = \frac{kT}{h} \exp(\Delta S^*/R) \tag{10}$$

Approximation Method Using the Horowitz-Metzger Equation[16]

The Horowitz-Metzger method is illustrative of the approximation methods. These authors derive the relation

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{E^*\theta}{2.303\,RT_s^2} \qquad \text{for } n = 1 \tag{11}$$

where $n = 1$, the LHS of eqn. (10) would be log $-\ln/1 - \alpha$. For a first order kinetic process the Horowitz Metzger equation may be written in the form

$$\log\left[\log\frac{w_\alpha}{w_r}\right] = \frac{E^*\theta}{2.303\,RT_s^2} - \log 2.3030 \tag{12}$$

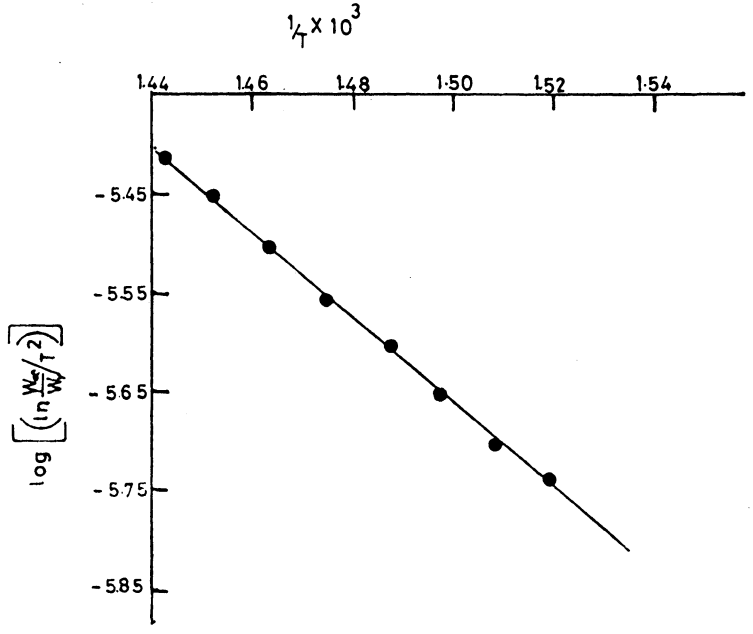

Fig. 6. Coats Redfern plot for $Pt(LH)_2Cl_2$

where $\theta = T - T_s$ and the other terms are described earlier. A plot of log [log (w_α/w_r)] vs θ was drawn and was found to be linear f rom the s lopes of

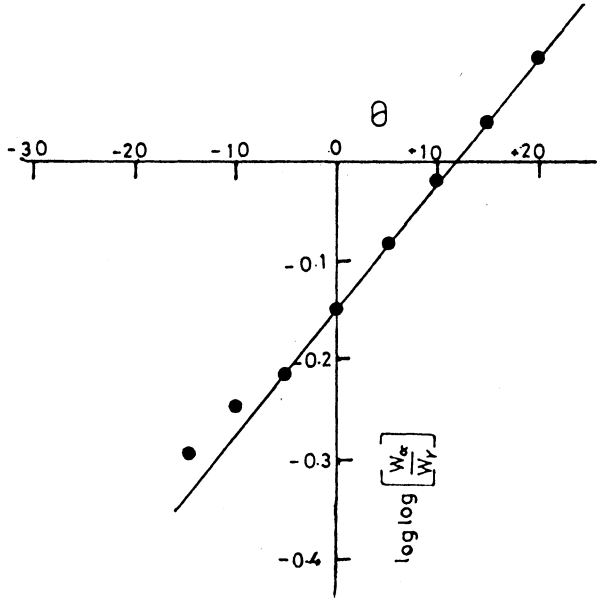

Fig. 7 Horowitz Metzger Plot for PdL2

which E^* was calculated. Typical plots are given in (Figs. 7 and 8). the pre-exponential factor A was calculated from the equation

$$\frac{E^*}{RT_s^2} = \frac{A}{\phi \exp(-E^*/RT_s)} \tag{13}$$

The entropy of activation ΔS^* was obtained from the Eq. (10) used earlier for the purpose.

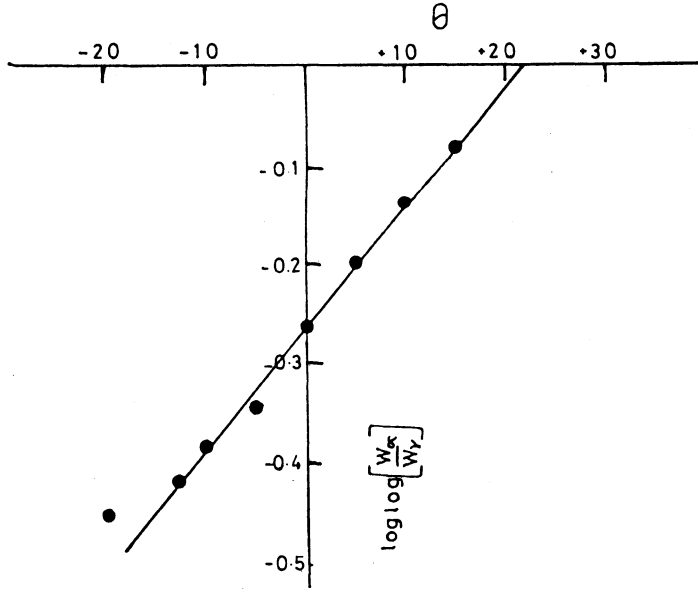

Fig. 8 Horowitz Metzger plot for $Pt(LH)_2Cl_2$

Zsako's Modified Doyle Method[16].

The trial and error method of Doyle was modified by Zsako by introducing the standard deviation instead of curve fitting method for calculations. The value of $g(\alpha)$ was calculated for various values of 'n' in the general equation

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

where 'n' can be considered as apparent reaction order. The values of 'n' taken are $n = 0, 0.5, 1$ or 2.

If the logarithm of Doyle's equation is taken,

$$\log AE^*/R\phi = \log g(\alpha) - \log P(x) = B \tag{14}$$

where $g(\alpha)$ is a certain function of α, where α stands for the fraction of initial compound reacted, A = frequency factor, E^* = activation energy, R = gas constant and ϕ = heating rate.

The values of the integral

$$P(x) = \frac{e^{-x}}{x}\int_x^\infty \frac{e^{-u}}{u}\,du \quad (\text{where } u = E^*/RT) \tag{15}$$

were calculated and tabulated by Doyle for x values covering a range from 10 to 50 and these values were used in calculating 'B'. The average of B values, as obtained at different temperatures, was taken and $\partial = \sqrt{(Bi - \overline{B})^2/r}$ where Bi is any value, $\overline{B}$ is arithmetical mean and r is the number of values. ∂ values for various 'B' values are calculated and given in Table 2. The ∂ value is minimum if the apparent order of reaction n is taken as 1, i.e., first order reaction. Thus from tested 'n' values, $n = 1$ is the best.

TABLE 2
ZSAKO'S MODIFIED METHOD ∂ VALUES

Substance	E^*	$n = 0$	$n = 0.5$	$n = 1$	$n = 2$
$[PdL_2]$	18	0.0070	0.0027	0.0043	0.0292
	20	0.0096	0.0016	0.0001	0.00116
	22	0.0015	0.0080	0.0046	0.0241
	24	0.0070	0.0118	0.0157	0.0347
$[Pt(LH)_2Cl_2]$	18	0.0013	0.0053	0.0018	0.0292
	20	0.0051	0.0041	0.0029	0.0262
	22	0.0046	0.0087	0.0005	0.0267
	24	0.0084	0.0092	0.0008	0.0236

RESULTS AND DESCUSSION

The decomposition temperature ranges in DTA and DTG for the two metal chelates are given in Table 1. Data from independent pyrolysis experiments (carried out by heating weighed samples taken in porcelain crucibles in an atmosphere of air) are also included in Table 1. Kinetic parameters calculated by employing the Coats Redfern and Horowitz Metzger equations are summarised in Table 3. the overall loss of mass from the TG curves is 20% for PdL_2 and 26.3% for $Pt(LH)_2Cl_2$, while the calculated loss in mass for these conversions are

$$PdL_2 \rightarrow PdO \qquad 20.03\%$$

$$Pt(LH)_2Cl_2 \rightarrow Pt \qquad 25.25\%$$

TABLE 3
KINETIC DATA

Substance	Parameters	From Coasts-Redfern equation	From Horowitz Metzger equation
$[PdL_2]$	E^* (kJ mol^{-1})	95.7	100.5
	A (S^{-1})	1.93×10^5	3.02×10^5
	ΔS^* (JK mol^{-1})	−150.2	−146.3
$[Pt(LH)_2Cl_2]$	E^* (kJ mol^{-1})	87.1	97.8
	A (S^{-1})	1.19×10^4	7.27×10^4
	ΔS^* (JK mol^{-1})	−173.7	−158.7

The end products are confirmed to be PdO and Pt from their X-ray diffraction pattern.

The fluorenone thiosemi-carbazone chelates of palladium and platinum are found to be anhydrous, based on elemental analysis, on the absence of hydroxyl bands in i.r. spectra. The initial decomposition temperature is frequently used to define the relative thermal stability of metal chelates[19]. On the basis of experimental findings in the present course of studies and the observartions made by earlier workers[20, 21] the relative thermal stability of the above chelate can be given as

$$[Pt(LH)_2Cl_2] > [PdL_2]$$

Decomposition Kinetics

The analysis of data using the Zsako's modified Doyle method[16] by calculation of standard deviation gives the order of the decomposition reaction near unity in all cases. Based on this value of the order of reactions, the kinetic parameters are evaluated. The Coats Redfern method seems to be more accurate but considerable time consuming. The approximation methods may give reasonably good values, but, however, they have to be considered mathematically less accurate than integral methods. The values of activation energy E^* obtained by three methods for the two chelates are given in Table 1. The results show that the values obtained by various methods are comparable. Because of their similar structures the complexes show similar thermal behaviour, as is evidenced from their comparable values of E^* and A.

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