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THERMAL DECOMPOSITION KINETICS OF SALICYLIDENEAMINOFLUORENE COMPLEXES OF COBALT(II) AND NICKEL(II)

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ABSTRACT

The thermal decomposition of cobalt(II) and nickel(II) complexes of the novel Schiff base salicylideneaminofluorene was studied by TG. The chelates show exactly similar TG plots when heated in an atmosphere of air. Thermoanalytical data (TG and DTG) of these chelates are presented in this communication. Interpretation and mathematical analysis of these data and evaluation of order of reaction, energy and entropy of activation based on the differential method employing the Freeman–Carroll equation, the integral method using Coats–Redfern equation and the approximation method using the Horowitz–Metzger equation are also given.

INTRODUCTION

Transition metal complexes of Schiff bases have important technical applications. Wendlandt and co-workers [1–5] and Hill and co-workers [6,7] studied the thermal properties of metal chelates with different types of complexing ligands. A study of thermal decomposition of Schiff base complexes of nickel and cobalt has been reported by Bhaskare et al. [8]. Recently Lehtinen has made a report of the thermal stability and kinetics of Cu(II) and Ni(II) chelates of the Schiff bases derived from 5-bromosalicylaldehyde and some medicinal sulfonamides [9]. In continuation of our work [10,11] on thermal decomposition kinetics of metal chelates we report in this paper, the thermoanalytical data of two typical complexes: salicylideneaminofluorene chelates of cobalt(II) and nickel(II).

EXPERIMENTAL

The metal complexes of salicylideneaminofluorene ($C_{20}H_{15}ON$) were prepared by refluxing a 1 M methanolic solution of the metal chloride with a 2 M methanolic solution of the ligand for about 10 h. The precipitates were filtered, washed with methanol and dried in a vacuum desiccator. The

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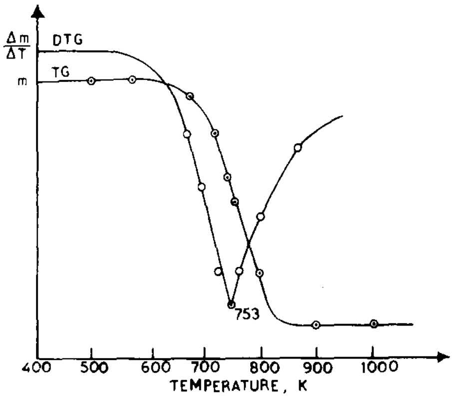

Fig. 1. TG and DTG traces of CoL_2.

structure of these chelates was found to be of the general formula ML_2 (M = Co(II), Ni(II); LH = salicylideneaminofluorene).

Apparatus

TG curves were recorded on a Stanton recording thermobalance (Model TR-1). The heating rate was 4 K min^{-1} and chart speed was 6 in. h^{-1}. The atmosphere was static air. Buoyancy correction was applied.

Treatment of data

The instrumental TG curves were re-drawn as mass vs. temperature (TG) curves and also as the rate of mass loss vs. temperature (DTG) curves. Typical TG and DTG curves are presented in Figs. 1 and 2.

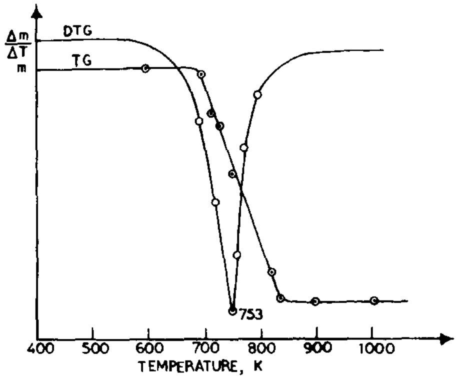

Fig. 2. TG and DTG traces of NiL_2.

The TG curves were studied in greater detail. The curves for CoL_2 and NiL_2 each exhibited a characteristic, well-defined and non-overlapping decomposition pattern. The mass loss considerations and X-ray diffraction data indicated the products to be Co_3O_4 and NiO. The relevant portion of the TG curve was re-drawn on an expanded scale, using standard curve sets. Three different methods were used to evaluate kinetic data from these TG traces.

Differential method using the Freeman–Carroll equation [12]

The Freeman–Carroll equation was used in the form

$$\frac{\Delta \log \frac{\mathrm{d}w}{\mathrm{d}t}}{\Delta \log w_\gamma} = \frac{(-E^*/2.303R)\,\Delta(T^{-1})}{\Delta \log w_\gamma} + n \tag{1}$$

where $w_\gamma = w_\alpha - w$, w_α = mass loss at the completion of the reaction; w = mass loss up to time t; T = absolute temperature at time t; n = order of reaction; R = gas constant (cal); and E^* = activation energy (J mol^{-1}). Of the above terms, w_γ and T can be directly obtained from the TG traces. The mass–temperature gradient ($\mathrm{d}w/\mathrm{d}T$) could be obtained by drawing tangents. The temperature slopes, $\mathrm{d}w/\mathrm{d}T$, were converted into time slopes, $\mathrm{d}w/\mathrm{d}t$ using the relation

$$\frac{\mathrm{d}w}{\mathrm{d}t} = \left(\frac{\mathrm{d}w}{\mathrm{d}T}\right)\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right) = \left(\frac{\mathrm{d}w}{\mathrm{d}T}\right)\phi \tag{2}$$

where ϕ is the heating rate. A plot of $[\Delta(T^{-1})]/(\Delta \log w_\gamma)$ versus $[\Delta \log(\mathrm{d}w/\mathrm{d}t)]/(\Delta \log w_\gamma)$ was drawn and found to be linear from which the order of reaction and the activation energy were obtained from the intercept and slope, respectively (Figs. 3 and 4). The order of reaction (n)

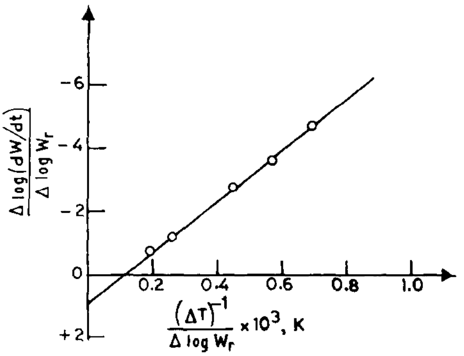

Fig. 3. Freeman–Carroll plot for CoL_2.

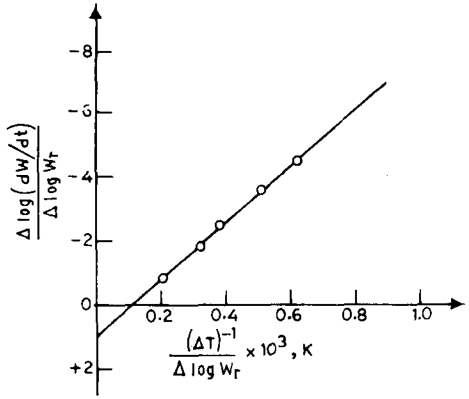

Fig. 4. Freeman–Carroll plot for NiL_2.

was found to be 0.98 for CoL_2 and 1 for NiL_2. The usual first-order rate law expression

$$(dx/dt) = k(a - x) \tag{3}$$

can be put in the following form using the terms w and w_γ

$$(dw/dt) = kw_\gamma \tag{4}$$

combining this with the Arrhenius equation, i.e.

$$k = Z\exp(-E^*/RT) \tag{5}$$

we get

$$\log[(dw/dt)/w_\gamma] = \frac{-E^*}{2.303RT} + \log Z \tag{6}$$

A plot of the left-hand side (LHS) of eqn. (6) against (T^{-1}) was found to be linear, from the slope of which E^* was calculated. Z was calculated from the intercept and the entropy of activation, ΔS^*, was obtained from the equation

$$Z = \frac{kT}{h}\exp(\Delta S^*/R) \tag{7}$$

where k is the Boltzmann constant, h is the Planck constant and T_s is the peak temperature from DTG. Typical curves concerning application of the Freeman–Carroll equation ($n = 1$) to CoL_2 and NiL_2 are given in Figs. 5 and 6, respectively.

Integral method using the Coats–Redfern equation [13]

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

$$\int_0^\alpha d\alpha|(1-\alpha)^n = Z|\phi\int_0^T \exp(-E^*/RT)dt \tag{8}$$

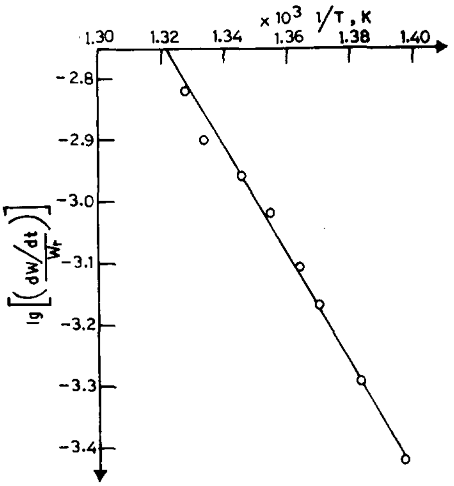

Fig. 5. Freeman–Carroll plot (modified) for CoL_2.

The LHS of eqn. (8) has two different solutions, namely

$$1-(1-\alpha)^{1-n}/(1-n) \quad \text{for } n \neq 1 \tag{9}$$

and

$$-\log(1-\alpha) \quad \text{for } n=1 \tag{10}$$

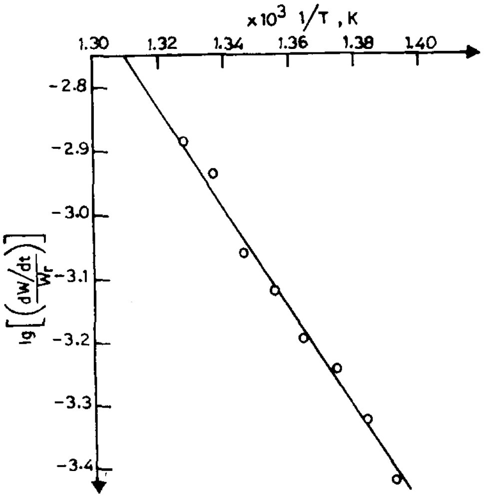

Fig. 6. Freeman–Carroll plot (modified) for NiL_2.

In both cases, the right-hand side of eqn. (8) has the solution

$$\frac{ZRT^2}{\phi E^*}\left(1 - \frac{2RT}{E^*}\right) \exp(-E^*/RT) \tag{11}$$

Equations (12) and (13) are obtained after taking logarithms

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\left[\frac{ZR}{\phi E^*}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT} \quad \text{for } n \neq 1 \tag{12}$$

and

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\left[\frac{ZR}{\phi E^*}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT} \quad \text{for } n = 1 \tag{13}$$

In ordinary thermal decomposition reactions, $\log[ZR/\phi E\ (1 - 2RT/E^*)]$ is practically constant, and plots of

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] \text{ vs. } 1/T \quad \text{for } n \neq 1 \tag{14}$$

and

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] \text{ vs. } 1/T \quad \text{for } n = 1 \tag{15}$$

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. (14) and $n = 1$ in eqn. (15). The application of eqns. (14) and (15) to our data on the Co(II) and Ni(II) chelates revealed that a better straight line results with eqn. (15) and, hence, the order of reaction is unity.

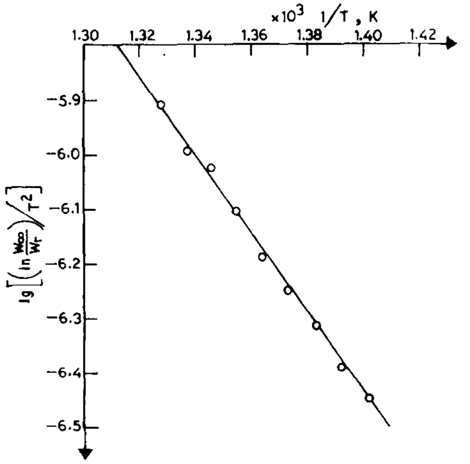

Fig. 7. Coats–Redfern plot for CoL_2.

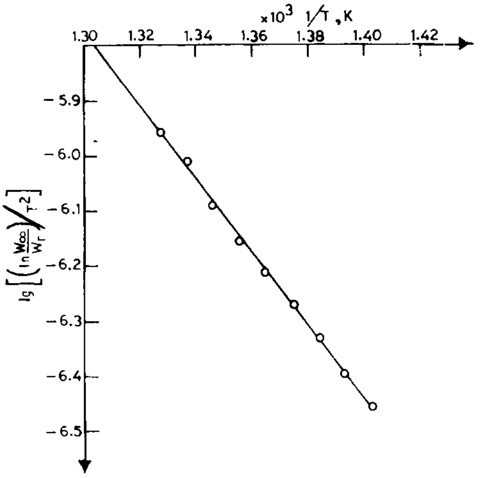

Fig. 8. Coats–Redfern plot for NiL_2.

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

$$\log\left[\frac{\ln(w_\alpha/w_\alpha - w)}{T^2}\right] = \log\left[\frac{2R}{\phi E^*}\left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT} \qquad (16)$$

Since $1 - (2RT/E^*) \approx 1$, a plot of LHS of eqn. (16) against $1/T$ was drawn (Figs. 7 and 8), from the slope of which E^* was calculated. Using this value of E^*, Z was calculated from the intercept.

Approximation method using the Horowitz–Metzger equation [14]

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

$$\log\left[\frac{1 - (1 - \alpha)^{1-n}}{1 - n}\right] = \frac{E^*\theta}{2.303RT_s^2} \quad \text{for } n \neq 1 \qquad (17)$$

When $n = 1$, the LHS of eqn. (17) would be $\log[-\ln(1 - \alpha)]$. For a first-order kinetic processs the Horowitz–Metzger equation may be written in the form

$$\log\left(\log\frac{w_\alpha}{w_\gamma}\right) = \frac{E^*\theta}{2.303RT_s^2} - \log 2.303 \qquad (18)$$

where $\theta = T - T_s$ and the other terms are as described earlier. A plot of $\log[\log(w_\alpha/w_\gamma)]$ vs. θ was drawn and was found to be linear from the slope of which E^* was calculated. Typical curves are given in Figs. 9 and 10. The

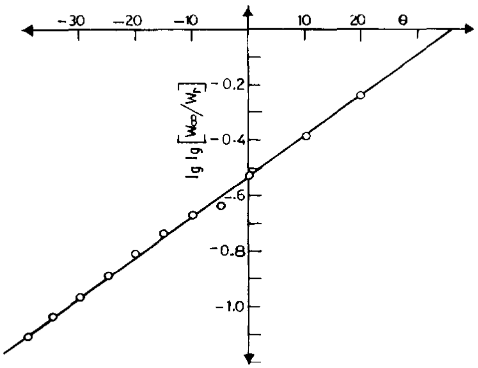

Fig. 9. Horowitz–Mestzger plot for CoL_2.

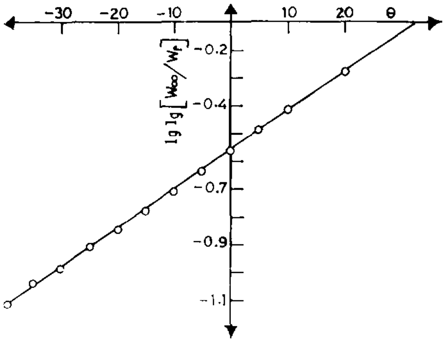

Fig. 10. Horowitz–Metzger plot for NiL_2.

pre-exponential factor, Z, was calculated from the equation

$$\frac{E^*}{RT_s^2}=\frac{Z}{\phi \exp(-E^*/RT_s)} \tag{19}$$

The entropy of activation, ΔS^*, was calculated as earlier from eqn. (7).

RESULTS AND DISCUSSION

Thermal behaviour

The TG curves for CoL_2 and NiL_2 give single well defined, non-overlapping peaks at the same temperature, as may be seen from Table 1. Mass loss at the end of this stage, read from the TG curves, is 87% for CoL_2 and 86% for NiL_2. The theoretical mass loss at this stage would be 88.1% for the decomposition $CoL_2 \rightarrow Co_3O_4$ and 87.2% for the decomposition $NiL_2 \rightarrow$

TABLE 1

Thermal decomposition data

Substance [a]	Decomposition temp. range (K)	% Mass loss			Peak temp. from DTG (K)	Order of reaction, Freeman–Carroll method
		Observed from TG	From independent pyrolysis	Calculated		
CoL_2	623–823	87.0	88.5	87.2	753	0.98
NiL_2	613–823	86.0	89.1	88.1	753	1.00

[a] L = salicylideneaminofluorene.

NiO. The end products are confirmed to be Co_3O_4 and NiO from their X-ray diffraction patterns.

In a recent work [10,15] certain transition metal chelates of the Schiff base vanillideneanthranilic acid were studied by TG and DTG as well as by IR, EPR and NMR spectroscopy, including those of cobalt and nickel, which are hydrated, polymeric chelates. But salicylideneaminofluorene chelates of cobalt and nickel are found to be anhydrous, based on elemental analysis, on the absence of dehydration peaks in DTG and on the absence of hydroxyl bands in IR spectra.

Decomposition kinetics

In studying the decomposition kinetics, three methods mentioned in the literature were chosen: Freeman–Carroll, Coats–Redfern, and Horowitz–Metzger. In the case of the derivation method, the most precise kinetic data are obtained when moderately steep sections of the thermogravimetric curves are taken for computation. The Coats–Redfern method seems to be more accurate but considerably time consuming.

The activation energy obtained from application of the Freeman–Carroll equation are for CoL_2, $E^* = 159.6$ kJ mol^{-1} and for NiL_2, $E^* = 147.3$ kJ

TABLE 2

Kinetic data

Substance	Parameter	From Freeman–Carroll equation	From Coats–Redfern equation	From Horowitz–Metzger equation
CoL_2	E^* (kJ mol^{-1})	159.6	147.3	167.7
	Z (s^{-1})	1.76×10^8	2.37×10^7	9.06×10^8
	ΔS^* (J K^{-1} mol^{-1})	−94.7	−111.5	−96.9
NiL_2	E^* (kJ mol^{-1})	147.3	147.4	155.0
	Z (s^{-1})	2.28×10^7	2.14×10^7	1.25×10^8
	ΔS^* (J K^{-1} mol^{-1})	−111.8	−112.3	−97.4

mol^{-1}. The Coats–Redfern equation gives activation energy values, $E^* = 147.3$ kJ mol^{-1} for the decomposition of CoL_2 and $E^* = 147.4$ kJ mol^{-1} for the decomposition of NiL_2. Somewhat similar values are obtained by application of the Horowitz–Metzger equation: for CoL_2, $E^* = 167.7$ kJ mol^{-1} and for NiL_2, $E^* = 155$ kJ mol^{-1}.

The entropies of activation for the two chelates are comparable. The negative values indicate that the activated complexes have a more ordered structure than the reactants, and that the reactions are slower than normal [16].

Because of their similar structures, both the complexes show similar thermal behaviour, as evidenced from their peak temperatures and comparable values of activation energy.

SUMMARY

The thermal analysis of cobalt(II) and nickel(II) complexes of the Schiff base salicylideneaminofluorene was studied by the TG technique. Thermoanalytical data (TG and DTG) of these chelates are presented in this communication. Interpretation and mathematical analysis of these data and evaluation of order of reaction, energies of entropy and activation based on the differential method employing the Freeman–Carroll equation, the integral method using Coats–Redfern equation and the approximation method using the Horowitz–Metzger equation are also given. Because of their similar structures both complexes show similar thermal behaviour, as evidenced from their peak temperatures and comparable values of activation energy.

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