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Short Communication

Non-isothermal Degradation and Kinetic Parameters of Some Complexes

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ABSTRACT

Complexes of Co(II), Ni(II), Cu(II) and Pd(II) with ligand 4-s-benzyl-1-p-chlorophenyl-5-phenyl-2,4-isodithiobiurate (BPPTB) have been prepared. The TG data of decomposition of complexes have been analyzed for kinetic parameters, employing Freeman- Carroll and Sharp-Wentworth non-isothermal methods.

Keywords: Freeman-Carroll, Sharp-Wentworth, Thermal degradation, Kinetic parameters.

INTRODUCTION

It have been seen that a great attention is being paid in isolating the thermally stable complexes and determining their energy of activation as well as kinetic parameters from thermal decomposition data to know about their kinetic stabling and course of reaction kinetics. Thermal decomposition studies of the complexes are useful in predicting the thermal stability of the complexes as the chemical changes in the complexes can be studied with the help of TGA, DTG and DTA studies [1]. Kinetic studies of thermal decomposition reaction are useful in calculating the important parameters like activation energy (E*), free energy change (ΔG*), enthalpy change (ΔH*), entropy change (ΔS*) and pre-exponential factor (A). Several methods are reported in literature for evaluation of kinetic parameters [2-6].

Here attempts are made of evaluate the kinetic and thermodynamic parameters of the complexes using methods viz, "Freeman and Carroll" [7] and "Sharp-Wentworth" methods [8]. Former is used to analyses kinetic parameters such as entropy change, free energy change, frequency factor, apparent energy change while latter is used to determine activation energy and order of reaction. On the basis of these data thermal stability of complexes has been suggested.

In the present communication we report relative thermal stabilities of some coordination complexes of Co(II), Ni(II), Cu(II) and Pd(II) metal ions with ligand 4-s-benzyl–1-p-Chlorophenyl-5-phenyl-2, 4-isodithiobiurate (BPPTB). On the basis of their activation energies, calculated from non-isothermal TG data using Freeman-Carroll (FC) and Sharp- Wentworth (SW) methods. These methods for estimation of kinetic parameters are based on the assumption that the Arrhenius equation is valid and thermal and diffusion barriers are negligible [9].

MATERIALS AND METHODS

All the chemicals used were of AnalaR grade, solvents were distilled before use. The ligand used in the present work was synthesized by known method [10]. Metal salts of Co (II), Ni(II), Cu(II) were taken in the form of acetates while Pd (II) was used in the form of chloride. All the solutions of metal salts except Pd (II) were prepared in aqueous medium while later was prepared in dilute HCl adjusting its pH between 0.5 and 1.0. Ligand solution was prepared in methanol. The aqueous metal salts solution was gradually added with stirring to solution of ligand in the 1:2 (M:L) molar ratio. The solution was diluted with distill water till the coloured complex appears out. It was digested over water bath for 15 minutes, cooled, filtered and washed with hot mixture of water and ethanol. Product re-crystallized from solvent ether. Estimation of metal was done by classical method [11]. Nitrogen and sulphur were estimated by standard Kjeldahl method and Messenger method respectively [12].

Thermogravimetry (TG): The non-isothermal Thermogravimetric analysis of metal complexes was done on thermobalance fabricated at Central Instrumentation Centre, Nagpur University, Nagpur. All measurements were made at a linear heating rate of 5^0C min^{-1}. in air. These measurements were carried out from 40^0C to 700^0C taking sample masses ranging 2 to 4 mg at regular intervals of 20^0C until the mass loss was complete. TG curve for each complex were obtained by plotting percentage mass loss as a function of temperature.

RESULTS AND DISCUSSION

Thermograms of M(II) $(BPPTB)_2$ complexes are shown in fig. 1 where M=Co, Ni, Cu and Pd. In general water of hydration may be considered as crystal or as coordinated water. According to Nikolaev et.al [13], water eliminating below 150^0C can be treated as crystal water and water eliminating above 150^0C may be due to its coordination to metal ion. In present study Co (II) and Ni (II) complex contains no water of hydration is evidenced by observing their mass loss curve in graph 1. Co (II) $(BPPTB)_2$ complex is stable up to 110^0C while Ni (II) $(BPPTB)_2$ shows stability up to 200^0C. After that both complexes decompose rapidly due to oxidation – reduction reaction.

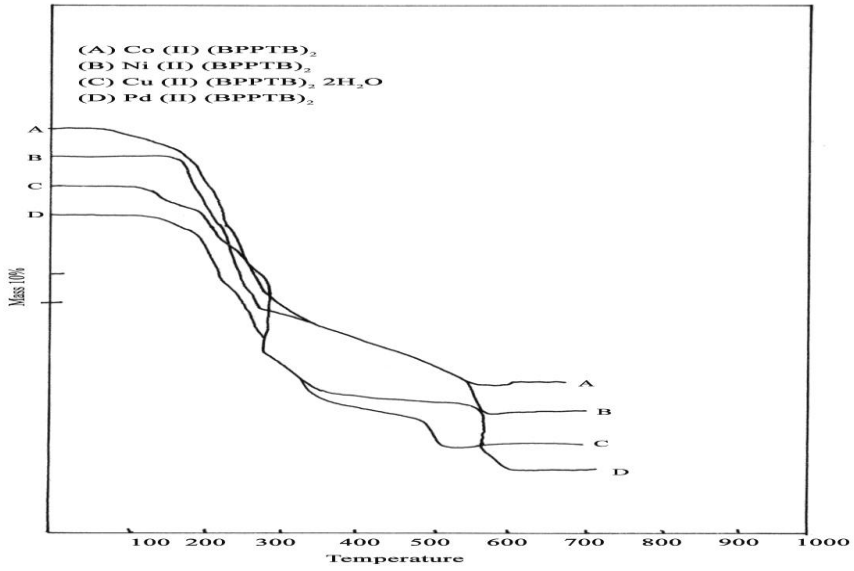

Fig. 1: TG curves of M (II) $(BPPTB)_2$ complexes

Cu (II) complex appears to be stable in temperature range 100 to 200^0C corresponds to weight loss of two moles water (3.80% found, 3.90% cal.). Complex shows rapid mass loss above 200^0C. Pd (II) $(BPPTB)_2$

complex contains no water of hydration and is stable up to 160^0C. Thermal stability of metal complexes of BPPTB follows the order Co (II) > Ni (II) > Cu (II) > Pd (II) respectively. As stated earlier, to determine kinetic parameters of the complexes Freeman-Carroll and Sharp-Wentworth methods have been used.
In Freeman-Carroll method following equation is used to evaluate various kinetic parameters.

$$\frac{\Delta \log (dw / dt)}{\Delta \log Wr} = \frac{- (E^* / 2.303\ R)\ \Delta (1/T)}{\Delta \log W} + n$$

Where Wr = Wα – W, Wα is mass loss at the completion of reaction, W is the mass loss up to time t, T is absolute temperature, n is order of reaction. R is the gas constant in calories and E* is the energy of activation in Kcal mol^{-1}.

By plotting

$$\frac{\Delta \log (dw / dt)}{\Delta \log Wr} \quad \text{against} \quad \frac{\Delta (1/T)}{\Delta \log W}$$

n is obtained as an intercept on former axis and Ea* is the slope of line.The following expression is used to evaluate Ea* by Sharp-Wentworth method.

$$\log \frac{(dc / dT)}{(1 - c)} = \log (A / \beta) - (Ea / 2.303\ RT)$$

Where, dc / dT is rate of change of mass with time t, T is temperature and $\beta = \Delta T/dt$.

The linear plot obtained by plotting

$$\log \frac{(dc / dT)}{(1 - c)} \quad \text{vs} \quad 1/T$$

Whose slope gives the value of Ea and from intercept A may be calculated.

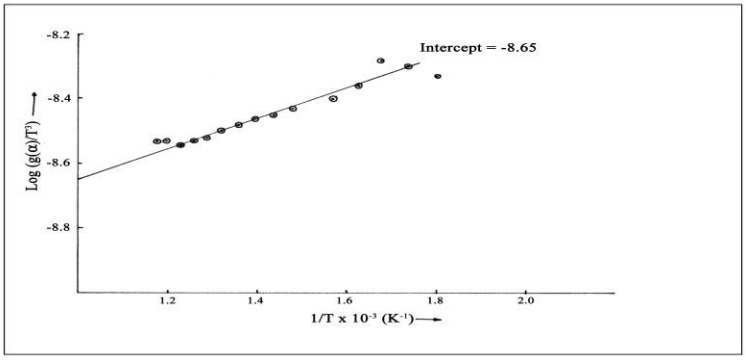

Fig. 2: Freeman – Carroll Plot of Ni (II) $(BPPTB)_2$ complex

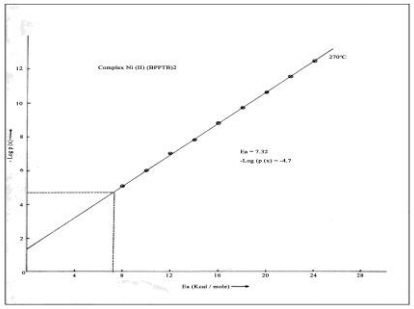

Fig 3: Calculation of log p(x) at270^0 C using Doyel graph

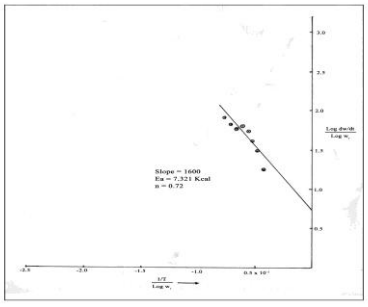

Fig 4: Freeman-Carroll plot of Ni (II) $(BPPTB)_2$ complex

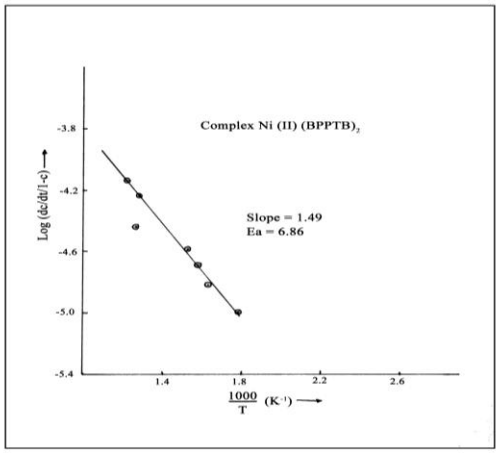

Fig. 5 : Sharp-Wentworth plot of Ni (II) $(BPPTB)_2$ complex

By using above methods thermal activation energies and thermodynamic parameters calculated are tabulated in table 1. Complex Ni (II) $(BPPTB)_2$ is taken as representative example and its kinetic plots are shown in fig. 2, 3, 4 and 5.

Table 1: Kinetic parameters of M (II) $(BPPTB)_2$ complexes using FC and SW methods

Complex	Decomposition Temp ^{0}C	Activation energy (Ea) K cal/mole		-Δ S (Cal)	Δ F (K cal)	Z (Sec^{-1})	S* (K cal)	n
		FC	SW					
Co (II) $(BPPTB)_2$	220	4.57	4.42	87.50	37.96	139.10	25.10	1(0.8)
Ni (II) $(BPPTB)_2$	200	7.32	6.86	87.89	34.83	148.54	22.73	1(0.72)
Cu (II) $(BPPTB)_2 2H_2O$	190	4.57	4.28	85.94	31.47	135.42	25.14	1(0.78)
Pd (II) $(BPPTB)_2$	150	5.12	4.98	89.39	33.10	186.35	24.85	1(0.66)

FC-Freeman Carroll method, SW-Sharp-Wentworth method. Figures in parentheses denote actual order found.

From the thermal decomposition data (Table 1), it is seen that thermal stability of metal complexes for BPPTB are in the order Co(II) > Ni(II) > Cu(II) > Pd(II) respectively. Values of activation energies calculated using SW and FC methods are harmony with each other. This is good agreement with finding of T. Ozawa

Ni(II) > Pd(II) > Co(II) > Cu(II)

Change in entropy for the complexes shows following orders Co(II) > Ni(II) > Pd(II) > Cu(II) respectively. Low values of Z for complexes may be due to classical slow reaction and hence other probable reason cannot be given. Analysis of data obtained by different equation indicates that decomposition of these complexes follow first order kinetics.

APPLICATIONS

Thermal decomposition studies of the complexes are useful in determining stability of the complexes with the help of Thermogravimetry. Methods reported in the present paper are useful in determination kinetic parameters such as activation energy, free energy change, enthalpy change and entropy change and pre-exponential factor.

CONCLUSIONS

Thermograms of M (II) $(BPPTB)_2$ complexes shows activation energy calculated by FC and SW methods are in good agreement with each other. Thermal decomposition of the complexes follows first order kinetics.

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