Thermodynamic Kinetic Parameters of Some Transition Metal Complexes of Schiff Base

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Complexes of Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) with Schiff base are prepared by condensation of 3-acety-6-methyl-(2H)-pyran-2,4(3H)dione (dihydroacetic acid) with *o-toluidine*. The ligand acts as bidentate molecule. The kinetic parameters for their decomposition have been evaluated by Coats-Redfern method from TG data. The values of kinetic and thermodynamic parameters are comparable and the decomposition follows a reaction mode.

INTRODUCTION

Schiff bases are known for their biological, industrial and analytical importance[1,2]. Metal complexes of various Schiff bases have been the subject of intensive research but comparatively little attention has been given to the Schiff bases derived from dihydroacetic acid and no report is available for the kinetic parameters of such complexes. The present communication deals with the synthesis, thermal degradation and evaluation of kinetic parameters of complexes of Cu(II), Ni(II), Co(II), Fe(III) and Mn(II) with Schiff base derived from dihydroacetic acid and *o*-toluidine.

EXPERIMENTAL

The Schiff base was synthesised by adding an ethanolic solution of the appropriate amine (*o*-toluidine) to an ethanolic solution of lactone (dihydroacetic acid) in 1:1 molar ratio and refluxing the resulting mixture on an RML Rotamantle for 4–6 h. The white product was crystallised from ethanol. Purity of the compound was checked by TLC.

The metal complexes were synthesised by adding a methanolic solution of the appropriate metal salt $MCL_2 \cdot xH_2O$ (0.02 mol) to a methanolic solution of Schiff base (DHA—*o*-toluidine) (0.02 mol) and the reaction mixture was refluxed on an RML Rotamantle for 2 h. To the cold solution, 10% alcoholic ammonia solution was added dropwise till the precipitate was formed. The complexes of different metals were precipitated at different pH. The precipitate of complex was filtered in hot condition, washed with hot methanol followed by petroleum ether (40–60°C). The metal complexes were dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator.

The TG curves were recorded at RSIC, Chennai, with heating rate 10°C per min from room temperature to 1000°C in nitrogen atmosphere.

RESULTS AND DISCUSSION

The analytical data and physico-chemical data of the ligand and complexes

are presented in Table-1. The conductivity data of all complexes (in 10^{-4} M DMSO) show the non-electrolytic nature of these complexes

TABLE-1
PHYSICAL DATA AND MAGNETIC DATA OF THE COMPLEXES.

Compound*	Colour	m.p. (°C)	μ_{eff} (B.M.)
DHA-2-methyl phenyl anil (L_1)	White	164	—
[Cu(II)-(L_1)$_2$]	Green	252	1.81
[Ni(II)-(L_1)$_2$]	Brown	>300	3.31
[Co(II)-(L_1)$_2$]	Green	>300	4.45
[Fe(II)-(L_1)$_2$]	Brown	248	5.59
[Mn(II)-(L_1)$_2$]	Black	>300	5.13

*All compounds gave satisfactory C, H and N analysis.

The infrared spectra of the ligands show a broad weak band around 2600–2400 cm^{-1} attributed to intramolecular hydrogen bonding[3]. The O—H$\cdots$N stretching at 2600–2400 cm^{-1} observed in the ligand is absent in all the complexes which confirms the deprotonation of enolic O—H and cooordination of oxygen with metal ions. This is further supported by an upward shift ν(C—O) (1250 cm^{-1}) the extent of 20–30 cm^{-1} in all the complexes. Infrared spectrum of ligand shows a strong band at 1670 cm^{-1}(C=N) which is shifted to lower frequency region (1650 cm^{-1}) in the complexes indicating the participation of azomethine group in chelation. The new bands at 580 cm^{-1} and 460 cm^{-1} in the metal complexes have been assigned to ν(M—O) and ν(M—N) mode respectively[4].

On the basis of magnetic moment value (Table-1) octahedral geometry for compounds **1–4** and tetrahedral geometry for compound **5** are suggested.

Thermal Studies

[Cu(II)-(L_1)$_2$] **complex:** TG curve of Cu(II)-(L_1)$_2$ complex shows that there is no weight loss up to 260°C indicating the absence of lattice or coordinated water. Therefore, the complex exhibits high thermal stability and decomposes at > 300°C. The thermogram shows one step exothermic peaks at 314.6°C which indicate the decomposition temperature of Cu(II) complex. Endothermic peak observed in differential thermal curve around 439.9°C and 589.7°C may be due to decomposition of the organic ligand and subsequent slow oxidation[5]. The thermogravimetric curve attains stability at 700°C and the horizontal line has been observed after 700°C in the complex and the residue corresponds to the respective metal oxide.

[Ni(II)-(L_1)$_2$] **complex:** A careful analysis of thermogram indicates that the complex is stable up to 280°C. The metal chelate follows single step decomposition. The thermogravimetric curve shows a single exothermic peak at 343.5°C which indicates decomposition temperature of the metal chelate and shows absence of lattice or coordinated water. Finally NiO is obtained as the end product.

[Co(II)-(L$_1$)$_2$] complex: The observed weight loss within 40–105°C temperature range could be correlated with the loss of water of crystallisation or lattice water[6]. The second step was encountered at 240°C where the organic constituents of the complex start breaking and the decomposition at 337°C shown in thermogravimetric curve is supported by two endothermic peaks at 312 and 486°C in differential thermal curve. The formation of metal oxide is observed at 697°C.

[Fe(III)-(L$_1$)$_2$] complex: The thermogravimetric curve of Fe(III) complex shows an exothermic peak at 87.9°C which corresponds to water of crystallisation. However, the temperature 274°C may be the decomposition temperature of organic matter and the exothermic peak at 328°C indicates decomposition temperature of the complex. FeO is obtained as the end product at 554°C.

[Mn(II)-(L$_1$)$_2$] complex: The thermogravimetric curve of Mn(II) complex shows a weight-loss by a weak exothermic peak at 61°C, indicating the presence of lattice or water of crystallisation[7]. The organic part completely decomposing in the range 231–289°C was supported by differential thermal curve. Finally, MnO is obtained at 621°C.

Thermal studies indicate that all the metal complexes do not contain coordinated water and that they are thermally quite stable. Decomposition of all the complexes started at relatively higher temperature and was completed above 650°C and the weights of the residue correspond to the formation of metal oxide. The thermal behaviours of Cu(II) and Ni(II) complexes are almost same, while the others differ from them.

Kinetic Parameters for Thermal Decomposition: The fractional weight loss (α) and the corresponding $(1 - \alpha)^n$ have been calculated from TG curves at different temperatures, where n depends upon the reaction model and $\alpha = (\omega_t - \omega_f)/(\omega_0 - \omega_f)$. The T *vs.* $(1 - \alpha)$ curves were constructed on the basis of thermogravimetric data for all the five complexes. The decomposition reaction for the loss of Schiff base moiety from the complexes was subjected to non-isothermal kinetic studies. The weighed least-square method (LSM) was used for obtaining best-fit linear plots by applying the data of various equations and thus the kinetic parameters were evaluated. The values of slope, intercept and energy of activation were obtained from plots. The value of frequency factor (Z) was evaluated using eqn. (1) for Coats-Redfern method and the entropy of activation was calculated using eqn. (2).

$$\text{Intercept} = \log (ZR/\beta E_a) \qquad (1)$$

$$\Delta S = 2.300R \log Zh/KT_m \qquad (2)$$

where K is the Boltzmann constant, h the Planck's constant, β the rate of heating, R the molar gas constant and T_m the peak temperature.

The values of E_a, Z and ΔS are given in Table-2 and the apparent order of the reaction is one. The values of kinetic parameters have been calculated by Coats-Redfern method[8]. The higher value of activation energy suggests the higher stability. In the present study, the numerical values of activation energy (E_a), frequency factor (Z) and entropy of activation (ΔS) indicate the smoothness of

the feasibility and reaction rate of the initial reactants and intermolecular stage compounds.

TABLE-2

THERMAL KINETIC PARAMETERS OF THE COMPLEXES OF Cu(II), Ni(II), Co(II), Fe(III) AND Mn(II) BY COATS-REDFERN METHOD

Compound No.	Decomposition stage/temp. (°C)	E_a (kJ mol^{-1})	Z (S^{-1})	$-\Delta S$ (kJ mol^{-1})
[Cu(II)-(L$_1$)$_2$]	I/314	33.26	326	202.40
[Ni(II)-(L$_1$)$_2$]	I/343	12.31	204	206.00
[Co(II)-(L$_1$)$_2$]	I/240	8.75	117	209.00
	II/337	32.21	323	202.86
[Fe(III)-(L$_1$)$_2$]	I/274	4.38	62	215.84
	II/328	10.44	152	209.01
[Mn(II)-(L$_1$)$_2$]	I/256	20.88	248	203.80
	II/449	75.35	533	214.00

The negative values of entropy of activation indicate that the activated complexes have a more ordered or more rigid structure than the reactants.

Kinetic parameters for these compounds have been determined individually at the first and second decomposition stages. Usually the first decompostition temperature lies in the range 240–343°C and the second one in the range 328–449°C. The order of thermal stability of compounds comes to be $2 > 1 > 4 > 5 > 3$ ($343 > 314 > 274 > 256 > 240$°C) (on the basis of first decomposition stage) and $5 > 3 > 4$ (on the basis of second decompostiion stage). The order of stability of the compounds on the basis of the values of activation energy can be set as $1 > 5 > 2 > 3 > 4$ (for first step) and $5 > 3 > 4$ (for second step). The variation in the trend might be interpreted to be due to some intermolecular interactions (structural as well as electronic) occurring therein. These are besides several experimental factors[9].

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