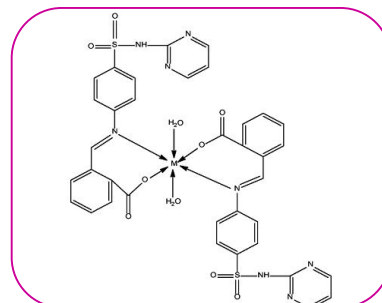_____

THERMAL DECOMPOSITION AND KINETIC PARAMETERS OF SOME SCHIFF BASE METAL COMPLEXES : A THERMAL STUDY

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ABSTRACT

The nature of water molecules indicated in the IR spectra was further ascertained by thermal analysis. The thermal stability of the polymeric metal chelates up to the decomposition point indicates that they are thermally stable. Aromatic back bone units are much more widely stable than aliphatic one, and they have a significantly higher melting temperature. It is known that the rather high thermal stabilities of the poly Schiff bases over the polychelates are due to numerous factors, such as molecular weight, stearic effects and resonance energy along the backbone of the chain. Marval and Torkoy reported the thermal stability of poly Schiff bases derived from 5, 5-methylene-bis-salicylaldehyde. They observed the heat stability of polychelates to be in the order Ni>Co>Cu. The water molecule (lattice or coordinated) was calculated by considering the amount of residue at 250^0C. Water in inorganic salts may be classified as lattice or coordinated water. There is, however, no definite borderline between the two. The former term denotes water molecules trapped in the crystalline lattice, either by weak hydrogen bonds to the anion or by weak ionic bonds to the metal or by both. Whereas the latter denotes water molecules bonded to the metal through partially covalent bonds. Studies of vibrational spectra are also useful for this purpose. It should be noted, however, that the spectra of water molecules are highly sensitive to their surroundings.

KEYWORDS: *nature of water, molecular weight,water molecules.*

INTRODUCTION

In general, lattice water absorbs at 3550-3200 cm^{-1} (anti-symmetric and symmetric OH stretching) and at 1630-1600 cm^{-1} (HOH bonding). According to Freeman, water eliminated below 150^0C can be considered as lattice water and above 150^0C coordinated to metal ion.   We have used a dynamic method by heating about 10-20 mg of the sample with increase of 10^0C per min from room temperature to 1000^0C in nitrogen atmosphere. On the basis of % loss in weight the thermal decomposition of the complexes can be discussed as follows:

Cu(II) complexes:

The presence of water molecules in coordination sphere was further checked by thermogravimetric analysis. TG curve shows that there is no weight loss up to 260^0C indicating the absence of lattice or coordinated water in Cu(II) complexes. Therefore the complexes exhibits high thermal stability and decompose at 300^0C. The TG thermogram (Fig. 4.26) shows one step exothermic peak at 314.6^0C which indicates the decomposition temperature of Cu(II) complexes. Endothermic peak observed in DT curve around 270.9^0C followed by two broad exothermic peaks at 439.9^0C and 589.7^0C may be due to decoposition of the organic ligand and subsequent slow oxidation. The TG thermogram attains stability at ~700^0C and the

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horizontal curve has been observed after 700^0C in these complexes and the residue corresponds to the respective metal oxide.

Ni(II) complexes:

A careful analysis of thermogram indicates that the complexes are stable up to 280^0C. The TGA date of these complexes reveal that metal chelates follow single step decomposition. The TG thermogram (Fig. 4.27) shows a single exothermic peak at 343.5^0C which indicate decomposition temperature of the metal chelates and absence of lattice or coordinated water. The complexes start decomposing partially giving metal oxide at 343.5^0C. The organic part completely decompose in the temperature range 335-492^0C as indicated by DT curve. Finally NiO is obtained as the end-product.

Co(II) complexes

The observed weight-loss within 40-105^0C temperature range could be correlated with, the loss of water of crystallization or lattice water, while the weight-loss within 110-220^0C could be correlated with the removal of coordinated water. The weight, losses for Co(II) complexes ecountered at 110.5^0C supported by broad exothermic peak in TG curve (Fig. 4.28) which is the characteristic of lattice water. The second step was encountered at 240^0C where the organic constituent of the complex starts breaking and decomposes at 337^0C shown in TG curve supported by two endothermic peaks at 312 and 486^0C in DT curve. Then the constant weight region corresponds to cobalt oxide, the final pyrolysis product.

Fe(III) complexes:

The TG curve (Fig. 4.29) of Fe(III) complexes shows a exothermic peak at 87.9^0C. corresponds to one molecule of water of crystallization. However, the temperature 274^0C may be the decomposition temperature of organic matter and the exothermic peak at 328^0C indicate decomposition temperature of the complex. The FeO is obtained as the end product at 554^0C showed in DT curve. All the complexes finally decompose to their metal oxide.

Mn(II) complexes:

The TG thermogram (Fig. 4.30) of Mn(II) complex show the weight loss by a weak exothermic peak at 61^0C, indicating the presence of lattice water or water of crystallisation. The chelates decompose at 256.9^0C indicated by a sharp peak in TG thermogram. The organic part completely decompose in the range 231-289^0C was supported by DT curve. Finally MnO is obtained as the end product at 621^0C indicated by endothermic peak in DT curve.

Thermogravimetric studies indicate that 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 complete above 650^0C and the weights of the residues correspond to the formation of metal oxide. The thermal behavior of Cu(II) and Ni(II) complexes are almost same while the other differs from them.

METHODOLOGY
THERMAL DECOMPOSITION AND KINETIC PARAMETERS OF Cu(II), Ni(II), Co(II) and Mn(II) COMPLEXES.
Theoretical considerations:

Thermal decomposition kinetic studies of thermal reactions are useful in studying parameters like free energy change (ΔF), enthalpy change (ΔS), activation energy (Ea) and pre-expontial factor (A) or frequency factor (Z). This concept was first proposed somewhere in 1928. Since then so many methods and equations have been put forward for studying thermal decomposition kinetics of the reaction. Thermal decomposition studies of materials are useful in predicting the thermal stability so that the chemical changes in the material can be studied with the help of TGA, DTG and DTA studies. Thermal decomposition kinetics were proposed by Flynn. In 1958. Freeman and Carroll published their method of kinetic analysis of thermo

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analytical data. Since then various methods for kinetic analysis have been proposed. On the basis of non-isothermal concept, some methods derived for estimation of the kinetic parameters are Coats-Redfern, Horowitz-Metzger, DharwadkarKarkhannawala, Zsako Doyle and Fuoss et al.

Horowitz-Metzger method gives reasonably good results while the other methods seems to be more accurate but they are a considerable time-consuming methods. Horowitz-Metzger method is therefore, used for finding the kinetic parameters of some representative transition metal complexes in the present work. Thermal decomposition reaction of many coordination compounds of transition metals by this method have been reported.

The method that was used to evaluate the kinetic parameters from TG traces of complexes is presented below.

Horowitz-Metzger method[6]

The method of Horowitz-Metzger is illustrative of the approximation methods. They derived the relation for such reactions by the following equation.

$$\log (\log W_c/W_r) = Ea\theta/2.3\,R\,Tm^2 - \log 2.3$$

The energy of activation (Ea) was calculated from the slope of the plots of

$$\log (\log W_c/W_r) \text{ vs}\,\theta$$

Where $W_r = W_c - W$ (W_c = weight-loss at completion of reaction and W = total weight-loss up to time t)

The frequency factor (Z) was calculated by

$$\text{Intercept} = \log (ZR/\beta Ea)$$

And the entropy of activation (ΔS) was calculated as

$$\Delta S - 2.303\,R\,\log Z\,h/k\,T_m$$

Where k is the Boltzman constant, h the plank's constant, β the rate of heating, R the molar gas constant and T_m the peak temperature.

RESULTS AND DISCUSSION

The non-isothermal kinetic parameters of Cu(II), Ni(II), Co(II), Fe(III), and Mn(II) with Schiff base DHA-4-methyl phenyl anil (L_1) have been calculated from the thermograms (Figs. 4.26-4.30). The log (log W_c/W_r)vsθ curves constructed on the basis of TG data for all the five complexes. The decomposition reaction for the loss of Schiff base moiety from the complex was subjected to non-isothermal kinetic studies at a uniform heating rate of 10^0/min. the weighted least-squares method was used for obtaining best-fit linear plots by applying the data of HM method and the kinetic parameters were calculated. The values of slops, intercept and energy of activation were obtained from the plots.

The thermograms of the Cu(II) and Ni(II) complexes show one stage thermal decomposition with a single DTG peak at 314.6 and 343.5 C respectively. The thermograms of Co(II), Fe(III) and Mn(II) show more than one stage of decomposition. Theoretically, with decreasing the value of Ea, the value of Z increases and the higher value of activation energy suggests the higher stability. However some other inherent physical and chemical factors may cause a change or deviation in this trend. The higher values of activation energy (Table 1) of Cu(II) and Ni(II) complexes show higher stability than Co(II), Fe(III) and Mn(II) complexes. Higher

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values of activation energy (Ea) and lower values of frequency factor (Z) favour the reaction rate of the initial reactants and intermolecular stage compounds.

The negative values for entropy of activation indicates that the activated complexes have a more ordered or more rigid structure than the reactants or intermediate and the reactions are slower than normalwhich is further.

Table 1
Thermal kinetic parameters of the complexes on the basis of Horowitz-Metzger (HM) method.

Complex	Decomp. Stage/temp. (^{0}K)	Ea (KJmol^{-1})	-ΔS (Jk^{-1}mol^{-1})	ΔF (kJmol^{-1})	Z (S^{-1})
1. L_1-Cu(II)	I/587	96.59	197.00	110.10	623
L_2 –Cu(II)	I/583	99.63	197.98	111.46	600
2. L_1-Ni(II)	I/616.5	63.42	162.66	75.48	317
L_2 –Ni(II)	I/610	66.08	164.57	78.15	302
3. L_1-Co(II)	I/513.4	22.22	197.03	123.33	549
	II/610.4	15.70	199.74	137.54	470
	III/824	14.31	199.24	137.54	653
4. L_1-Mn(II)	I/529.9	63.06	203.61	174.43	264
	II/722	30.45	204.31	153.24	167
5. L_1-Fe(III)	I/547	24.74	205.49	133.63	204
	II/601	38.93	209.74	190.41	168

Supported by low Z values. The order to thermal stability of compounds comes to be 2>1>4>5>3 (on the basis of first decomposition stage) and 4>3>5 (on the basis of second decomposition stage). The order of the stability of compounds on the basis of the values of activation energy can be set as 1>2>4>5>3 ((for first stage) and 5>4>3 (for second stage). The variation in the trend might be interpreted to be due to some intermolecular interactions (structural as well as electronic) occurring there in. There are besides several experimental factors.

On the application of the above mentioned method on the TGA traces of these complexes, Ea, Z, ΔS and ΔF values were obtained for the thermal decomposition reactions (Table 1). Ea values are sufficiently high while ΔS have negative values. These values are comparable with other observations

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Fig. 4.27 Thermogram of Ni(II) complex

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Fig. 4.28 Thermogram of Cu(II) complex

Fig. 4.29 Thermogram of Fe(III) complex

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Fig. 4.36 Thermogram of Mn(II) complex