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Thermal Decomposition Studies of Some Polymeric Complexes

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The thermal analysis of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) chelates with 4,4′-dihydroxy-3-3′-diacetyl biphenyl-2-mercapto-4,6-diamino triazine has been carried out in air atmosphere. All chelates show somewhat similar TG patterns. The activation energies of the chelates were calculated by using both the freeman-Carrol and Sharp-Wentworth methods. Various thermodynamic parameters have been evaluated by using thermal data. The order of thermal stability of chelates is found to

Cu(II) > Co(II) > Ni(II) > Fe(II) > Mn(II).

INTRODUCTION

In continuation of our work[1-4] on metal polychelates, the thermal decomposition studies of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) polychelates derived from 4-4′-dihydroxy-3,3′-diacetylbiphenyl-2-mercapto-4,6-diamino triazine(DDBMT) have been reported here. Very few systems are reported showing the relationship between thermal stability of metal chelates and structure of chelating agents[5]. Choudhari *et al.*[6] and Bhave *et al.*[7] studied the thermal properties of metal chelates with various chelating ligands. The purpose of this study is to report thermal stability and to ascertain the water of coordination/water of hydration in metal chelates.

EXPERIMENTAL

Preparation of the metal chelates: Metal polychelates of DDBMT were synthesized by interfacial polycondensation[8]. All the chelate polymers in the form of coloured powders were found to be insoluble in common organic solvents. Dynamic TGA were recorded by the TGS-2, Perkin-Elmer thermogravimetric analyser at Regional Sophisticated Instrumentation Centre, Nagpur University, Nagpur in air atmosphere. The heating rate was maintained at 10°C/min.

Energy of activation and order of reaction of thermal decomposition of complexes of DDBMT are determined by Freeman-Carrol[9] method using relation,

$$\frac{\frac{-E}{2.303}\Delta(1/T)}{\Delta \log w_r} = -X + \frac{\Delta \log dw/dt}{\Delta \log w_r}$$

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where E = Energy of activation, T = Temperature in K, R = Gas constant, W_c = Weight loss at completion of reaction, W = Weight loss up to time t, $W_r = W_c - W$, dw/dt = Rate of change of weight loss, X = Order of reaction.

From the graph

$$\frac{\Delta \log dw/dt}{\Delta \log W_r} \text{ vs } \frac{\Delta(1/T)}{\Delta \log W_r}$$

The order of feaction and energy activation were determined. Slope of the graph gave the value of $\frac{-E}{2.303R}$ and the order of the reaction was determined from Y-intercept.

While using Sharp_Wentworth[10] method following equation was used,

$$\log\left(\frac{dc/dT}{1-c}\right) = \log\frac{A}{\beta} - \frac{E_a}{2.303R}\cdot\frac{1}{T}$$

for a linear heating rate $\beta = dT/dt$.

Thus a linear plot is obtained on plotting $\log\left(\frac{dc/dT}{1-c}\right)$ vs $\frac{1}{T}$, whose slope gave the value of E_a and from the intercept, A may be evaluated.

RESULTS AND DISCUSSION

From the thermal curves various thermoanalytical data, including initial decomposition temperature (T_a), inflexion point temperature (T_b) and per cent-mass loss (%W) due to the oxidation-reduction reactions are incorporated in Table-1.

The presence of coordinated water molecules which is suggested from the IR spectra is confirmed by the thermogravimetric data. In general, the water of hydration may be considered as being either within the crystal lattice or coordinated. According to Nikolaev *et al.*[11], water eliminated below 150°C can be considered at lattice water, and that eliminated above 150°C may coordinated to the metal atom present. In the present study, in case of the Mn(II), Fe(II), Co(II), and Ni(II) polychelates the loss near 150–210°C equal to 7.94, 9.30, 8.60 and 9.50% respectively. These weight losses correspond to two coordinated water molecules per repeating unit of polychelates. The Cu(II) polychelate show weight losses in one step between 100–150°C equal to 8.10% which is probably due to two lattice water molecules. In the present studies initial decomposition temperature (T_a) and inflection temperature (T_b) have been used to determine thermal stability of metal chelates[11]. On the basis of experimental findings in the present course of studies, the relative thermal stability for DDBMT chelates can be given as Cu(II) > Co(II) > Ni(II) > Fe(II) > Mn(II). From TG it can be seen that there are three distinct stages in the degradation process. In the first stage upto 210°C there is about 7.94–9.50% weight loss and during second stage there is further weight loss. Ultimately the polychelates decomposes at 700°C leaving behind a residue which corresponds to the formation of Mn_3O_4, Fe_2O_3, Co_3O_4, NiO and CuO respectively[12]. In all the chelates the rate of decomposition in the

TABLE-1
RESULTS OF THERMOGRAVIMETRIC ANALYSIS OF DDBMT POLYCHELATES

Compund	T_a (°C)	T_b (°C)	% W	Activation FC(KJ/mole)	Energy SW	$-\Delta S$ (J)	ΔF (KJ)	Z sec^{-1}	$-S^*$ (J)	n
$[Mn(II)(DDBMT)2H_2O]_n$	250	350	78	18.77	18.26	287.10	116.06	81.25	107.76	0.65
$[Fe(II)(DDBMT)2H_2O]n$	270	360	76	25.10	22.27	309.40	124.09	99.17	104.66	0.65
$[Co(II)(DDBMT)2H_2O]n$	290	400	78	35.86	31.36	318.62	135.59	44.13	101.03	0.66
$[Ni(II)(DDBMT)2H_2O]n$	280	360	79	30.59	28.21	318.51	130.29	190.95	104.33	0.58
$[Cu(II)(DDBMT)2H_2O]n$	300	360	78	20.06	16.97	332.86	124.31	81.38	107.92	0.72

T_a = Temperature of initial decomposition.
T_b = Temperature at inflextion point.
%W = Calculated from mass loss curve.
FC = Freeman-Carroll.
SW = Sharp-Wentworth.

first stage is fast compared to the second stage. The thermal activation energy was calculated by employing the both Freeman-Carrol and Sharp-Wentworth methods and the values which are comparable are summerised in Table-1.

Considering the thermal data obtained using the Freeman-Carrol method, it is also possible to calculate thermodynamic parameters such as entropy change (ΔS), free energy change (ΔF), apperent entropy (S^*), and frequency factor Z for the polychelates. These values are also incorporated in Table-1. Their values are all very similar, which indicates a common reaction mode[13]. The abnormally low values of Z conclude that the decomposition reaction of the polychelates can be classed as a slow reaction[14].

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