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NOTE

Thermal Decomposition Kinetic Studies of Some Metal Complexes

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Thermogravimetric analysis was used to determine kinetic parameters such as order of reaction, activation energy, frequency factor etc. of some metal complexes based on the method of Freeman and Carroll.

Key Words: Kinetics, Metal Complexes, Thermogravimetric.

Thermogravimetric method is one among them which provides primarily chemical rather than physical information about the samples. Depending upon the properties measured and the temperature programs[1-3] more than a dozen thermal methods are recognized. Considerable work has been done on thermal decomposition kinetics of Schiff base complexes[4-8].

In this work, we reported the thermo-analytical data of Co^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+} and Pb^{2+} complexes of 1,5-(3,4-dihydroxybenzaldehyde) thiocarbohydrazone and 1,5-bis(3-hydroxy-4-methoxybenzaldehyde) thiocarbohydrazone and calculated the energy of activation (E), Arrhenius factor (A) and entropy of activation (ΔS).

Thermal analysis was carried out using a Perkin-Elmer series thermal analysis system in static air atmosphere. A constant heating rate of 10°C/min and sample mass of 2–5 mg were employed for the entire study.

Complexes of some metals, *e.g.*, Co^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+} with 1,5-bis(3,4-dihyroxybenzaldehyde) thiocarbohydrazone and 1,5-bis(3-hydroxy-4-methoxy benzaldehyde) thiocarbohydrazone were prepared by usual methods and the ligand by condensation of thiocarbohydrazone with 3,4-dihydroxybenzaldehyde and 3-hydroxy-4-methoxybenzaldehyde respectively in aqueous ethanol.

Thermogravimetric analyses of the M(II) chelates were done on universal $V_1$12E-TA thermal analysis system. It was found that there is no loss in weight up to 650°C for ML_1 (where L_1 = 1,5-bis(3,4-dihydroxybenzaldehyde) thiocarbohydrazone) and up to 730°C for ML_2 (where L_2 = 1,5-bis(3-hydroxy-4-methoxybenzaldehyde) thiocarbohydrazone). The loss in weight above 650 and 730°C in both the metal chelates complexes is due to the decomposition of

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chelates and loss of ligand molecules. Weight of final residue corresponds to MO. The observed loss and weight of residue agree well with the loss and weight expected as per formula of chelate in which M : L ratio is 1 : 2 in both the complexes.

The kinetics of decomposition of metal chelates to metal oxides was studied here. The kinetic parameters like energy of activation (E), frequency factor (Z) and entropy of activation (ΔS^*) were calculated by using Freeman-Carroll[9] method.

In this method, for the first order reaction, gives the relation

$$\log [(dw/dt)/w_r] = -E/2.303RT + \log Z$$

Here, $w_r = w_\alpha - w \cdot w_\alpha$ is the mass loss at the completion of the reaction and w the mass loss up to time t. The temperature slope dw/dT is converted into time slope dw/dt by using the relation

$$dw/dt = (dw/dT)(dT/dt) = (dw/dT)\phi$$

where ϕ is the heating rate.

Thus, a plot of $\log [(dw/dt)/w_r]$ *vs.* 1/T is a straight line with slope –E/2.303R and intercept $\log Z \cdot \Delta S^*$ is calculated by the relation

$$\Delta S^* = [\log Z - \log (kT_s/h)]2.303R$$

The E, Z and ΔS^* obtained by this method are given in Table-1.

TABLE-1
FREEMAN-CARROLL METHOD

Sample	T_i	T_f	T_s	E (kJ/mol)	Z (min^{-1})	ΔS^* ($J\ K^{-1}\ mol^{-1}$)
CoL_1	478	680	653	230.2	1.2×10^{21}	298.7
NiL_1	563	590	578	299.8	1.8×10^{24}	360.4
ZnL_1	565	653	635	267.4	1.1×10^{23}	170.8
HgL_1	427	562	548	463.2	1.4×10^{28}	272.6
PbL_1	442	680	660	270.2	1.2×10^{23}	369.6
CoL_2	427	653	624	312.4	2.3×10^{25}	483.2
NiL_2	536	623	596	238.0	2.2×10^{22}	193.2
ZnL_2	543	593	580	298.6	2.5×10^{25}	178.4
HgL_2	481	559	514	293.8	2.7×10^{26}	238.5
PbL_2	445	632	619	408.1	2.4×10^{32}	258.3

L_1 = 1,5-bis(3,4 dihydroxybenzaldehyde) thiocarbohydrazone
L_2 = 1,5-bis(3-hydroxy-4-methoxybenzaldehyde) thiocarbohydrazone

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