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Kinetic and Thermal Stability of Cobalt(II)-imipramine Complexes

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New six cobalt(II)-imipramine complexes have been thermally explored in great detail to evaluate the kinetic and thermodynamic parameters such as activation energy E_a, preexponential factor ln A, enthalpy ΔH, free energy ΔG and entropy ΔS. The enthalpy values and activation energy values are in the range 2.90–139.22 kJ mol^{-1} and 6.54–9.95 kJ mol^{-1}, respectively.

INTRODUCTION

The thermogravimetric studies of metal complexes[1–4] find extensive application in determining the purity, metal-ligand bond strength, melting points, etc. The synthesis and characterization of cobalt(II)-imipramine complexes have been reported earlier[5]. The present paper describes the kinetic and thermodynamic parameters of the title complexes employing TGA studies at a heating rate of 10°C min^{-1}.

EXPERIMENTAL

DuPont 9900 computer/thermal analyser with 951 TG module thermobalance was used to recording TG curves. About 8–10 mg of complexes were taken for analysis on TGA over a temperature range of 30–800°C in the atmosphere of nitrogen at a heating rate 10°C min^{-1}.

The thermograms curves were analysed to give percentage weight loss as a function of temperature. The activation energy E_a and pre-exponential factor ln A were obtained by Broido's method[6]. The Integral Procedure Decomposition Temperature were obtained by Doyle's mthod[7].

RESULTS AND DISCUSSION

In order to determine thermal stability trend, the termperature characteristics such as T_0 (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), T_{20} (temperature for 20% weight loss), T_{max} (temperature of maximum rate of degradation) and IPDT (integral procedure decomposition temperature) of the degradation process were calculated.

The T_0, T_{10} and T_{20} are three main criteria indicating the heat stability of complexes and they are also the sole features of thermogravimetric curves. The literature survey reveals that, higher the values of T_0, T_{10} and T_{20} higher the thermal stability of the system[8]. To obtain a quantitative assessment of the relative stability, IPDT values can be regarded as having significant importance because they represent the overall nature of the TG curves.

In these complexes cobalt(II)-thiocyanato complex show relatively high thermal stability and cobalt(II)-chloride complex show low thermal stability. The higher stability may be due to a great heat resistance character of the sulphur linkage to central metal ion[9] while the lowest stability of cobalt(II)-chloride complex may be ascribed to a purely high electronegative nature of chloride ion. The increased trend of the thermal stability of complexes is in the order

$$Cl^- < CH_3COO^- < Br^- < NO_3^- < SO_4^{2-} < SCN^-.$$

A graph of [ln (ln 1/Y)] *vs* 1/T (where Y is the fraction of the number of initial molecule not yet decomposed) for all three stages of degradation were ploted. The kinetic parameters such as activation energy E_a and pre-exponential factor ln *A* of the degradation process of complexes have been calculated by using the methods of Broido's[6] and are given in Table-1. The activation energies are low in first stage transition (6.54–9.95 kJ mol^{-1}) and the activation energies are high in third stage (121.48–156.53 kJ mol^{-1}). The lowest value for first steps due to this low energy is utilised to remove the coordinated water molecule. The abnormal values of ln *A* indicate that the decompostion reaction of the complexes can be classified as a slow reaction[10].

TABLE-1

KINETIC AND THERMODYNAMIC PARAMETERS FOR THE DEGRADATION PROCESS OF COMPLEXES

Complex	Process	$E_a \pm 2$ (kJ mol^{-1})	ln A ± 2 (min^{-1})	ΔH (kJ mol^{-1})	ΔS (JK^{-1})	ΔG (kJ mol^{-1})
$[Co(IP)_2(H_2O)_2Cl_2]$	I	08.54	10.87	05.02	–47.31	250.37
	II	38.93	17.96	34.07	02.00	329.45
	III	142.16	31.53	135.42	112.30	447.05
$[Co(IP)_2(H_2O)_2Br_2]$	I	09.95	11.63	06.97	–39.06	209.60
	II	40.08	19.32	35.81	13.31	289.83
	III	145.13	35.58	139.22	141.50	387.57
$[Co(IP)_2(H_2O)_2(NO_3)_2]$	I	07.74	10.62	04.33	–48.75	243.21
	II	32.10	17.40	27.98	–00.36	281.65
	III	128.00	31.47	121.80	108.47	409.65
$[Co(IP)_2(H_2O)_2(CH_3COO)_2]$	I	07.94	10.63	04.44	–48.81	249.50
	II	36.45	17.54	31.76	–00.46	320.33
	III	132.33	31.22	125.82	105.63	431.05
$[Co(IP)_2(H_2O)_2SO_4]$	I	06.59	09.96	02.90	–53.23	264.87
	II	24.56	14.70	19.85	22.18	323.41
	III	121.48	28.51	114.63	84.05	454.56
$[Co(IP)_2(SCN)_2]$	I	33.48	16.38	28.40	–10.62	348.91
	II	46.83	15.62	39.72	–10.67	488.49
	III	156.53	29.88	148.27	94.20	587.24

Considering the thermal decompostion data obtained from TG curves, it is also possible to evaluate thermodynamic parameters such as enthalpy (ΔH), free energy (ΔF) and entropy (ΔS) for all the complexes and the values are also given in Table-1. The comparison of the values of enthalpy with those of T_0 (from the t. g. curve) for complexes shows that with decreasing value of enthalpy the decomposition temperature also decreases.

The bond strength approximately characterizes from enthalpy value, together with the values of the activation energies. The free energy values are positive. The ΔH values are low in first stage and high in third stage. This may be ascribed to low energy of first stage which is sufficient to break the bond between the water molecule and metal ion. The second step's enthalpy values compared with third step show that in the second step the values are low, which may be due to the fact that metal-organic bond is weaker than the inorganic ligand-metal bond. The free energy values are negative in first two steps and positive in the third step. The entropy values are compensated by the value of enthalpies of activation, leading to almost the same values for the free energies of activation[11].

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