Thermal Decomposition Kinetics of Co (II) and Ni(II) Schiff Base complexes

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Abstract: The thermal behaviour of Co (II) and Ni(II) complexes derived from thiocarbohydrazone Schiff base was studied by thermogravimetric analysis(TG). The thermodynamic analysis shows that the complexes lose lattice and coordinated water molecules in the first step and decomposition of ligand moiety in the further steps leading to formation of stable metal oxide. The decomposition curves were analyzed and the parameters like order of reaction, energy of activation and apparent entropy were calculated by using Broido and Horowitz-Metzger methods. On the basis of half decomposition temperature, the thermal stability of the complexes was determined.

Keywords: Thiocarbohydrazone, Metal complexes, Thermal decomposition.

INTRODUCTION

Schiff base complexes derived from thiocarbohydrazone ligands containing strong donor sites such as oxygen, sulfur and azomethine nitrogen atom have been the subject of particular investigation, not only due to variety of ways in which they can bonded to metal ions, their spectroscopic properties and biological applications [1-7], but also due to their remarkable thermal stability as compared to the Schiff base ligands [8-10]. In this paper we report kinetics of the thermal decomposition pattern of Co(II) and Ni(II) complexes prepared by using thiocarbohydrazone ligand. The thermal parameters were calculated using Broido [11] and Horowitz-Metzger [12] methods. The complexes are thermally stable and their thermal decompositions are multistage processes. The complexes are subjected to a TG analysis from 50-850°C.

MATERIAL AND METHODS

All the chemicals used as a starting material for the synthesis of the ligand and their metal complexes were of AR grade or chemically pure, solvents were purified and dried before use. The metal complexes were prepared by mixing the ethanolic solution of metal salt with the solution of ligand by setting the suitable reaction conditions. The Co(II) and Ni(II) metal acetates were used for the preparation of complexes. Thermal analysis results of the complexes were obtained at a rate of 10^0C per minute on a Rijaku-Thermo plus EVO2 thermodilatometer.

Synthesis of the Schiff base ligands:

The ligand was prepared by the addition of hot ethanolic solution of thiocarbohydrazide (0.05 mol) into hot ethanolic solution of 4-Diethylamino-2-hydroxybenzaldehyde (0.10 mol). The reaction mixture was refluxed in a water bath for 4-6 hrs. The colored products so obtained were filtered off and recrystallized from dimethyl formamide.

Synthesis of Co(II) and Ni(II) Complexes:

Equimolar quantities of respective metal salt and the ligand were dissolved separately in absolute ethanol (30 ml). Both the solutions were filtered and mixed in hot condition. The reaction mixture was refluxed for 5 hrs in a water bath. The colored products obtained were filtered, washed several times with hot water followed by ethanol and diethyl ether.

RESULTS AND DISCUSSION

Thermogravimetric analysis of the complexes:

All the complexes are stable up to 800°C and are decomposed into two stages. The Co(II) and Ni(II) complexes remain stable up to ~210°C indicating absence of coordinated and lattice water molecules. Elimination of ligand moiety takes place in the first step and a part of coordinate ligand decomposed in second step followed by horizontal level beyond 650°C in all the complexes due to formation of stable metal oxides. The above pattern confirms the formation of metal complexes. The half decomposition temperature, entropy change (ΔS), free energy change (ΔF) and frequency factor (Z) of compounds were calculated by employing Broido and Horowitz-Metzger methods [22-24]. The kinetic parameter data for the complexes are given in the Table 3. On the basis of half decomposition temperature, the thermal stability of the Co(II) and Ni(II) metal complexes is found to be: CO-L_2 > Ni-L_2 > L_2 respectively.

Table 1 Thermal decomposition data of L_2 complexes.

Sr. No.	Complex	Half decomposition temperature (°C)	Activation Energy Ea (kJ mole^{-1})		(n)	Entropy Change -ΔS (J/mol/K)	Free Energy Change ΔF (kJ/mol)	Apparent Entropy Change S* (kJ)
			BR*	H-M**				
1.	L_2	410	20.00	31.1	0.92	-329.87	115.01	-24.21
2.	CO-L_2	390	11.77	15.14	0.96	-332.78	109.33	-33.34
3.	Ni-L_2	160	9.56	19.23	0.95	-220.06	88.88	-30.25

CONCLUSION

The activation energy calculated by the Broido and Horowitz- Metzger methods are in good agreement with each other. Thermodynamic parameters have been calculated on the basis of thermal activation energy and values are given in Table 1. The thermal stability of the compounds can be correlated with the substituent group attached to the ligands. It is found that more substituted ligands may have more thermal stability than more substituted ligands.

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