Asian Journal of Chemistry Vol. 10, No. 3 (1998), 587–590

Kinetic Parameters from TG Analysis of Co^{2+}, Ni^{2+} and Cu^{2+} Complexes

M.M. ALAM*, H.K. SINHA† and V.P. SINGH†
Department of Chemistry
M.G. College, Gaya, India

Kinetics of thermal decompositions of pyridine and morpholine complexes of Co^{2+}, Ni^{2+} and Cu^{2+} ions have been studied. Kinetic parameters, *viz.*, apparent activation energy, frequency factor, activation entropy and apparent order of reaction have been determined using the graphical method of Freeman and Carrol and results were compared by Coats-Redfern method. It was found that the data by both the methods are in good agreement.

INTRODUCTION

Literature survey reveals that thermodynamic study of complexes of bivalent metal ions[1–5] with a number of ligands have been made. The values of activation energy have been computed by the method.[6, 7] It is often difficult to choose a suitable equation to describe the kinetics of thermal decomposition reactions, specially of a complex where rate is governed by one or more rate determining processes. The basis of the calculation of kinetic data from TG curve is based on the formal kinetic equation $-dx/dt = kx^n$ where x is the amount of the sample undergoing reaction, n is the order of reaction, and k is specific rate constant and the latter's dependence on temperature is expressed as $k = Ae^{-E/Rt}$ where A is the pre-exponential factor, E is the activation energy and R is the gas constant.

EXPERIMENTAL

Thermogravimetric analyses of all the metal complexes were carried out on the thermogravimetric analyser of Stanton-Redcroft make Model TG 750 operating on 1.0 mv full seals for obtaining thermometric curve and a recorder for temperature versus time curve has been used. A heating rate of 10°/min was employed. The chart speed was maintained at 120 mm/hr. The medium was static air in all the heating. Experimental results were recorded in Table-1.

Preparation of the sample: Pyridine and morpholine complexes of isothiocyanate of Co, Ni and Cu are prepared by the method described by Kauffman *et al.*[1]

RESULTS AND DISCUSSION

The graphical method developed by Freeman and Carroll was used for the determination of activation energy E_a and the order of reaction 'b' from linear plot between $\Delta \log dw/dt/\Delta \log wr$ and $\Delta(T)^{-1}/\Delta \log wr$, where $wr = w_c - w$,

†Department of Chemistry, A.B. College, Gaya, India.

w_c = weight (mg) loss at completion of reaction, w = total weight loss up to time t, T = absolute temperature. The intercept having the value zero corresponds to the order of reaction and the slope is equivalent to $E_a/2.3R$ and the values of E_a in all the cases are shown in Table-2.

TABLE-1

Temp. (°C)	$Co(NCS)_2 \cdot 4L_1$ Wr (mg)	$Co(NCS)_2 \cdot 4L_2$ Wr (mg)	$Ni(NCS)_2 \cdot 4L_1$ Wr (mg)	$CO(NCS)_4 \cdot 4L_1$ Wr (mg)	$Cu(NCS)_2 \cdot 2L_1$ Wr (mg)	$Cu(NCS)_2 \cdot 2L_1$ Wr (mg)
70	2.05	—	—	—	—	—
80	1.95	—	—	—	—	—
90	1.80	—	1.65	—	—	—
100	1.55	0.54	1.55	—	1.90	—
110	1.25	0.46	1.40	—	1.75	—
120	0.65	0.40	1.15	—	1.50	—
130	—	0.30	0.73	—	0.70	—
140	—	0.20	0.25	—	—	—
150	—	0.12	—	—	—	—
160	—	0.05	—	—	—	—
170	—	—	—	—	—	—
180	—	—	—	—	—	—
190	—	—	—	—	—	0.30
200	—	—	—	1.75	—	0.25
210	—	—	—	1.63	—	0.22
220	—	—	—	1.38	—	0.15
230	—	—	—	0.88	—	0.08
240	—	—	—	0.18	—	—

L_1 = pyridine; L_2 = morpholine

The results were compared with Coats-Redfern method.[7] This was done by linear plot of log $f(\alpha)T^2$ *vs.* 1/T and results obtained were recorded in Table-2. The values of collision frequency was obtained by the equation Z = antilog (intercept) E_q/R.

Sample weight and log $g(\alpha)$ data at different temperatures was otained. The value of α is calculated with the equation given below.

$$\alpha = (W_0 - W)/(W_0 - W_t)$$

where W, W_0 and W_t are actual, intial and final weights of the sample respectively.

When $b = 0$, $g_0(\alpha) = \alpha$; when $b = 1$, $g_1(\alpha) = -\ln(1 - \alpha)$ and when $b = 2$, $g_2(\alpha) = \alpha/(1 - \alpha)$, where 'b' stands for order of kinetic thermal decomposition of complexes.

From the comparative study of results, it is clear that thermal decomposition of complexes follows the identical path as in each case, order of thermal decomposition is found to be zero.

TABLE-2
KINETIC PARAMETERS OF PYRIDINE AND MORPHOLINE COMPLEXES OF Co^{2+}, Ni^{2+} and Cu^{2+} IONS

Kinetic Parameters	Freeman-Carroll						Coats-Redfern					
	Pyridine complexes			Morpholine complexes			Pyridine complexes			Morpholine complexes		
	Co^{2+}	Ni^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
n (order)	Zero	Zero	Zero	Zero	Zero	Zero	Zero	Zero	Zero	Zero	Zero	Zero
E_a (Kcal mol^{-1}) (Activation energy)	2.08	1.90	2.45	2.20	3.20	4.30	1.46	1.20	1.32	3.16	4.17	4.22
$Z \times 10^5$ (Frequency factor)	3.52	3.42	3.71	3.61	4.32	4.81	2.62	2.59	2.72	4.12	4.61	4.76
$\Delta S^{\#}$ (E.U.) (Entropy of activation)	–34.14	–34.18	–33.20	–34.45	–34.06	–33.72	–34.72	–34.73	–34.42	–34.18	–33.93	–33.74

The apparent activation energy of these complexes are in the order given below:

$$Co > Ni < Cu \text{ (in pyridine complexes)}$$

and $$Co < Ni < Cu \text{ (in morpholine complexes)}$$

These orders are in good agreement with results of Freeman-Carroll[6] and Coats-Redfern.[7] The order is also according to the order as suggested by Irving-Williams.[8]

The activation entropy of these complexes has been calculated by the relationship given below:

$$\Delta S^{\#} = 2.303R \log (zh/kT)$$

where h = Planck constant, k = Boltzman constant, T = absolute temperature at which the weight loss is half of the total weight loss during the considered step.

Results obtained for $\Delta S^{\#}$ have been shown in Table-2. From this table, it is clear that the entropy of activation is negative in each case. The value of $\Delta S^{\#}$ indicate that there is formation of strong complex with greater order in their molecules. At last, we come to the conclusion that pyridine and morpholine attached to the metal ions with similar type of linkage.

REFERENCES

1. B. Georg Kauffman, A. Richard Albers and L. Fred Harlan, in: Robert W. Parry, Inorganic Synthesis, Vol. XII, McGraw-Hill Book Company, New York, p. 251.
2. R.Berg, *Z. Anal. Chem.*, **76**, 191 (1929).
3. M. Borrel and R. Paris, *Anal. Chem. Acta*, **4**, 267 (1950).
4. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd edn., p. 479.
5. F.J. Welcher, Organic Analytical Reagent, D. Van Nostrand Co., Inc., New Jersey, pp. 1–4 (1948).
6. E.S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
7. A.W. Coats and J.P. Redfern, *Nature (London)*, **201**, 68 (1964).
8. H.M. Irving and R.J.P. Williams, *Nature (London)*, **162**, 746 (1984).

(*Received*: 31 December 1997; *Accepted*: 17 February 1998) AJC-1443