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NOTE

Kinetics of Metal Complexes of Methylmorpholine

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Thermodynamic study has been made to know the coordinating ability of thiocyanate and isothicocyanate complexes of Fe^{2+}, Cd^{2+} and Cu^{2+} ions with methylmorpholine. Study of thermodynamic parameters suggests that (–SCN) has more coordinating power than (–NCS) complex.

Key Words: Kinetics, Complexes, Methylmorpholine.

Literature survey indicates that thermodynamic study of complexes of bivalent ions[1-3] with a various ligands have been made, but thermodynamic of metal complexes of thiocyanate and isothiocyanate in methyl morpholine appears to be scanty. Hence efforts have been made to study the complexes of Fe^{2+}, Cd^{2+} and Cu^{2+} thermodynamically and results are used to characterize the coordinating ability (–SCN) and (–NCS) on the basis of thermodynamic parameters computed by Freeman Caroll and Coats-Redfern method based in TG curves obtained after thermal decomposition of complexes of Fe^{2+}, Cd^{2+} and Cu^{2+} ions.

Kinetic data are obtained on the basis of thermal decomposition of complexes of these metals of considering

$$\text{(solid) A} \rightarrow \text{B (solid)} + \text{C (gas)} \tag{1}$$

The above thermal decomposition takes place in several steps (destruction of the crystal lattice) formation of crystal lattice of the solid product B and gaseous product C. Kinetics of the above type of the reaction is studied and Freeman and Carrolls method are applied and the following equations are used for calculating activation parameter (Ea) and order of reaction.

$$\frac{d\alpha}{dt} = \left(\frac{Z}{a}\right) e^{\frac{-E\alpha}{Rt}} f(\alpha) \frac{dT}{dt} \tag{2}$$

where α = dT/dt (Linear heating rate), Z = frequency factor, Ea = activation energy, R = gas constant, T = Absolute temperatures and $d\alpha/dt$ = rate of sample loss per degree, $d\alpha$ = fractional weight of the total weight loss and $f(\alpha)$ = function of the weight loss and from eqn. 1 we may write

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$$-\frac{d\alpha}{dt} = K.X^n \text{ when X = amount of sample}$$

Methylmorpholine complexes of isothiocyanets and thiocyanates of Fe^{2+}, Cd^{2+} and Cu^{2+} are prepared by the method of Kaufmann *et al.*[4] and then thermogravimetric analysis of these complexes are carried out by the method described by Alam *et al.*[2,3] and the experimental results are tabulated in Table-1.

TABLE-1

Temp. (ºC)	[Fe(NCS)$_2$ 2L] Wr (mg)	[Cd(NCS)$_2$ 2L] Wr (mg)	[Cu(NCS)$_2$ 2L] Wr (mg)	[Fe(SCN)$_2$ 2L] Wr (mg)	[Cd(SCN)$_2$ 2L] Wr (mg)	[Cu(SCN)$_2$ 2L] Wr (mg)
0	2.06	–	–	–	–	–
70	1.96	–	–	–	–	–
80	1.81	–	1.64	–	–	–
90	1.56	0.55	1.54	–	1.90	–
100	1.26	0.47	1.39	–	1.75	–
110	0.66	0.41	1.14	–	1.49	–
120	–	0.31	0.72	–	–	–
130	–	0.21	0.24	–	–	–
140	–	0.13	–	–	–	–
150	–	0.16	–	–	–	–
160	–	–	–	–	–	–
170	–	–	–	–	–	–
180	–	–	–	–	–	–
190	–	–	–	–	–	0.29
200	–	–	–	1.74	–	0.25
210	–	–	–	1.62	–	0.21
220	–	–	–	1.37	–	0.14
230	–	–	–	1.87	–	0.07
240	–	–	–	0.17	–	–

L = Methylmorpholine.

The graphical method developed by the freeman and Caroll is used for the determination of activation energy and the order of the decomposition from linear plot of

$$\Delta\log\frac{dw/dt}{\Delta\log wr}\text{against}\frac{\Delta T(\Delta T-1)}{\Delta\log wr}$$

where, Wr = (We - W); We = wt loss at completion of reaction and W = wt loss after time 't', T = absolute temp. The intercept gives the value of order of reaction and slope is equivalent to Ea/2.303R and the values obtained are tabulated in Table-2.

TABLE-2
KINETIC PARAMETERS OF METHYLMORPHOLINE THIOCYANATE AND ISOTHIOCYANATE COMPLEXES OF Fe^{2+}, Cd^{2+} AND Cu^{2+}

Freeman-Carroll					Coats-Redfern				
Complex	Order	E_a (kcal/mol)	$Z \times 10^5$	$\Delta S^\#$ (E.U)	Complex	Order	E_a (kcal/mol)	$Z \times 10^5$	$\Delta S^\#$ (E.U)
Fe-SCN	Zero	2.05	3.42	-34.16	Fe-SCN	Zero	3.16	4.12	-34.14
Fe-NCS	Zero	1.90	2.59	-34.72	Fe-NCS	Zero	2.50	4.02	-34.96
Cd-SCN	Zero	4.10	4.32	-34.05	Cd-SCN	Zero	4.17	4.50	-34.18
Cd-NCS	Zero	3.20	4.60	-33.94	Cd-NCS	Zero	3.60	4.40	-33.06
Cu-SCN	Zero	4.50	4.64	-33.74	Cu-SCN	Zero	4.16	4.10	-33.96
Cu-NCS	Zero	3.30	4.81	-33.72	Cu-NCS	Zero	3.45	4.06	-33.64

The results obtained are compared with Coats-Redferns method. This is done by the linear plot of log $f(\alpha)^2$ *vs.* 1/T and the results obtained are recorded in the Table-2 and the values of 'x' are calculated using

$$\alpha = \frac{Wo - w}{w_c}$$

where w, wo, wc are actual, initial and final weights of the sample results tabulated in Table-2. It is observed that the thermol decomposition of complexes of Fe^{2+}, Cd^{2+} and Cu^{2+} follows similar path. The apparent activation energy of these complexes are in order : $Fe^{2+} < Cd^{2+} < Cu^{2+}$.

These order are according to Freeman-Carroll and Coals-Redfern. The activation entropy of these complexes has been calculated by the equation

$$\Delta S^+ = 2.303 \log\left(\frac{zh}{kt}\right)$$

where, h = Plank constant, k = Boltzamn constant, T = absolute temperature at which the weight loss is half of the total weight loss during the considered step. The entropy values (Table-2) indicates that there is formation of complex with greater order in their molecules.

From the persual of the Table-2, it is evident that the values of activation energy of –SCN complexes is more than that of –NCS. Hence the explanation of the above results is due to more coordinating ability of S in (–SCN) than that of nitrogen in (–NCS). The above suggection is justified due to difference of lone pairs on S and N in thiocyanate (–SCN) and isothiocyanate (–N=C=S) and this finding is identical with the results of Singh *et al.*[5].

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