Solid state kinetics of Co(II) complex containing nitrogen, sulphur ligand (5-Anilino-1,2,3,4-thiatriazole) from thermogravimetric analysis

[1]Ku. Sarita Prasad, [2]Akhilesh Prasad, [3]Ajay Kumar

University Department of chemistry,
Magadh University, Bodhgaya – 824234, India

***Abstract*: Co(II) chloride form 1:2complex with 5-anilino-1,2,3,4-thiatrizol. Kinetic parameters like entropy of activation, activation energy, apparent frequency factors have been by Freeman Carroll method and Doyl's method as modified by Zsako method using non-isothermal TG curve. The complex decomposes regularly.**

***Keywords*: 5-anilino-1,2,3,4-thiatrizol T.G. curve, activation energy, order of reaction, entropy of activation and frequency factors.**

Introduction:

In recent years thermal analysis technique is becoming a useful tool in different field of study such as chemical science biological science and mechanical science[1-8]. Transition metal complexes have been used as antifungal[9], antibacterial[10], antitumor[11], antiviral[12] andantimalarial[13], agents. Research study indicates that a cyclic ligand containing nitrogen, oxygen and Sulphur donor atoms in their structures can act as effective chelating agent for transition metal ion. It is observed that when the drugs are administrated as metal chelate there is increase in activity. Literature survey indicate that a metal complex plays important role in the development of coordination chemistry[14, 15, 16].

The present paper deals the solid state kinetics of Co(II) complex with 5-anilino1,2,3,4-thiatriazole and determine the kinetic parameters such as order of reaction, frequency factor, activation energy and entropy of activation using Freeman-Carroll method as well as Doyles method modified by Zsako[17, 18, 19].

Experimental

5-anilino-1,2,3,4-thiatriazole was prepared by condensation of ethanolic phenylisothiocyanate with hydrazine and aqueous sodium nitrite. The complex was prepared by refluxing slowly 40 ml of ethanolic solution of Co(II) chloride (0.01M) with 40 ml of ethanolic solution of (0.02M) ligand. A reddish brown colour precipitate was obtained. The precipitate was filtered off and washed with ethanol and dried in desiccator over anhydrous calcium chloride. Thermograms was recorded by "NETZSCH" simultaneous thermal analyser STA – 409" recorder.

RESULT AND DISCUSSION

First stage decomposition of complex was selected to study the solid state kinetics. The T.G. curve thus obtained has been used to calculate the kinetic parameters such as activation energy and order of reaction, using the Freeman and Carroll[19] graphical method. A linear plots was obtained when verses was plotted.

The existing weight of the complex at equal temperature interval i.e. 10^0C were noted from the T.G. curve.

Table – I

Thermoanalytical data and decomposition temperature for S

S.No.	Temperature range (^{0}C)	Species degraded
1	100 – 270	Loss of moisture and 2 Cl ions
2	270 - 290	Loss of whole ligand moiety
3	400	CoO formation

Table - II

Data obtained by Freeman and Carroll method:

Calculation of for different activation energy and δ_2 values of different temperature for *[Co(L₂)Cl₂]*

S.No.	*Temp.(^{0}C)*	*30 K Cal*	*32 K Cal*	*34 K Cal*
1	270	13.12067	13.98267	14.83667
2	280	13.30472	14.15372	15.25772
3	290	13.37417	14.20117	15.54617
4	300	13.40413	14.21813	15.79513
5	310	13.43998	14.24098	16.04098
6	320	13.47311	14.26511	16.27911
7	330	13.52114	14.30014	16.77513
8	340	13.58013	14.34713	16.52314
9	350	13.64418	14.40218	17.02618
10	360	13.71854	14.46254	17.27854
11	370	13.80576	14.53776	17.53976
12	380	13.94826	14.67226	17.85226
13	390	14.24860	14.96260	18.31660
	Average($\bar{B}$)	**13.58333**	**14.36510**	**16.54364**
	St. Deviation(δ_2)	**0.28437**	**0.24200**	**0.00461**

Initial weight at 260^{0}C = 8.75760 mg

Final weight at 400^{0}C = 1.36115 mg

Here $W_r = W_c - W$

Wc= weight loss at completion of reaction.

W= total weight loss up to time t.

Table: III

Data of logf(α) value for complex δ at different temperatures

B=0	***B=1***	***B=2***
E_a	***E_a***	***E_a***
Kcal/mole (δ_0)	***Kcal/mole (δ_1)***	***Kcal/mole (δ_2)***
14	**26**	**30**
0.37060	0.11773	0.28437
16	**28**	**32**
0.37824	0.09690	0.24200
18	**30**	**34**
0.39606	0.40774	1.00481

Initial weight at 260^{0}C = 8.75760mg

Final weight at 400^{0}C = 1,36115 mg

The intercept at suggesting the order of the reaction as and applying E_a= 2.303R x slope gave the value of activation energy to be equal to 28 Kcal/mole.

In the Doyle's method modified by the Zsako the wight of the complex at different temperature were noted from T.G. curve and f(α)

Values are calculated =

Here

W_0= Initial weight .

W_f= Final weight

W= Actual weight

The B_1 value for different order of reaction were calculated by the following equation.

$B_0 = \log\alpha - \log\delta(x)$

$B_1 = \log(\ln - \log\delta(x)$

$B_2 = \log(- \log\delta(x)$

The values of - logδ(x) were noted from Zsako table. Therefore, the values of minimum deviation were calculated by the

δ = 0.0969.

where r is the number of experimental data calculation of B. The value of δ and E_a corresponding to B_0, B_1 and B_2 are given in table number **IV**

Table – IV

	Methods	***Order of reaction***	***Activation energy***
1	*Freeman and Carroll*	*1.17*	*28.99426 Kcal/mole*
2	*J. Zsako*	*1*	*28.0000 Kcal/mole*

The least value for minimum deviation was δ_1 = 0.0969 when B= 12.53815 and hence order of reaction was 1 and activation energy was E_a = 28 Kcal/mole.

The apparent frequency factor and apparent entropy of activation were calculated using. logZ= $\bar{B} + logRq - logEa$ and the value calculated for Z and $\bar{B}$ were 4.11036x10^7 sec^{-1} and -104.84149 e.u respectively the TG graph is shown below. The value of kinetic parameter obtained by different methods are good agreement with each other hence are more reliable, thus there may be utilised in the study of solid state mechanism.

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