SOLID STATE KINETIC STUDY OF HG (II) COMPLEX WITH 1,2,3,4-THIATRIAZOLE

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I. ABSTRACT:

Complexation of 5-amino-1,2,3,4-thiatriazole with Hg(II) acetate form 2:1 complex in ratio. kinetic parameters like order of reaction, energy of activation, entropy of activation and frequency factor is determined by the graphical method of Freemann-Carroll and Doyle method as modified by Zsako.

Keywords: 5-amino-1,2,3,5-thiatriazole, Freemann and Carroll method, Doyle method, Zsako method.

II. INTRODUCTION:

Thermal analysis technique is used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated at a constant rate. It is non-isothermal method which has many advantages over currently used isothermal process. The wide range of measurements possible provide fundamental information on the material properties of the system under test so it is applicable in understanding the biochemistry of the compound. It is used in a wide range of disciplines from pharmacy, antibacterial, antiviral, antifungal agents, anticancer activities and foods to polymer science[1-4]. Decomposition of the complex is done with random nucleation mechanism[5] without any gap.

This paper deals with the kinetic study of Hg(II) complex with 1,2,3,4-thiatriazole and various kinetic parameters are calculated by Freemann and Carroll[6] graphical method and Doyle's[7] method as modified by Zsako[8].

III. MATERIAL AND METHODS:

Single thermogrametic curve was recorded by 'NETZSCH' with thermal analyser STA-409 recorder. 20 grams ice cold solution of thiosemicarbazide in 95 cc of 2.2 (N) HCl was added in three, 50 ml portions of $NaNo_2$ solution (in 150 ml water). Tiny white needle like crystal was obtained after washing, recrystallising and vaccum drying. The complex is prepared by mixing ligand and Hg(II) acetate in hot ethanoic solution. An orange coloured precipitate obtained was filtered, washed and dried over anhydrous $CaCl_2$.

IV. RESULT AND DISCUSSION:

The thermogram shows that the complex compound is stable up to 120°C and the initial pyrolysis begins after 120°C where all the acetate molecules escapes giving a probable ensemble of HgL. Further heating above 340°C, the complex is completely decomposed which is selected for the study of the kinetic parameters. Freeman & Carroll graphical method are employed to calculate the order of reaction and activation energy followed by Doyle's method modified by Zsako.

Table – I

Data obtained by Freeman and Carroll method for the complex

[Hg (5-ATTZ) $(CH_3COO)_2$]

Sl. No.	Temperature (°C)	Weight left	$\frac{\Delta \text{Log } \left(\frac{dw}{dt}\right)}{\Delta \text{ Log } dw_r}$	$\frac{\Delta T^{-1} (K^{-1}) \times 10^{-3}}{\Delta \text{Log Wr}}$
1.	280.00	2.35	5.20838	1.05236
2.	290.00	2.27	10.19374	1.55285
3.	300.00	2.20	3.06120	1.63639
4.	310.00	2.12	-2.55321	0.77781
5.	320.00	2.01	-4.15234	1.27581
6.	330.00	1.87	-2.25444	0.60206
7.	340.00	1.70	-1.31673	0.42241
8.	350.00	1.49	-0.96717	0.27591
9.	360.00	1.23	-0.59326	0.16220
10.	370.00	0.93	-0.20645	0.08162

Initial weight at 260°c = 2.67 mg

Final weight at 380°c = 0.63 mg

A plot Δlog *dw/dt*/ Δlog w_r verses $T^{-1} \times 10^{-3}$/ Δlog w_r gives a straight line intercepting at zero suggested the order of reaction; 0.00 giving slope 3.19600 and the activation energy,E*;14.72080Kcal/mol using E*=slope 2.303R relation for the step considered.

Table – II

Data of Log (α) values for the complex [Hg (5-ATTZ) $(CH_3COO)_2$]

& calculation at different temperatures

Sl. No.	Temperature (°C)	Weight left	$\alpha = W_0 - W_t / W_0 - W_f$	log α	log(ln1/1-α)	Log(α/1-α)
1.	270.00	2.48	0.09314	-1.03088	-1.00982	-0.98842
2.	280.00	2.35	0.15686	-0.80448	-0.76796	-0.73038
3.	290.00	2.27	0.19608	-0.70757	-0.66104	-0.61278

4.	300.00	2.20	0.23039	-0.63753	-0.58191	-0.52380
5.	310.00	2.12	0.26961	-0.56927	-0.50283	-0.43282
6.	320.00	2.01	0.32353	-0.49009	-0.40797	-0.32034
7.	330.00	1.87	0.39216	-0.40654	-0.30291	-0.19033
8.	340.00	1.70	0.47549	-0.32286	-0.19024	-0.04261
9.	350.00	1.49	0.57843	-0.23775	-0.06360	0.13738
10.	360.00	1.23	0.70588	-0.15127	0.08770	0.38021
11.	370.00	0.93	0.85294	-0.06908	0.28260	0.76343

Initial weight at 260°c = 2.67 mg

Final weight at 380°c = 0.63 mg

To affirm the validity of the values of different parameters Doyle and Zsako equations are adopted;

$$F(\alpha) = \frac{ZE}{Rq} P(x)$$

$$\log \left(\frac{ZE}{\alpha R}\right) = \log F(\alpha) - \log P(x) = \text{constant (B)}$$

At every 10^0/min of decomposition of complex, the weight of the compounds are noted from the TG method.

Using the corresponding values of $F(\alpha)$ and –log P(x), the different values necessary for further calculation at various temperatures where determined by using relations below;

b = 0; $B_0 = \log \alpha - \log P(x)$

b = 1; $B_1 = \log (\ln \alpha/1-\alpha) - \log P(x)$

b = 2; $B_2 = \log (\alpha/1-\alpha) - \log P(x)$

Table – III
calculation of B_0 for different activation energies and δ_0 values at different temperatures for the Hg (5-ATTZ) $(CH_3COO)_2$

Sl. No.	Temperature (°C)	14 Kcal	16 Kcal	18 Kcal
1.	270.00	6.88712	7.50312	8.70412
2.	280.00	6.99852	7.89752	8.78552
3.	290.00	6.98043	7.86643	8.74243
4.	300.00	6.94547	7.81447	8.67547
5.	310.00	6.90373	7.76373	8.61173
6.	320.00	6.88191	7.72991	8.56491
7.	330.00	6.86446	7.69946	8.52146
8.	340.00	6.85214	7.67414	8.48714
9.	350.00	6.84725	7.65525	8.45425
10.	360.00	6.84473	7.64173	8.42773
11.	370.00	6.83892	7.62392	8.40192
12.	$\overline{B_0}$	6.89497	7.71543	8.57970
13.	δ_0	0.05359	0.10986	0.12690

The values of B_0, B_1 and B_2 along with the corresponding values of standard deviation are tabulated in Table III, IV and V, respectively.

Table – IV
calculation of B_1 for different activation energies and δ_1 values at different temperatures for the Hg (5-ATTZ) $(CH_3COO)_2$

Sl. No.	Temperature (°C)	16 Kcal	18 Kcal	20 Kcal
1.	270.00	7.52418	8.72518	9.62118
2.	280.00	7.93404	8.82204	9.70004
3.	290.00	7.91296	8.78896	9.65296

4.	300.00	7.87009	8.73109	9.57809
5.	310.00	7.83017	8.67817	9.51217
6.	320.00	7.81203	8.64703	9.46703
7.	330.00	7.80309	8.62509	9.43709
8.	340.00	7.80676	8.61976	9.41876
9.	350.00	7.82940	8.62840	9.41940
10.	360.00	7.88070	8.66670	9.44470
11.	370.00	7.97560	8.75360	9.51760
12.	$\overline{B_1}$	7.83446	8.69873	9.52446
13.	δ_1	0.11200	0.06663	0.09500

Table – V

calculation of B_2 for different activation energies and δ_2 values at different temperatures for the complex

[Hg (5-ATTZ) $(CH_3COO)_2$]

Sl. No.	Temperature (°C)	20 Kcal	22 Kcal	24 Kcal
1.	270.00	9.64258	10.52458	11.39958
2.	280.00	9.73762	10.60662	11.46962
3.	290.00	9.70122	10.55322	11.40322
4.	300.00	9.63620	10.48020	11.31720
5.	310.00	9.58218	10.41318	11.23718
6.	320.00	9.55466	10.37266	11.18366
7.	330.00	9.54967	10.35367	11.15167
8.	340.00	9.56639	10.35839	11.14239
9.	350.00	9.62038	10.39838	11.17438
10.	360.00	9.73721	10.50621	11.26921

11.	370.00	9.99843	10.75943	11.50943
12.	$\overline{B_2}$	9.66605	10.48423	11.29614
13.	δ_2	0.12371	0.11884	0.12591

A comparison of the value incorporated in the previous tables are given in the table-VI showing that least value of $\delta_{min} = 0.05359$, corresponds with the order of the reaction, b = 0, activation energy E*= 14kcal/mol and $B_0 = 6.89497$.

Table – VI

b = 0		b = 1		b = 2	
E* Kcal/mol δ_o		E* Kcal/mol δ_1		E* Kcal/mol δ_2	
14	0.05359	16	0.11200	20	0.12371
16	0.10986	18	0.06663	22	0.11884
18	0.12690	20	0.09500	24	0.12591

The values, order of reaction and activation energies, evaluated by the two different methods are given in the table VII and are in good agreement within limit.

Table – VII

Methods	Order of reaction[n]	Activation Energy [E*]
Freeman and Carroll	0.00	14.72080Kcal/mol
J. Zsako	0.00	14.00000Kcal/mol

The frequency factor Z was calculated using the equation:

$$\text{Log } Z = \overline{B} + \log Rq - \log E^*$$

Where, $\overline{B} = 6.89497$

q = heating rate 10°/minute

E* = 14 Kcal/ mol

Thus, the frequency factor for the thermolysis step under consideration was found to be 1.86948×10^{2} sec^{-1}.

On solving the following relation given below, the apparent entropy of activation was calculated to be -207.40980 e.u.

$$\Delta S^{\#} = R \ln Zh/kT$$

The value for the absolute temperature T was taken as the temperature at which the weight lost was half of the total weight lost for the considered step i.e., 613 K.

V. REFERENCES:

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