

The study of solid state kinetics of Co (II) complex with 5-amino-1,2,3,4-thiatriazole

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Abstract: 5-amino-1,2,3,4-thiatriazole forms 2:1 complex with Co(II) acetate. The graphical method of Freemann-Carroll and Doyle method as modified by Zsako is used to determine kinetic parameters like order of reaction, activation energy, frequency factor and entropy of activation. It undergoes two steps decompositions.

(Key words : Solid State kinetics, Freemann method, Doyle method, Zsako method, 5-amino-1,2,3,5-thiatriazole)

Introduction

The technique of thermogravimetric analysis is used in various fields such as; medical science, chemical science, biological science, polymer science etc.¹⁻⁸. As it is a continuous non-isothermal process, so thermal kinetics and decomposition of the complex have advantages in understanding the biochemistry of the compound over many isothermal processes. Heterocyclic compound containing transition metal are widely used in phamarceutical field such as; antibacterial⁹, antiviral¹⁰, antitumour¹¹, antimalarial¹² and antifungal¹³ activities.

The basis of the calculation of the kinetic data from a T.G. curve is based on the formal kinetic equation; $-dx/dt = kx^n$ where 'x' is the amount of sample undergoing reaction, 'n' is the order of reaction and 'k' is the specific reaction rate constant and the dependence of temperature is expressed as; $k = A e^{-E/RT}$. In this paper, kinetics of thermal decomposition of complex of Co(II) with 5-amino-1,2,3,4-thiatriazole is studied and various kinetic parameters are calculated by Freemann and Carroll¹⁴ graphical method and Doyle's¹⁵ method as modified by Zsako¹⁶.

Experimental

Thermogram was recorded by "NETZSCH" simultaneous thermal analyzer STA-409 recorder. To an ice cold solution of 20 grams of thiosemicarbazide in 95 cc of 2.2 (N) HCl, three, 50 ml portions of NaNO₂ solution containing a total of 14.7 gram of NaNO₂ (in 150 ml water) was added. The diazotization of thiosemicarbazide gives the product which was washed with ice cold water, recrystallised with methyl alcohol and dried in vaccum yield tiny, colourless needle like crystal decomposed at 136°C with slight explosion. The complex was prepared by refluxing ligand and Co(II) acetate with hot ethanol. A pink precipitate was separated out which was filtered, washed with ethanol and dried over anhydrous CaCl₂.

Results and Discussion

The second Stage of decomposition was selected to study the kinetics parameters such as; order of reaction, activation energy by Freeman & Carroll method. The initial weight of the complex and the decomposition of complex at 10⁰/min equal temperature intervals are noted.

A plot $\Delta \log dw/dt / \Delta \log w_r$ verses $T^{-1} \times 10^{-3} / \Delta \log w_r$ gives a straight line intercepting at 1.00 suggested the order of reaction; 1.00 and the activation energy, E*; 40.27123 Kcal/mol using $E^* = \text{slope} \times 2.303R$ relation for the step of the reaction under consideration.

Here $w_r = w_c - w_t$

Where w_c = weight loss at completion of reaction
 w_t = total weight loss upto time 't'.

Table-I
Data obtained by Freeman and Carroll method for the complex [Co (5-ATTZ)₂(CH₃COO)₂]

S. No.	Temperature (°C)	Weight left	$\frac{\Delta \log (dw/dt)}{\Delta \log w_r}$	$\frac{\Delta T^{-1}(K^{-1}) \times 10^{-3}}{\Delta \log w_r}$
1.	230	2.72	5.94427	1.91880
2.	240	2.69	27.60891	3.55395
3.	250	2.65	-8.34195	1.02439
4.	260	2.57	-9.52657	1.13516
5.	270	2.44	-3.71071	0.52499
6.	280	2.37	7.91082	0.97986
7.	290	2.30	0.00000	0.10803
8.	300	2.18	-3.27150	0.43325
9.	310	2.01	-1.19010	0.23547
10.	320	1.81	-0.31815	0.13040

Initial weight at 210°C = 2.86 mg

Final weight at 330°C = 1.51 mg

Table-2
Data of Log F(α) values for the complex [Co (5-ATTZ)₂(CH₃COO)₂]
calculation at different temperatures

S. No.	Temperature (°C)	Weight left	$\alpha = \frac{W_o - W_t}{W_o - W_f}$	log α	log (ln1/1-α)	log $\frac{\alpha}{1-\alpha}$
1.	220	2.78	0.05926	-1.22724	-1.21405	-1.20071
2.	230	2.72	0.10370	-0.98421	-0.96065	-0.93666
3.	240	2.69	0.12593	-0.89988	-0.87099	-0.84143
4.	250	2.65	0.15556	-0.80811	-0.77192	-0.73469
5.	260	2.57	0.21481	-0.66794	-0.61648	-0.56291
6.	270	2.44	0.31111	-0.50708	-0.42867	-0.34523
7.	280	2.37	0.36296	-0.44014	-0.34589	-0.24430
8.	290	2.3	0.41481	-0.38215	-0.27098	-0.14944
9.	300	2.18	0.50370	-0.29782	-0.15454	0.00643
10.	310	2.01	0.62963	-0.20091	-0.00294	0.23045
11.	320	1.81	0.77778	-0.10914	0.17727	0.54407

Initial weight at 210°C = 2.86 mg

Final weight at 330°C = 1.51 mg

Doyle¹⁵ applied an equation for the determination of activation energy;

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

Where, Z = Frequency factor

E = activation energy R = gas constant

q = heating rate

Zsako¹⁶ tried to simplify Doyle's method by logarithm as:

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

where 'B' depends on the nature of the compound and the heating rate.

Table-3
Calculation of B_0 for different activation energies and δ_0 values at different temperatures for the complex $[\text{Co}(\text{5-ATTZ})_2(\text{CH}_3\text{COO})_2]$

S. No.	Temperature ($^{\circ}\text{C}$)	38 KCal	40 KCal	42 KCal
1.	220.00	18.81676	18.67976	19.55676
2.	230.00	18.70879	18.59479	19.45279
3.	240.00	18.65612	18.36012	19.20412
4.	250.00	18.21789	18.14489	18.97589
5.	260.00	18.04706	17.98706	18.80606
6.	270.00	17.90592	17.86392	18.67092
7.	280.00	17.68786	17.65586	18.44486
8.	290.00	17.45685	17.44285	18.22285
9.	300.00	17.26618	17.27018	18.03618
10.	310.00	17.10109	17.11909	17.87209
11.	320.00	16.93886	16.96686	17.71186
12.	$\bar{B}_0$	17.89121	17.82594	18.63221
13.	δ_0	0.63198	0.56059	0.60210

Table - IV
Calculation of B_1 for different activation energies and δ_1 values at different temperatures for $[\text{Co}(\text{5-ATTZ})_2(\text{CH}_3\text{COO})_2]$ Complex

Sl. No.	Temperature($^{\circ}\text{C}$)	38 Kcal	40 Kcal	42 Kcal
1.	220.00	18.82995	18.69295	19.56995
2.	230.00	18.73235	18.61835	19.47635
3.	240.00	18.68501	18.38901	19.23301
4.	250.00	18.25408	18.18108	19.01208
5.	260.00	18.09852	18.03852	18.85752
6.	270.00	17.98433	17.94233	18.74933
7.	280.00	17.78211	17.75011	18.53911
8.	290.00	17.56802	17.55402	18.33402
9.	300.00	17.40946	17.41346	18.17946
10.	310.00	17.29906	17.31706	18.07006
11.	320.00	17.22527	17.25327	17.99827
12.	$\bar{B}_1$	17.98802	17.92274	18.72902
13.	δ_1	0.55936	0.48759	0.52907

The values of α is calculated for each temperature which gives the value of $\log F(\alpha)$ at different temperatures ranging 330k to 673k for the order of reaction $b=0, 1$ and 2 by using equation; $\alpha = w_0 - w_t/w_0 - w_f$

At various temperatures, using the corresponding values of $F(\alpha)$ and $-\log P(x)$, the

different values of B_0, B_1 and B_2 are calculated for the order of reaction; $0, 1$ and 2 and are tabulated in Table III, IV and V respectively.

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

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

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

The harmony in experimental data can be achieved by the standard deviation of individual B_i values from their arithmetical mean $\bar{B}$.

$$\delta = \sqrt{\frac{(B_i - \bar{B})^2}{r}}$$

Where 'r' is the number of experimental data used for the calculation of $\bar{B}$. $\delta_{\min}$ indicates maximum consistency with experimental data.

Table -V
Calculation of B2 for different activation energies and δ_2 values at different temperatures for [Co (5-ATTZ)₂ (CH₃COO)₂] Complex

Sl. No.	Temperature (°C)	44 Kcal	46 Kcal	48 Kcal
1.	220.00	20.46029	21.33229	22.20629
2.	230.00	20.36134	21.21934	22.07634
3.	240.00	20.48058	20.95157	21.79057
4.	250.00	19.88031	20.70831	21.53531
5.	260.00	19.65609	20.54409	21.35309
6.	270.00	19.63077	20.43377	21.23477
7.	280.00	19.43070	20.22070	21.00370
8.	290.00	19.23356	20.00956	20.77956
9.	300.00	19.10643	19.86843	20.63043
10.	310.00	19.05545	19.80545	20.55345
11.	320.00	19.10307	19.84507	20.57907
12.	$\bar{B}_2$	19.67260	20.44896	21.24933
13.	δ_2	0.52828	0.52776	0.57072

The least $\delta_{\min}$ value is 0.48759 which corresponds to the order of the reaction, b=1 and activation energy $E^*=40$ kcal/mol in the table-VI.

Table - VI

b = 0		b = 1		b = 2	
E*	δ_0	E*	δ_1	E*	δ_2
38	0.63198	38	0.55936	44	0.52835
40	0.56059	40	0.48759	46	0.52776
42	0.60210	42	0.52907	48	0.57072

Table - VII

Methods	Order of reaction[n]	Activation Energy [E*]
Freeman and Carroll	1.00	40.27123 Kcal/mol
J. Zsako	1.00	40.00000 Kcal/mol

The frequency factor Z was calculated to be $6.97525 \times 10^{12} \text{ sec}^{-1}$ for the thermolysis step under consideration using the equation:

$$\log Z = B + \log Rq - \log E^*$$

Where, $B = 17.92274$;

R = gas constant

q = heating rate $10^\circ/\text{minute}$;

$E^* = 40 \text{ Kcal/mol}$

The apparent entropy of activation was calculated to be -4.46474 e.u. from the relation;

$$\Delta S^\ddagger = R \ln Zh/kT$$

Where, T stands for the absolute temperature i.e 573 K at which the step under consideration was half complete.

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.

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