

Solid state kinetics of Zn(II) complexes with 5-anilino-1,2,3,4-thiatriazol

Basundhara Kumari

University Department of Chemistry, Magadh University, Bodh Gaya

Email : basundhara82@gmail.com

Manuscript received online 25 May 2020, accepted on 31 August 2020

Abstract : 5-Anilino-1,2,3,4-thiatriazol forms 1:1 complex with Zn(II) Chloride. Kinetic parameters like order of reaction, activation energy, entropy of activation and frequency factors have been determined by graphical method of Freeman and Carroll and Doyle's method as modified by Zsako using TG curve. The complex decomposes regularly. First stage of decomposition is selected for the determination of kinetic parameters.

(Keywords : 5-anilino-1,2,3,4- Thiatriazol, TG curve, order of reaction, activation energy. Entropy of activation, frequency factor)

Introduction

In recent years thermal analysis technique is becoming a useful tool in different field to study ad chemical science, polymer science biological and medical sciences.¹⁻⁸ The organic compounds contains N, and produce more sensational result *in vivo*⁹. The metal complexes have increased interest in the field of biological activities as antibacterial, antiviral, antifungal, agents.¹⁰⁻¹² Research study indicates that a cyclic ligand containing nitrogen, oxygen and sulphur donor atoms in their structure can acts as effective chelating agents for transition metal ion. It is observed that when the drugs are administered as metal chelate there is increase in activity.

Transition metal complexes which usually contain nitrogen, sulphur and oxygen as ligand atoms are becoming increasingly important because these Schiff bases can bind with different metals centers involving various co-ordination site and allow successful synthesis of metallic

complexes with interesting stereochemistry. The thermal decomposition products of the complexes having nitrogen/ sulphur ligands are apparently of significances in understanding the biochemistry of the complexes. Thus paper deals the solid state kinetics of Zn (II) complex with 5-anilino- 1,2,3,4, Thiatriazol and calculation of kinetic parameters i.e. order of reaction, activation energy. Apparent frequency factor and activation entropy using Freeman and Carrall method as well as Zsako method.

Experimental

Thermograms were recorded by Mettler TGA. Ligand with 5- anilino- 1,2,3,4, thiatriazol was prepared by condensation of ethanolic solution of phenyliso thiocyanate with hydrazine and aqueous sodium nitrite. Zn(II) complex was prepared by refluxing slowly 40 ml. ethanolic solution of 0.01 M Zn(II) chloride and 40 ml ethanolic solution of ligand. A white ppt was separated out gradually, which was filtered and dried over anhydrous CaCl₂.

Results and Discussion

The first stage of decomposition was selected to study the solid state kinetics. The kinetic parameters such as order of reaction, activation energy, were determined using the existing weight of the complex at equal temperature intervals, i.e., 10°C by Freeman and Carrall method. A linear plot were obtained when

$$\frac{\Delta \log dw / dt}{\Delta \log w_r} \text{ Vs } \frac{\Delta T^{-1} \times 10^{-3}}{D \log W_r}$$

was plotted

Table-1
Data obtained by Freeman and Carrall method

Temp °C	Weight	$W_r = W_c - W$	$\frac{\Delta \log dw / dt}{\Delta \log w_r}$	$\frac{\Delta T^{-1} \times 10^{-3}}{D \log W_r}$
01	140	3.71886	11.47321	1.57773
02	150	3.67792	03.39476	1.78206
03	160	3.64645	04.26689	2.06115
04	170	3.60597	02.97047	1.42509
05	180	3.53758	03.26336	0.71399
06	190	3.42591	01.46360	0.32772
07	200	3.26904	00.41508	0.57523

Initial weight at 120°C = 3.79 mg.

Final weight at 210°C = 3.14 mg.

Here $W_r = W_c - W$

W_c = Weight loss at completion of reaction

W = total weight loss upto time t .

the value of activation Energy to be equal to 18.66000 K cal/ mole.

In the Doyle's method¹³ modified by Zasko¹⁴ the weight at the compound at different temperate were noted from T.G cuve and $F(\infty)$ values are calculated (Table II)

The line intercepted at 1.8 suggesting the order of reaction as 1.8 and applying $E = 2.3R$ slop gave

Table II
Data of $\log F(\infty)$ values for the complex calculated at different temperatures

Temp °C	Weight (mg)	$\infty \frac{W_o - W_t}{W_o - W_f}$	$\log \infty$	$\log \left(\ln \frac{1}{1 - \infty} \right)$	$\log \frac{\infty}{1 - \infty}$
130	3.77142	10.02979	-1.52607	-1.51952	-1.51294
140	3.71886	01.11122	-0.95381	-0.92846	-0.90261
150	3.67797	0.17459	-0.75798	-0.71698	-0.67465
160	3.64645	0.22343	-0.65085	-0.59710	-0.54103
170	3.60597	0.28615	-0.54340	-0.47226	-0.39701
180	3.53758	0.39213	-0.40656	-0.30295	-0.19038
190	3.42591	0.56517	-0.24782	0-.07945	0.11385
200	3.26904	0.80825	-0.09245	-0.21789	0.62481
210	3.14530	1	0	0	0

Initial weight at 120°C = 3.79 mg.

Final weight at 210°C = 3.14 mg.

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f}$$

Here W_0 = Initial weight
 W_f = Final weight
 W = Actual weight

The Bi values for different order of reaction were calculated by the following equation

$$B_0 = \log \alpha - \log(v)$$

$$B_1 = \log\left(\frac{1}{1-\alpha}\right) - \log p(x)$$

$$B_2 = \log\left(\frac{\alpha}{1-\alpha}\right) - \log p(x)$$

The values of $-\log p(x)$ were noted from Zsako table. Therefore the values of minimum deviation were calculated by the

$$\delta = \sqrt{\frac{(B_1 \cdot B_2)^2}{r}}$$

Where r is the no of Experimental data for the calculation of B. The value of S and E corresponding to B_0 , B_1 and B_2 are give in table III

Table III

B_0		B_1		B_2	
Kcal/ mole	δ_0	Kcal/ mole	δ_1	Kcal/mole	δ_2
12	0.12324	12	0.15181	18	0.1556
14	0.14656	14	0.14397	20	0.13978
16	0.13235	16	0.14670	22	0.18347

The least value for minimum deviation was 0.12324 when $f=0$ and $E=12$ Kcal/ mole and $B_0=7.69222$. It indicates that the order of reaction and activation Energy are 0 and 12 KCal/ mole respectively. The apparent frequency factor and apparent entropy of activation were calculated using.

$$\log_z = \bar{B} + \log R_q - E \text{ and}$$

$$Ds \neq 8.31431 \log \frac{z \cdot h}{k t}$$

found to $Z = 3.56738 \times 10^7 \text{ sec}^{-1}$ and

$$\Delta S \neq -103.370 \text{ e.u.}$$

Respectively. The value of kinetic parameters obtained by different methods are in good agreement with each other.hence are more reliable.

Thus these may be utilised in the study of solid state mechanism.

References

1. M. F: Fleszor *Thermal Anal* (49) 219 (1997).
2. S Vyazarkin : *Int Res. Phys. Chem.* 19, 45 (2000).
3. N. Hurdev, M. Prayinaru, A. Creanga, S. Alazaroie N. Hurdne, *Rev mat plast* (41), 41 (2001).
4. R. K. Agrawal, S. Prasad, Gahlot N Turk *J. Chem.* (28) 691 (2004).
5. Chen. Luoy, P. Zhao FQ, Hurz, Li sw, Goa, Y, Chin. *Thermal Anal cal*, (91) 897 (2008).
6. A.B. Sigueria, G. Bannach, Rodriguer EC, Carvalho CT, J. *Thermal Anal cal*, (91) 897 (2008).
7. Z. H. Wang, Goyz, Zhang J, Mal. Song h B *J Agri food Chem.*, 58, 2715 (2010).

8. Z. J. Fan, Yang, Zharg HMN, wongsH, Coi F, Zuox, Zheng Q, Zhijin hs, *J food Chem. Agirc* (58) 2630 – 36 (2010)
9. M. G. Bhowan, J. Saina, RT Lanlloo, *Transition Metal Chemistry* (26) 329 (2001).
10. J.P. Scovill, D. L. Klayman, C.F. Fronchino, *J Med Chem.* (25) 126 (1982)
11. M. N. Hossain, M.N. Alam, J. Begum, *Inorganic Chin Act.* **249**, 207, (1996).
12. D. X. West, S. B. Podhy, P.B. Sonawane, *Chikte Rc, Strct, Bond*, (76). 1-50 (1991)
13. Doyle, C. D.J. *Appl. Palym. Sc.* **5**, 285 (1961)
14. J. Zsako, *J. Phys, Chem*, **72**, 2406 (1968)