Solid state kinetics of Cu(II) complex of [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] from thermo gravimetric analysis

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Abstract The ligand [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] (L) is a schiff base derived from condensation reaction of 1,2,3,4-thiatriazole-5-ylamine and Salicylaldehyde. Synthesis of the ligand (L) and the complex $[Cu(II)(L)_2] \cdot 2H_2O$ have been studied in our previous work (Bharti et al., Asian J Chem 23(2):773–776, 2011). Thermal decomposition behavior of synthesized Cu(II) complex has been investigated by thermo gravimetric (TG) analysis at heating rate of $10\ °C\ min^{-1}$ under nitrogen atmosphere. The mechanism of decomposition of Cu(II) complex has been established from TG data. Kinetic parameters such as order of reaction (n), activation energy (E_a), frequency factor (Z) and entropy of activation ($\Delta S^{\neq}$) were calculated by using Freeman and Carroll (J Phys Chem 62:394–397, 1958) as well as Doyle's methods as modified by Zsako (J Phys Chem 72(7):2406–2411, 1968).

Keywords Solid state kinetics · Thermal decomposition · Thermo gravimetric analysis · [2-(1,2,3,4-Thiatriazole-5-yliminomethyl)-phenol] · Kinetic parameters

Introduction

In recent years thermal analysis technique is becoming a useful tool in different fields of study such as chemical science, polymer science, biological, and medical sciences [1–15]. The Schiff bases have found wide applications in the field of co-ordination chemistry. Schiff base ligands containing strong donor sites like phenoxy oxygen atoms as well as imine nitrogen atoms, sulphur atoms have special co-ordination ability with transition metal ions and excellent for catalysis, biological replication [16–18]. Transition metal complexes of Schiff base ligands have increased interest in the field of biological activities such as antibacterial, antiviral and antifungal agents [19–21]. Schiff bases are potential anticancer drugs [22] and when administered as their metal complexes the anticancer activity of such complexes is enhanced in comparison to the free ligand [23]. Thiadiazoles [24, 25], triazoles [26, 27], and their derivatives are also known for there biological activities [28, 29]. The thermal kinetics and decomposition products of the complex are apparently of significance in understanding the biochemistry of the compounds [30].

This paper deals the solid state kinetics of Cu(II) complex with Schiff base of [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] and calculation of kinetic parameters, i.e., order of reaction, activation energy, entropy of activation, and frequency factor using Freeman and Carroll as well as Doyle's methods as modified by Zsako.

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Experimental

The ligand and the complex have already been synthesized and characterized in our previous studies [1]. The thermal analysis of synthesized Cu(II) complex of Schiff base [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] was carried out to investigate their degradation patterns and kinetic parameters such as order of reaction (n), activation energy

(E_a), and entropy of activation ($\Delta S^{\neq}$) were calculated by using Freeman and Carroll [2] as well as Doyle's methods as modified by Zsako [3]. The thermal behaviors of the compound were investigated using Universal V4.2E, TG 2950 TA Instruments USA. Generally, 20–30 mg of the complexes were taken in an alumina crucible and then subjected to a controlled heating rate of 10 °C min^{-1} in a temperature range of 30–1000 °C under nitrogen atmosphere.

Methodology and kinetic analysis

Freeman and Carroll method

The existing percentage mass of the complex at equal temperature intervals, i.e., 10 °C were noted directly from TG curve for a particular stage of thermal decomposition. A plot of $[\Delta \log \mathrm{d}w/\mathrm{d}t]/[\Delta \log W_r]$ versus $[\Delta T^{-1}]/[\Delta \log W_r]$ has been drawn for the stage of decomposition under consideration where $W_r = W_C - W$, W_C = total mass loss on completion of reaction, and W = total mass loss up to time t.

The straight line obtained is suggestive of the order of reaction from their intercept on Y-axis and the activation energy is equal to 2.303 $R \times$ slope. Freeman and Carroll had suggested that a good straight line is obtained, however, in the present cases remarkable deviations have many times been observed possibly on account of experimental factors, compactness, particle size, etc., over which there were no control.

Doyle's method as modified by Zsako

The validity of this graphical method has been supported by the Doyle method as modified by Zsako employing standard deviations in the calculations instead of curve fitting procedure. Doyle's equation for TG curve is

$$F(\alpha) = \left(\frac{ZE}{aR}\right)p(x) \tag{1}$$

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \tag{2}$$

where W = actual mass, W_0 = initial mass, and W_f = Final mass of the sample. $F(\alpha)$ can easily be calculated with the help of Eq. 2 for different presumed kinetic equations.

The percentage mass of the complex at equal temperature intervals, i.e., 10 °C were noted directly from TG curve for a particular stage of thermal decomposition and $F(\alpha)$ values are calculated.

The B_i values for different order of reaction were calculated by the following equations.

$$B_0 = \log \alpha - \log p(x) \tag{3}$$

$$B_1 = \log(\ln 1/1 - \alpha) - \log p(x) \tag{4}$$

$$B_2 = \log(\alpha/1 - \alpha) - \log p(x) \tag{5}$$

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

$$\delta = \sqrt{\frac{(B_i - \bar{B})^2}{r}} \tag{6}$$

where r is the number of experimental data used for the calculation of $\bar{B}$.

The values for order of reaction and activation energy were revised by this method for the particular stage of transformation as in case of calculations by Freeman and Carroll procedure. This minimum deviation δ min for particular B_i value and E_a value suggest the order of reaction and activation energy for the considered stage of transformation.

The apparent frequency factor and the apparent activation entropy were also calculated from the equation:

$$\log Z = \bar{B} + \log Rq - \log E_a \tag{7}$$

$$\Delta S^{\neq} = 2.303 \log Zh/KT. \tag{8}$$

where R = gas constant, $\bar{B}$ = arithmetical mean of most consistent series of B_i values, q = heating rate, E_a = activation energy, h = Planck's constant, K = Boltzmann's constant, AND T = absolute temperature at half of the total loss in mass for the considered step of paralysis.

Results and discussion

Thermo gravimetric analysis of coordination complex of [Cu(L)$_2$]·2H$_2$O

The thermo gravimetric (TG) curve, which characterizes the thermal decomposition of the Cu(II) complex of Schiff base of salicyaldehyde and 5-amino-1,2,3,4-thiatriazole (L) in nitrogen atmosphere at a heating rate of 10 °C min^{-1} are given in Fig. 1. Close examination of the TG curve reveals that the decomposition of Cu(II) complex occurred in four steps. In first step, there is mass loss from 100 to 120 °C (obsd: 17.27%; cal: 17.66%), which may be due to elimination of water molecules (2H$_2$O) and two –CH=N– moiety. In second step mass loss from 180 to 240 °C (obsd: 51.17%; cal: 51.47%). It may be due to loss of two ( ) moiety. At third step gradual mass loss from 300 to 700 °C (obsd: 81.01%; cal: 81.86%) may be due to mass loss of two moiety. Residue obtained may be due to
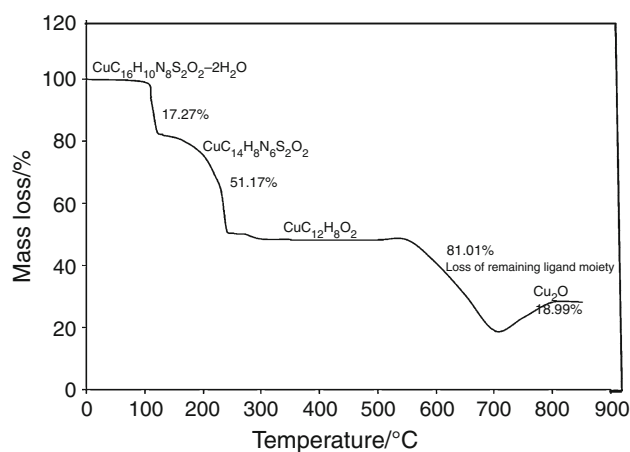
Fig. 1 TG plot of [Cu(L)$_2$]·2H$_2$O complex

Cu$_2$O (obsd: 28%; cal: 28%). It can be seen clearly (Table 1) that the mass losses obtained from the TG curves and that calculated for the corresponding molecules are in

good agreement. Slight increase in mass above 700 °C is due to internal oxidation of moiety.

The second stage of transformation was considered for study of chemical kinetics. The residual mass existing at equal temperature gaps were read directly from the TG curve and data were calculated by Freeman and Carroll method which are given in Table 2.

The plot [Δlog dw/dt]/[Δlog W_r] versus [ΔT^{-1}]/[Δlog W_r] (Fig. 2) with the value tabulated above gives a straight line with an intercept at suggesting the order of reaction 0.9 and activation energy 18.05 kcal/mol as calculated from $E_a = 2.303 R \times$ slope.

Further the mass read at different temperatures were used to calculate data adopting Doyle's methods as modified by Zsako for the same step of the reaction.

log $F(\alpha)$ values obtained in Table 3 were used to calculate B_0, B_1, B_2 and δ_0, δ_1, δ_2 values for different activation energies at different temperature which are given in Table 2 for different presumed order of reaction. The minimum value of δ indicates the best E value. At the same

Table 1 Thermo analytical data and decomposition temperature for [Cu(L)$_2$]·2H$_2$O complex

S. No.	Temperature/°C	Species degraded	Mass loss/%	
			Found	Cal.
1	100–120	Loss of 2H$_2$O molecule and two –CH=N– moiety	17.27	17.66
2	180–240	Loss of two [thiadiazole structure] moiety	51.17	51.47
3	300–700	Loss of two [methylbenzene structure] moiety	81.01	80.86
4	Above 700	Cu$_2$O formation	28 (residue)	28

Table 2 Data obtained by Freeman and Carroll Method

S. No.	Temperature/°C	Mass/%	[Δlog dw/dt]/[Δlog W_r]	[ΔT^{-1}]/[Δlog W_r]
1	140	81.63	−8.0628	7.3957×10^{-3}
2	150	81.13	−7.9549	5.7508×10^{-3}
3	160	80.53	−8.2591	4.1622×10^{-3}
4	170	79.76	−7.1061	2.8378×10^{-3}
5	180	78.72	−4.7909	1.9434×10^{-3}
6	190	77.34	−7.7592	1.3055×10^{-3}
7	200	75.51	−5.5125	7.7388×10^{-4}
8	210	72.86	−2.6489	4.2185×10^{-4}
9	220	68.99	-0.5943	2.2610×10^{-4}
10	230	64.00	0.2106	1.4740×10^{-4}
11	240	59.63	1.1924	1.5401×10^{-4}
12	250	57.44	0.9923	1.4762×10^{-4}
13	260	56.21	0.2156	8.2043×10^{-5}

Initial mass% at 130 °C = 82.06, final mass% at 270 °C = 55.22
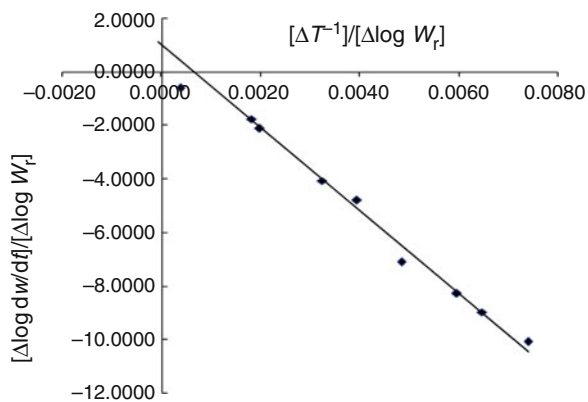
Fig. 2 Plot of $[\Delta \log \mathrm{d}w/\mathrm{d}t]/[\Delta \log W_r]$ versus $[\Delta T^{-1}]/[\Delta \log W_r]$

time, the least value δ min is a measure of the consistency of the decomposition process with the presumed function $F(\alpha)$. Presuming other kinetic equation and calculating the corresponding δ min values, the least value of δ min indicates $F(\alpha)$ among the tested ones which ensure the maximum consistency with experimental data.

Comparative value of δ along with their activation energies for the presumed order of order of reaction are given in Table 4.

A comparison of the δ min values for different presumed orders incorporated in the previous table are given in Table 4 showing that $\delta_0 = 0.0649$ is the minimum value which corresponds to the order of reaction $b = 1$, activation energy $E_a = 18$ kcal/mol and $\bar{B}_0 = 10.4144$.

With the help of above values, the apparent frequency factor $Z = 4.7770523 \times 10^5$ s^{-1} and apparent entropy of activation $\Delta S^{\neq} = -16.9065$ e.u. which is calculated for the

Table 4 Comparative value of δ along with their activation energies for the presumed order of order of reaction

$b = 0$		$b = 1$		$b = 2$	
E_a/kcal/mol	δ_0	E_a/kcal/mol	δ_1	E_a/kcal/mol	δ_2
12	0.0869	16	0.0878	22	0.2058
14	0.1084	**18**	**0.0649**	24	0.1956
16	0.2243	20	0.1330	26	0.2196

The bold values show the minimum deviation for the activation energy 18 kcal

Table 5 Orders of reaction (n) and activation energy (E_a) by both the adopted procedures

Methods	Order of reaction/n	Activation energy E_a/kcal/mol
Freeman and carroll	0.9	18.05
J. Zasko	1	18

considered stage of transformation using following equations

$$\log Z = \bar{B} + \log Rq - \log E_a \qquad (9)$$

and

$$\Delta S^{\neq} = 2.303R \log Zh/kT \qquad (10)$$

where T is the absolute temperature, i.e., 503 K at which the mass lost is half of total mass lost.

Thus resemblance of the value for kinetic terms obtained for the same stage of decomposition evaluated by two different methods is comparable and is given in the Table 5

Table 3 Data of $\log F(\alpha)$ values for the complex $[Cu(L)_2] \cdot 2H_2O$ calculated at different temperatures

S. No.	Temparature/°C	$\alpha = (W_0 - W_t/W_0 - W_f)$	$\log \alpha$	$\log(\ln 1/1 - \alpha)$	$\log(\alpha/1 - \alpha)$
1	140	0.0157	−1.8044	−1.8010	−1.7976
2	150	0.0339	−1.4694	−1.4620	−1.4544
3	160	0.0558	−1.2532	−1.2408	−1.2283
4	170	0.0839	−1.0762	−1.0573	−1.0381
5	180	0.1219	−0.9142	−0.8863	−0.8577
6	190	0.1722	−0.7640	−0.7236	−0.6819
7	200	0.2390	−0.6217	−0.5637	−0.5031
8	210	0.3356	−0.4741	−0.3883	-0.2965
9	220	0.4768	−0.3216	−0.1885	−0.0403
10	230	0.6589	−0.1812	0.0316	0.2859
11	240	0.8183	−0.0871	0.2318	0.6536
12	250	0.8982	−0.0466	0.3589	0.9457
13	260	0.9431	−0.0254	0.4573	1.2193
14	270	0.9792	−0.0091	0.5881	1.6729

Initial mass% at 130 °C = 82.06, final mass% at 270 °C = 55.22

Conclusions

The results obtained from the TG curve confirm the hydration and the stoichiometry of the prepared Cu(II) complex that is established by elemental analysis and spectral analysis [1]. The statistical way of working up experimental data and the minimization of standard deviation ensure accuracy in estimating apparent activation energy which is consistent with the presumed kinetic equation. Calculations can be carried out relatively simply using $-\log P(x)$ and can be easily programmed electronic computers.

Since the standard deviation, δ, is a quantitative measure of the consistency between experimental data and the presumed kinetic equation, the Doyle's methods as modified by Zsako can be very useful in testing the validity of different kinetic equations. The kinetic parameter determined by using Freeman and Carroll method as well as Doyle's methods as modified by Zsako are found to be in good agreement as shown in Table 5.

References

1. Bharti, Verma UN, Mukhopadhyay K. Synthesis, spectral and thermal properties of Cu(II) complex of Schiff base derived from Salicylaldehyde and 1,2,3,4-thiatriazole-5-ylamine. Asian J Chem. 2011;23(2):773–6.
2. Freeman ES, Carroll B. The application of thermoanalytical techniques to reaction kinetics. The thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. J Phys Chem. 1958;62:394–7.
3. Zsako J. Kinetic analysis of thermogravimetric data. J Phys Chem. 1968;72(7):2406–11.
4. Vyazovkin S. Kinetic concepts of thermally stimulated reactions in solids: a view from a historical perspective. Int Rev Phys Chem. 2000;19:45–60.
5. Afzal AB, Akhtar MJ, Svensson L-G. Thermal studies of DBSA doped polyaniline/PVC blends by isothermal microcalorimetry. J Therm Anal Calorim. 2010;100(3):1017–25.
6. Bagdi K, Molna'r K, Puka'nszky B Jr, Puka'nszky B. Thermal analysis of the structure of segmented polyurethane elastomers: relation to mechanical properties. J Therm Anal Calorim. 2009; 98(3):825–32.
7. Krongauz VV, Ling MTK. Photo-crosslinked acrylates degradation kinetics. J Therm Anal Calorim. 2009;96(3):715–25.
8. Hurduc N, Prajinaru M, Creanga A, Alazaroaie S. The non-isothermal kinetic study of the thermal degradation processes of some aso-polymeric liquid crystals. Rev Mat Plast. 2004;4:41–4.
9. Siqueira AB, Bannach G, Rodrigues EC, Carvalho CT, Ionashiro M. Solid-state 2-methoxybenzoates of light trivalent lanthanides synthesis, characterization and thermal behaviour. J Therm Anal Calorim. 2008;9:897–902.
10. Agarwal RK, Prasad S, Gahlot N. Synthesis, spectral and thermal properties of some penta-coordinated complexes of oxovanadium(IV) derived from thiosemicarbazones of 4-aminoantipyrine. Turk J Chem. 2004;28(6):691–702.
11. Zhang HY, Zhang JJ, Ren N, Xu SL, Tian L, Bai JH. Synthesis, crystal structure and thermal decomposition mechanism of the complex $[Sm(p\text{-}BrBA)_3bipyH_2O]_2$ H_2O. J Alloys Comp. 2008;464:277–81.
12. Fleszar MF. Thermal behavior of teflon/phenolic liners in self-lubricating bearings. J Thermal Anal. 1997;49:219–26.
13. Kurnoskin AV. Thermal oxidative destruction of epoxy polymers. JMS Rev Macromol Chem Phys. 1993;35:419–94.
14. Luo Y, Chen P, Zhao FQ, Hu RZ, Li SW, Gao Y. Kinetics and mechanism of the thermal decomposition reaction of 3,3-bis(azidomethyl)oxetane/tetrahydrofuran copolymer. Chin J Chem. 2004;22(7):1219–24.
15. Thomas J, Parameswaran G. Structural, thermoanalytical and antitumour studies of metal chelates of anthracene-9-carboxaldehyde thiosemicarbazone. Asian J Chem. 2002;14:1354–64.
16. Mary NL, Parmeswaran G. Kinetics and mechanism of the thermal decomposition of Schiff base complexes of cobalt and nickel by TG and DSC studies. Asian J Chem. 1993;5:597–605.
17. Singh NK, Singh SB, Shrivastav A, Singh SM. Spectral, magnetic and biological studies of 1,4-dibenzoyl-3-thiosemicarbazide complexes with some first row transition metal ions. Proc Indian Acad Sci (Chem Sci). 2001;113:257–73.
18. Scovill JP, Klayman DL, Franchino CF. 2-acetylpyridine thiosemicarbazones. 4. Complexes with transition metals as antimalarial and antileukemic agents. J Med Chem. 1982;25:1261–4.
19. Hossain ME, Alam MN, Begum J, et al. The preparation, characterization, crystal structure and biological activities of some copper(II) complexes of the 2-benzoylpyridine Schiff bases of S-methyl- and S-benzyldithiocarbazate. Inorg Chim Acta. 1996;249:207–13.
20. West DX, Padhy'e SB, Sonawane PB, Chikte RC. Structural and physical correlation in the biological properties of transition metal N-heterocyclic thiosemicarbazones and S-alkyldithiocarbazate complexes. Struct Bond. 1991;76:1–50.
21. Phatak P, Jolly VS, Sharma K. Synthesis and biological activities of some new substituted aryl azo Schiff base. Orient J Chem. 2000;16:493–4.
22. Salimon J, Salih N, Hameed A, Ibraheem H, Yousif E. Synthesis and antibacterial activity of some new 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives. J Appl Sci Res. 2010;6:866–70.
23. Wang ZH, Guo YZ, Zhang J, Ma L, Song HB, Fan ZJ. Synthesis and biological activity of organotin 4-methyl-1,2,3-thiadiazole-5-carboxylates and benzo[1,2,3]thiadiazole-7-carboxylates. J Agric Food Chem. 2010;58:2715–9.
24. Fan ZJ, Yang Z, Zhang H, Mi N, Wang H, Cai F, Zuo X, Zheng Q, Zhijin HS. Synthesis, crystal structure, and biological activity of 4-methyl-1,2,3-thiadiazole-containing 1,2,4-triazolo[3,4-b][1,3,4]thiadiazoles. J Agric Food Chem. 2010;58:2630–6.
25. Mohan TP, Vishalakshi B, Bhat KS, Rao KS, Kendappa GN. Synthesis and insecticidal activity of some 1,3,4-oxadiazole derivatives containing phenoxy fluorophenyl group. Indian J Chem. 2004;43B:1798–801.
26. Gupta AKS, Misra HK. Synthesis and biological activity of 1,2,4-triazoles. Indian J Chem. 1979;17:185–7.
27. Mishra RK, Tiwari RK, Bahel SC. Synthesis and antifungal activity of some 1,4-disubstituted-5-mercapto-1,2,4-triazoles. J Indian Chem Soc. 1991;68:110–2.
28. Hussain S, Sharma J, Amir M. Synthesis and antimicrobial activities of 1,2,4-triazole and 1,3,4-thiadiazole derivatives of 5-amino-2-hydroxybenzoic acid. E J Chem. 2008;5(4):963–8.
29. Olar R, Badea M, Marinescu D, Lazar V, Chifiriuc C. New complexes of Ni(II) and Cu(II) with Schiff bases functionalized with 1,3,4-thiadiazole: spectral, magnetic, biological and thermal characterisation. J Therm Anal Calorim. 2009;97:721–7.
30. Kong H, Kucera RB, Jack WE. Characterization of a DNA polymerase from the hyperthermophile archaea *Thermococcus litoralis*. Vent DNA polymerase, steady state kinetics, thermal stability, processivity, strand displacement, and exonuclease activities. J Biol Chem. 1993;268(3):1965–75.