

Thermogravimetric and kinetic study of Fe(III) complex with thiatriazole derivative

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Abstract : Schiff bases and their complexes are versatile compounds and easily synthesized. 2-hydroxyl-acetanamide thiatriazole (L) has been synthesized and used as a ligand for the formation of Fe(III) complex. Fe (III) chloride forms 1:1 complex with 5-amino-1,2,3,4-thiatriazole. It undergoes two step decomposition. Kinetic parameters like activation energy, frequency factor, apparent entropy of activation and order of reaction have been determined employing graphical method of Freeman-Carroll and Doyle method as modified by Zsako introducing standard deviation in the calculation. The chemical structures were characterized using different spectroscopic methods. The elemental analyses revealed that the Fe(III) complex has the formulae $[\text{FeL}_2\text{Cl}_2] \cdot \text{Cl}$. Thermo gravimetric studies were carried out to identify the decomposition pattern and hence the stoichiometry as well as the geometry of the metal complexes.

(Keywords : Schiff base, Thermogravimetric analysis, Kinetic parameters, 5-amino-1,2,3,4-thiatriazole)

Introduction

Co-ordination chemistry, precisely, is the chemistry of metal atoms co-ordinated by atoms or molecules. Co-ordination chemistry has always been a challenge to the Inorganic chemist. Chemistry of Schiff bases have been intensively investigated in recent years owing to their co-ordination properties and diverse applications. The synthesis and structural investigation and reaction of transition metal Schiff bases have received a renewed attention in recent years because of their biological activities as antibacterial, antitumoral, antifungal and antiviral

activities. Thiosemicarbazones are a class of compounds obtained by condensation of thiosemicarbazide with suitable aldehydes or ketones. In most complexes Thiosemicarbazones¹ behave as bidentate ligands because they can bond to metals through sulphur and the hydrazinic nitrogen atoms, although in a few cases they behave as unidentate ligands and bond through only. Sulphur atom²⁻⁴. Thiosemicarbazones derivatives have demonstrated wide range of biological activity viz. antimicrobial⁵⁻¹⁰, antitumor¹¹⁻¹², sodium channel blocker¹³, anticancer¹⁴⁻¹⁵, antitubercular¹⁶, antiviral¹⁷.

Thermogravimetric analysis is a continuous non-isothermal method which has many advantages over currently used isothermal methods. The advantages are that a single experimental curve is sufficient to obtain an estimate of the apparent heat of activation and that kinetics can be probed over an entire temperature range in continuous manner without any gap. The basis of the calculation of kinetic data from TG curve is based as the formal kinetic equation $-dx/dt = kx^n$ where x is the amount of the sample undergoing dependence as temperature is expressed as:

$$K = A \cdot e^{-E/RT}$$

Kinetic constant of complex cited have been investigated from thermal analysis procedures eg: Freeman-Carroll¹⁸ and Doyle method¹⁹ as modified by Zsako²⁰. Freeman and Carroll first of all introduced the widely used differential method or determination of kinetic parameters from the thermogravimetry curves.

Thermal analysis is a useful tool in different field of study such as chemical science, polymer science, biological, medical science. The thermal kinetics and decomposition of the products of the complex are apparently of significance in understanding the biochemistry of the compound. The use of non-isothermal method for finding kinetics parameter like activation energy, frequency factor, apparent entropy of activation and order of reaction is investigated.

Experimental:

Single thermogravimetric curve was drawn on electrobalance "Perkin Elmer" with a recorder operating on 1MV full scale for recording the thermogram. A chromium aluminium thermocouple placed 3-4 mm below the sample holder was used for recording the thermogram.

Preparation of sample:

The ligand 5-amino-1,2,3,4-thiatriazole was prepared by described method²². Schiff base, thus derived from Thiatriazole and 2-hydroxy-1-naphthaldehyde is 2-hydroxy-1-acetamide thiatriazole. Complexation of Fe(III) chloride was then carried out. An ethanolic solution of Schiff base of thiatriazole (0.001M) with 2-hydroxy-1-naphthaldehyde (0.001M) were mixed with hot ethanolic solution of ferric chloride in 1:1 molar ratio and it was refluxed on water bath for 1 hours and then cooled. A brownish pale precipitate was obtained which was filtered, washed with alcohol and dried in desiccator over anhydrous CaCl_2 .

Results and Discussions

Elemental analysis data reveal that the complex contains the different percentage as shown in the table-1.

Fe (III) complex: $[\text{FeL}_2\text{Cl}_2]\text{Cl}$

Table -1 Analytical data for the metal complex

COMPOUND	COLOUR		%C	%H	%N	%S	%O	%Cl	%M
$[\text{Fe}(\text{ATTN})_2\text{Cl}_2]\text{Cl}$	Dark	Theo.	42.70	2.67	16.23	9.3	4.65	15.50	8.55
	Brown	Expt.	42.85	2.81	15.78	8.1	5.18	16.85	8.95

Freeman-Carroll graphical method was primarily employed to evaluate the order of reaction and activation energy of first stage of decomposition of complex from the data tabulated in table-II.

The values obtained have been finally corroborated by Doyle procedure²¹ as modified by Zsako.

Table-II DATA OBTAINED BY FREEMAN AND CARROLL METHOD

Sl. No.	Temperature ($^{\circ}\text{C}$)	%Weight left (Y)	$\frac{\Delta \log(dw/dt)}{\Delta \log w_r}$	$\frac{\Delta T^{-1}(\text{K}) \times 10^{-3}}{\Delta \log w_r}$
1	210	93.8		
2	220	93.1		
3	230	92.1	-30.6737	7.98536
4	240	90.6	-22.9082	5.04159
5	250	88.7	-10.3322	3.75114
6	260	85.9	-11.1748	2.38045
7	270	82.3	-5.40927	1.71242
8	280	77.5	-4.39157	1.17057
9	290	71.1	-3.04087	0.78175
10	300	62.7	-1.94893	0.51155
11	310	52	-1.1436	0.32571
12	320	38.3	-0.68807	0.18542
13	330	21.6	-0.26463	0.08606
14	340	6.6		

Initial weight at 210°C =93.8%

Final weight at 340°C = 6.6 %

The tabulated data showed straight line of the plot $\Delta \text{Log} dw/dt / \Delta \text{Log} W_r V s \Delta T^{-1} \times 10^{-3} / \Delta \text{Log} W_r$.

The line intercepted at 0.98 and gave a slope 5.18. The Values in turn were suggestive of the order of reaction one and activation energy 23.859 Kcal/mol for the step considered.

To affirm the validity of their values for order of reaction, energy of activation, frequency factor and entropy of activation Doyle's modified by Zsako procedure were adopted. The different values necessary for further calculation were evolved at various temperature employing relations:

$$B=0; \quad B_0 = \log(\alpha) - \log p(x)$$

$$B=1; \quad B_1 = \log(\ln 1/(1-\alpha)) - \log p(x)$$

$$B=2; \quad B_2 = \log(\alpha/(1-\alpha)) - \log p(x)$$

Table-III Data of log (α) values for the complex calculated at different temperatures						
Sl.No.	Temp. (°C)	% weight left (Y)	$\alpha = (w_0 - w_t) / (w_0 - w_i)$	Log α	Log ($\ln 1/(1-\alpha)$)	Log[$\alpha/(1-\alpha)$]
1	220	93.1	0.00802752	-2.09542	-2.0936694	-2.0919181
2	230	92.1	0.01949541	-1.71007	-1.7057994	-1.7015172
3	240	90.6	0.03669725	-1.43537	-1.4272732	-1.4191293
4	250	88.7	0.05848624	-1.23295	-1.2199254	-1.206773
5	260	85.9	0.09059633	-1.04289	-1.0224309	-1.0016461
6	270	82.3	0.13188073	-0.87982	-0.8494702	-0.818398
7	280	77.5	0.18692661	-0.72833	-0.6841684	-0.6384586
8	290	71.1	0.2603211	-0.58449	-0.5206564	-0.4535339
9	300	62.7	0.35665138	-0.44776	-0.3554939	-0.2562025
10	310	52	0.4793578	-0.31934	-0.1852916	-0.0358796
11	320	38.3	0.63646789	-0.19622	0.0051323	0.24323372
12	330	21.6	0.82798165	-0.08198	0.2455507	0.68244594
13	340	6.6	1	0		

Log (α)Log($\ln 1/(1-\alpha)$), log ($\alpha/(1-\alpha)$) values are tabulated in table III and -Log p(x) values were taken from Zsakochart. The values of B_0 , B_1 , and

B_2 along with the corresponding values of standard deviation are tabulated in table IV, V, VI respectively.

Table-IV Calculation of $B_0 = \log \alpha - \log p(x)$ for different activation energies & δ_0 values at different temperatures				
Sl.No.	Temperature (°C)	20 K cal.	22 K cal.	24 Kcal.
1	220	9.427582	10.39758	11.35558
2	230	9.622932	10.57093	11.51193
3	240	9.711633	10.64163	11.56563
4	250	9.732054	10.65005	11.55605
5	260	9.751111	10.65011	11.54411
6	270	9.751181	10.63318	11.50818
7	280	9.739671	10.60867	11.47167
8	290	9.729509	10.58151	11.43151
9	300	9.712244	10.55624	11.39324
10	310	9.69566	10.52666	11.35066
11	320	9.678776	10.49678	11.30778
12	330	9.658021	10.46202	11.26002
$\overline{B_0}$		9.684198	10.56461	11.43803
δ_0		0.085817	0.077485	0.099211

Table-V Calculation of $B_1 = \log \left(\ln \frac{1}{1-\alpha} \right) - \log p(x)$ for different activation energies & δ_1 values at different temperatures				
Sl. No.	Temperature ($^{\circ}\text{C}$)	22K cal.	24 K cal.	26 Kcal.
1	220	10.39933	11.35733	12.31133
2	230	10.57520	11.51620	12.45220
3	240	10.64973	11.57373	12.49173
4	250	10.66307	11.56907	12.47507
5	260	10.67057	11.56457	12.45257
6	270	10.66353	11.53853	12.44453
7	280	10.65283	11.51583	12.37283
8	290	10.64534	11.49534	12.33934
9	300	10.64851	11.48551	12.31151
10	310	10.66071	11.48471	12.29771
11	320	10.69813	11.50913	12.30913
12	330	10.78955	11.58755	12.37955
$\overline{B}_1$		10.64304	11.51646	12.38646
δ_1		0.090736	0.061564	0.07297

Table-VI Calculation of $B_2 = \log \left(\frac{1}{1-\alpha} \right) - \log p(x)$ for different activation energies & δ_2 values at different temperatures				
Sl.No.	Temperature ($^{\circ}\text{C}$)	26 K cal.	28K cal.	30 Kcal.
1	220	12.31308	13.26108	14.20408
2	230	12.45648	13.38748	14.31348
3	240	12.49987	13.41887	14.32687
4	250	12.48823	13.38423	14.28023
5	260	12.47335	13.35635	14.23035
6	270	12.4756	13.3116	14.1726
7	280	12.41854	13.27154	14.11554
8	290	12.40647	13.24647	14.08147
9	300	12.4108	13.2378	14.0598
10	310	12.44712	13.26112	14.07012
11	320	12.54723	13.34723	14.14423
12	330	12.81645	13.60345	14.38745
$\overline{B}_2$		12.47944	13.3406	14.19885
δ_2		0.116085	0.098863	0.105293

The table V indicate the $\delta_{\min}$ has the least values i.e. 0.061564 when the order of reaction is $b=1$, Corresponding to activation energy $E=24$ Kcal/mol & $\overline{B}_1=11.51646$.

Table-VII

B=0		B=1		B=2	
E*Kcal/mol	δ_0	E*Kcal/mol	δ_1	E*Kcal/mol.	δ_2
20.	0.085817	22	0.090736	26.	0.116085
22	0.077485	24	0.061564	28	0.098863
24	0.099211	26	0.072970	30	0.105293

The frequency factor z has calculated using the equation:-

$$\log z = \overline{B}_1 + \log Rq - \log E^*$$

$$\text{Where } = 11.51646$$

$$Q = \text{heating rate } 10^\circ\text{C/ minute}$$

$$E^* = 24 \text{ Kcal / mol.}$$

Thus, the frequency factor for the thermolysis step under consideration was found to be $Z=4.56 \times 10^6$

sec^{-1} & the apparent entropy of activation was calculated to be $\Delta S^\ddagger = -122.96564 \text{ e.u.}$ from the relation.

$$\Delta S^\ddagger = R \ln zh/kt$$

$$\text{Or, } \Delta S^\ddagger = 8.314 \log$$

Where t stands for the absolute temperature 578K at which the step under consideration was half complete.

Table-VIII

Methods	Order of reaction	Activation energy
Freeman &Carroll	0.98	23.85 kcal.
J. Zsako	1.00	24.00 kcal.

The values, order of reaction and activation energies, evaluated by two different methods are

given in the Table VIII and are in good agreement within limit.

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