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Thermogravimetric and kinetics study of Cr(III) complex with thiatriazole derivative

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Abstract: 2-hydroxy1-acetanamide thiatriazole(**L**) has been synthesized and used as a ligand for the formation of Cr(III) complex. Cr(III) chloride forms 1:2 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 complexeswhere M=Ni(II) and Cu(II) have the general formulae $[ML_2Cl_2]$, while the Cr(III) complex has the formula $[CrL_2Cl_2]Cl$.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:** 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 Thiosemicarbazones[1] 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 Sulphuratom[2-4]. Thiosemicarbazones derivatives have demonstrated wide range of biological activity *viz.* antimicrobial[5-10], antitumor[11-12], sodium channel blocker[13], anticancer[14-15], antitubercular[16],antiviral[17].

Thermogravimetric analysis is a continuous non-isothermal method which has many advantages over currently used isothermal methods. Theadvantages 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 expressd as:

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

Kinetic constant of complex cited have been investigated from thermal analysis procedures eg: Freeman-Carroll[18] and Doyle method[19] as modified by Zsako[20]. 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.

Experimetal

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 method[22].Schiff base, thus derived from Thiatriazole and 2-hydroxy1-napthaldehyde is 2-hydroxy1-acetanamide thiatriazole.40ml of ligand (0.02M) in ethanol were mixed with 40ml of Chromium Chloride (0.01M) in ethanol. The mixture were refluxed for half hour on a steam bath. Dark green colour precipitate was obtained. On cooling the contents, the colored complexes were separated out. Precipitate was filtered off with the help of filter paper. The resulting product washed with ethanol and dried in a desiccator over anhydrous $CaCl_2$. Purity of the complexes were checked.

Result and Discussions

Elemetal analysis data reveal that the complex contains the different percentage as shown in the table-1.Cr(III)complex:$[CrL_2Cl_2]Cl$

Table - 1 Analytical data for the metal complexes.

COMPOUND	COLOUR		%C	%H	%N	%S	%O	%Cl	%M
$[Cr(ATTN)_2Cl_2]Cl$	Dark Green	Theo.	45.42	2.52	17.66	10.09	5.04	11.04	8.20
		Expt.	44.07	2.02	18.08	11.35	5.95	12.00	8.12

Freeman-Carrollgraphical 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 procedure[21] as modified by Zsako.

Table-II Data Obtained by Freeman and Carroll method

Sl.No.	Temperature (^{0}C)	%Weight left (Y)	$\Delta\log(dw/dt)/\Delta\log w_r$	$\Delta T^{-1}(K)\times10^{-3}/\Delta\log w_r$
1	250	80.73	-6.039051185	1.954454
2	260	77.23	-5.224036438	1.267363
3	270	72.71	-2.810734511	0.874368
4	280	66.89	-1.93181286	0.586002
5	290	59.31	-1.314550902	0.367964
6	300	48.33	-0.951875494	0.183346
7	310	35.51	-0.190976876	0.084964

Initial weight at 230°C =85.13%
Final weight at 320°C = 25.26 %

The tabulated data showed straight line of the plotΔLogdw/dt /ΔLogWrvs$\Delta T^{-1}x10^{-3}$/ΔLogWr.

The line intercepted at 0.95 and gave a slope 6.60. The Values in turn were suggestive of the order of reaction one and activation energy 30.399 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; $B_0 = \log(\alpha) - \log p(x)$

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

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

Log (α), log (ln1/1-α), log (α/1-α) values are tabulated in table III and -Log p(x) values were taken from Zsako chart. The values of B_0, B1, and B2 along with the corresponding values of standard deviation are tabulated in table IV, V, VI respectively.

Table-III Data of log (α) values for the complex calculated at different temperatures

Sl.No.	Temp. (^{0}C)	% weight left (Y)	$\alpha=(w_0-wt)/(w_0-w_f)$	Log α	Log (In 1/(1-α)	Log[α/(1-α)]
1	**240**	83.22	0.031902455	-1.49618	-1.4891545	-1.4821
2	**250**	80.73	0.073492567	-1.13376	-1.1172865	-1.10061
3	**260**	77.23	0.131952564	-0.87958	-0.8492162	-0.81813
4	**270**	72.71	0.207449474	-0.68309	-0.6335789	-0.58211
5	**280**	66.89	0.304660097	-0.51618	-0.4396695	-0.35838
6	**290**	59.31	0.431267747	-0.36525	-0.2484549	-0.12016
7	**300**	48.33	0.614665108	-0.21136	-0.0206144	0.2028
8	**310**	35.51	0.828795724	-0.08155	0.24671957	0.684933

Table-IV
Calculation of B_0 =log α– log p(x)for different activation energies &$\delta_0$values at different temperatures

Sl.No.	Temperature (^{0}C)	24 K cal.	26 K cal.	28 Kcal.
1	**240**	11.50482	12.42282	13.34182
2	**250**	11.65524	12.56124	13.45724
3	**260**	11.70742	12.59542	13.47842
4	**270**	11.70491	12.61091	13.44691
5	**280**	11.68382	12.54082	13.39382
6	**290**	11.65075	12.49475	13.33475
7	**300**	11.62964	12.45564	13.28264
8	**310**	11.58845	12.40145	13.21545
$\overline{B_0}$		11.64063	12.51038	13.36888
δ_0		0.063306	0.073845	0.086164

Initial weight at 200°C =88.97%,
Final weight at 300°C = 2.38 %

Table-V

Calculation of $B_1 = \log\left(In\frac{1}{1-\alpha}\right)$ -log p(x) for different activation energies &$\delta_1$values at different temperatures

Sl. No.	Temperature (^{0}C)	28K cal.	30 K cal.	32 Kcal.
1	**240**	13.34885	14.25685	15.16285
2	**250**	13.47371	14.36971	15.25771
3	**260**	13.50878	14.38278	15.25778
4	**270**	13.49642	14.35742	15.21942
5	**280**	13.47033	14.31433	15.16333
6	**290**	13.45155	14.28655	15.11355
7	**300**	13.47339	14.29539	15.10939
8	**310**	13.54372	14.35272	15.15372
$\overline{B_1}$		13.47084	14.32697	15.17972
δ_1		0.053239	0.042192	0.055123

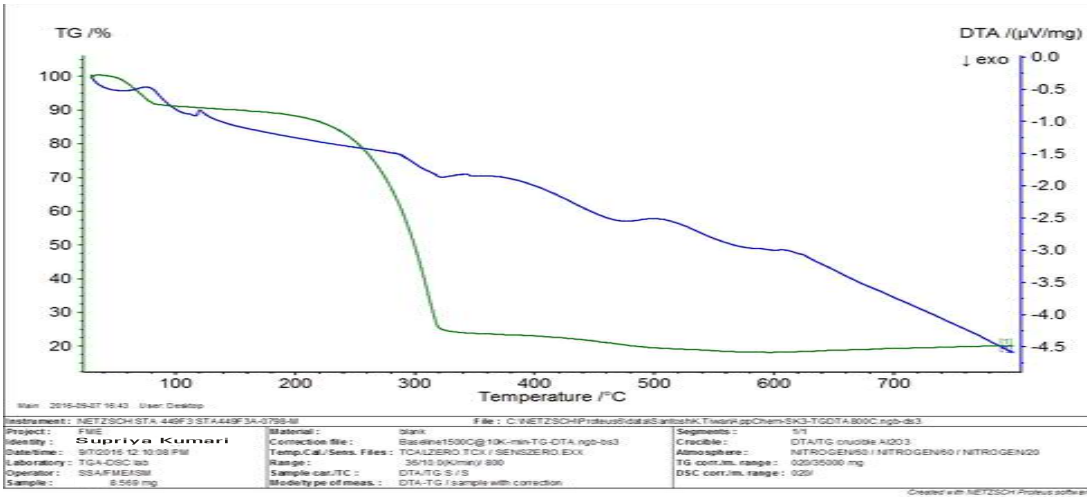

Fig: The TGA curves of the Cr(III) complex

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 (^{0}C)	34K cal.	36K cal.	38 Kcal.
1	**240**	16.0729	16.9719	18.0739
2	**250**	16.15939	17.07339	17.92539
3	**260**	16.16087	17.02987	17.29687
4	**270**	16.12489	16.97689	17.83089
5	**280**	16.08562	16.92462	17.76962
6	**290**	16.06984	16.89684	17.71884
7	**300**	16.1478	16.9608	17.7668
8	**310**	16.39393	17.18893	17.98693
$\overline{B}_2$		16.15191	17.00291	17.79616
δ_2		0.097999	0.087387	0.220305

The table V indicate the **δ**min has the least values i.e. 0.042192when the order of reaction is b=1, Corresponding to activation energy E=30 Kcal/ mol & $\overline{B_1}$ =14.32697.

Table-VII

B=0		B=1		B=2	
E*		E*		E*	
Kcal/mol	**δ_0**	**Kcal/mol**	**δ_1**	**Kcal/mol**	**δ_2**
240	.063306	280	.053239	340	.097999
260	.073845	300	.042192	360	.087387
280	.086164	320	.055123	380	.220305

The frequency factor z has calculated using the equation:-

Log z = $\overline{B_1}$ + log Rq – log E*

Where = 14.32697
Q = heating rate 10^0C/ minute
E* = 30 Kcal / mol.

Thus, the frequency factor for the thermolysis step under consideration was found to be Z=2.36×10^{-9} sec^{-1} & the apparent entropy of activation was calculated to be $\Delta s^{\#}$ = -70.981856 e.u. from the relation.

$\Delta s^{\#}$ = Rln zh/kt

Or, $\Delta s^{\#}$ = 8.3143 log

Where t stands for the absolute temperature 576K at which the step under consideration was half complete.

Table-VIII		
Methods	**Order of reaction**	**Activation energy**
Freeman &Carroll	0.95	30.39 kcal.
J. Zsako	1.00	30.00 kcal.

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