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Solid State Kinetics Of Hg(I) Complex Derived From Schiff Base Of 5-Amino1,2,3,4 Thiatriazole With-Ortho-Methoxybenzaldehyde.

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Abstract

Thermal analysis has become an established method in the study of thermal behavior of materials and finds wide applications. The mercury complex (Hg_2LCl_2) where L is Schiff base derived from 5-Amino [1,2,3,4] Thiatriazole was synthesized by refluxing the Schiff base with mercuric chloride, and gravimetric analysis. The molecular weight was found to be 692.18mg. Thermal analysis was performed using thermogravimetric Analysis (TGA) Which showed Three distinct stages of weight loss, initial loss of ligand moiety and finally two chloride ion. These steps were analyzed to determine kinetic parameters using freeman-Carroll and zasko's modified Doyle method.

The order of reaction for the main decomposition step was formed to be approximately 1M/Sec using freemen–Carroll and 1M/Sec using zasko's method. The corresponding activation energies were 23.45 kcal/mol and 26 kcal/mol respectively.

The apparent entropy of activation (ΔS±) was calculated as –389.343348759 e.u and the frequency factor(Z) was found to be 2.53705947×10^3 sec-1 These results obtained by different methods were in good agreement and support the reliability of the kinetic model. These findings help in understanding the thermal behaviors and stability of mercury-Schiff base complexes in the solid state.

Keywords: solid state kineties, thermo gravimetric analysis, Schiff base.

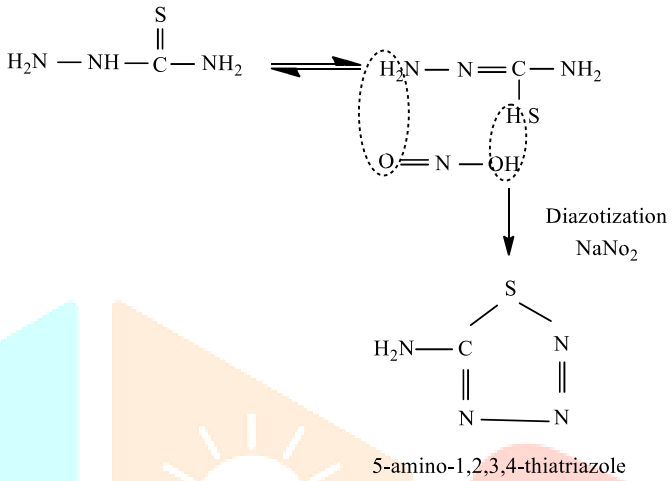
Introduction

In the recent years the coordination chemistry of transition metal and their derivatives have been widely studied due to their biological importance (1-3).A large number of Schiff bases and their complexes have been studied for their important properties e.g. their ability to reversibility bind oxygen transfer of an amino group and complexing ability towards some toxic metal (4-6) chemical parameters of Schiff bases have been determined with the help of thermogravimetric analysis. This technique involve change in weight of a system under examination with increase of temperature at a pre-determine preferably at a linears rate of study the solid state reaction. A number of workers have demonstrated its usefulness (7-8). Thermal analysis technique is becoming a usefull tool in different fields of study such as chemical science, polymer science, biological science and medical scince(8-16).

The present paper deals the solid state kinetics of Hg(I)complex with 5-amino-1,2,3,4-thiatriazole) and determine the kinetics parameters such as order of reaction, frequency factor, activation energy and entropy of activation using Freeman-Carroll method as well as Doyles method modified by Zsako17, 18, 19.

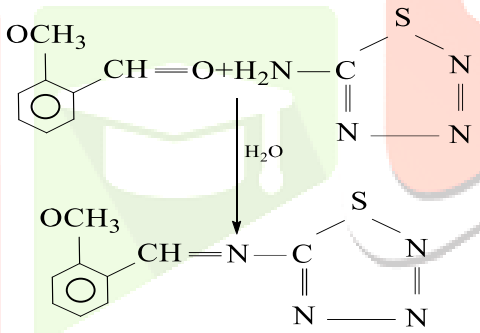
(A) Preparation of 5-amino-1,2,3,4-thiatrizole

An ice cold solution of 20 grams of thiosemicarbazide in 95 cc of 2.2(N) HCl, was added from a burette, with stirring in a total of 14.7 gram of $NaNo_2$ in 150 ml water. After each 50 ml was added, the product was collected and washed with 10 ml of ice water. The filtrate being returned to the reaction vessel the crude product was vacuum dried and recrystallized from methanol yielded fine, colorless needle which decomposed with a slight explosion of 136^0 in a capillary tube.



5-amino-1,2,3,4-thiatriazole

(B). Preparation of Schiff base: 1:1 molar solution of o-methoxy-benzaldehyde and 5-amino-1,2,3,4, thiatriazole in ethanol and condensed in acidic medium light yellow solid Schiff base is filtered and recrystallized with ethanol.



Preparation of Schiff base: 1:1 molar solution of o-methoxybenzaldehyde and 5-amino-1,2,3,4-thiatrizole in ethanol are mixed and condensed in acidic medium. Brown Schiff base is filtered and recrystallized with ethanol.

Instrumentation

Elemental analysis and mass spectrometery analysis are also determined the purity and composition of transition metal complexes.

Thermogravimetric Analysis (TGA)

TGA determine degradation kinetics, material purity and quality in industries from Pharmaceuticals to polymers**.**

Results and discussion

The result obtained by the usual elemental analysis and estimation of metal content are suggestive of the molecular formula [Hg_2LCl_2] and the molecular weight 692.18 to the complexes.

The basis of the calculation of kinetic parameter from a TG curve is based on the formal kinetic equation - $d\alpha/dt=k\alpha$

Where α is the fraction of the initial compound undergoing reaction and k is the specific rate constant.

The specific rate constant depends upon the temperature by the expression, $k = Ae^{-E/RT}$.

where A is the pre-exponential factor, E the activation energy and R is the gas constant.

The thermo-gram of the complex shows Three stages of the decomposition. Second stage of the decomposition was selected for the determination of kinetic parameter, i.e. order of reaction, activation energy, entropy of activation and frequency factor firstly by graphical method of Freeman – Carroll and Doyle's method as modified by Zsako.

The following table contains the data obtained by Freeman -Carroll method.

Table – II : Data obtained by Freeman and Carroll method

S.No.	Temp(^{0}C)	Weight (mg)	$\frac{\Delta \log dw/dt}{\Delta\, logWr}$	$\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log Wr}$
1	150	3.552007	-52.95580	15.90857
2	160	3.540703	-36.83261	8.94580
3	170	3.520052	-23.02167	4.58278
4	180	3.487010	-10.83956	2.64437
5	190	3.421578	-7.43879	1.19450
6	200	3.309192	-2.99522	0.58181
7	210	3.145939	-1.10136	0.29712
8	220	2.950296	-0.27386	0.14623

Initial weight at 130^{0}C = 3.563093mg.

Final weight at 230^{0}C = 2.741393mg

The tabulated data showed straight line of the plot

[$\Delta log \frac{dw}{dt}/\Delta logWr$] versus [$\Delta T^{-1}$] / [$\Delta$ log Wr]. The line intercepted at 0.8

which was suggestive of the order of reaction 1Mole/sec and activation energy 23.45Kcal/mole using 2.303R x slope.

Table – III : Data of log f(α) values for $[Hg_2LCl_2]$ complex calculated at different temperatures for complex:

S.No.	Temp(^{0}C)	Weight (mg)	$\alpha = \frac{W_0 - W_t}{W_0 - W_f}$	$log\,\alpha$	$log\left(ln\frac{1}{1-\alpha}\right)$	$log\left(\frac{\alpha}{1-\alpha}\right)$
1	140	3.563093	0.005290252	-2.276523647	-2.275372343	-2.274220021
2	150	3.552007	0.027248387	-1.564659193	-1.558673984	-1.552661153
3	160	3.540703	0.052380431	-1.280830934	-1.269200324	-1.257464955
4	170	3.520052	0.092592187	-1.033425658	-1.012497737	-0.991228173
5	180	3.487010	0.172222222	-0.763910811	-0.723513966	-0.681824575
6	190	3.421578	0.308994767	-0.510048876	-0.432258776	-0.349530212
7	200	3.309192	0.5076719	-0.294416875	-0.149592776	0.013328501
8	210	3.145939	0.745767312	-0.127396656	0.136563729	0.467371954
9	220	2.950296	0.745767312	-0.127396656	0.136563729	0.467371954

Initial weight at 130^{0}C = 3.563093mg.
Final weight at 230^{0}C = 2.741393mg.

Table – IV: Calculation of B_0 for different activation energies and δ_0 value at different temperature for $[Hg_2LCl_2]$ complex.

SN	Temp(^{0}C)	22 kcal	24 kcal	26 kcal
1	140	12.253476	13.381476	14.508476
2	150	12.362062	13.471062	14.570062
3	160	12.387341	13.468341	14.547341
4	170	12.400169	13.459169	14.511169
5	180	12.389574	13.427574	14.457574
6	190	12.411089	13.426089	14.440089
7	200	12.429951	13.423951	14.415951
8	210	12.414583	13.396583	14.366583

9	220	12.365603	13.323603	14.277603
	Average (B_0)	12.379317	13.419761	14.454983
	Standard deviation ($\delta 0$)	0.049151773	0.04461268	0.087446216

Table – V: Calculation of B_1 for different activation energies and δ_1 value at different temperature for[Hg_2LCl_2]complex.

SN	Temp(^{0}C)	24 kcal	26 kcal	28 kcal
1	140	13.382628	14.509628	15.632628
2	150	13.474008	14.573008	15.669008
3	160	13.474326	14.553326	15.623326
4	170	13.470800	14.522800	15.575800
5	180	13.448502	14.478502	15.505502
6	190	13.466486	14.480486	15.485486
7	200	13.501741	14.493741	15.480741
8	210	13.541407	14.511407	15.476407
9	220	13.587564	14.541564	15.489564
	Average (B_1)	13.483051	14.518274	15.548718
	Standard deviation (δ_1)	0.054302183	0.030769431	0.072284

Table – VI: Calculation of B_2 for different activation energies and $\delta_2$value at different temperature for $[Hg_2LCl_2]$ complex.

SN	Temp(^{0}C)	26 kcal	28 kcal	30 kcal
1	140	14.510780	15.633780	16.748780
2	150	14.575961	15.671961	16.763961
3	160	14.559339	15.629339	16.699339
4	170	14.534535	15.587535	16.632535
5	180	14.499772	15.526772	16.553772
6	190	14.522175	15.527175	16.532175
7	200	14.576470	15.563470	16.546470
8	210	14.674329	15.639329	16.605329
9	220	14.872372	15.820372	16.763372
	Average (B_2)	14.591748	15.622192	16.649526
	Standard deviation (δ_2)	0.110670411	0.084992683	0.090793786

By using the above table we calculate the minimum value of δ for B_0 , B_1, and B_2 i.e. for zero order, for zero order, first order and second order respectively as in table VII.

Table - VII

b = 0		b = 1		b = 2	
Ea		Ea		Ea	
k cal /mol	**δ0**	**k cal /mol**	**δ1**	**k cal /mol**	**δ2**
22	0.049151773	24	0.054302183	26	0.110670411
24	0.04461268	26	0.030769431	28	0.084992683
26	0.087446216	28	0.072284	30	0.090793786

The minimum value for B_1 is 0.030769431 and here order of reaction is 1M/sec and activation energy 26 kcal/mole.

The apparent frequency factor Z = 2.53705947 X $10^3 sec^{-1}$ and apparent entropy of activation.

where calculated using the equation $\log z = \bar{B} + \log Ra - logEa$

Where R is the gas constant and a is the heating rate. The frequency factor was calculated to be 2.53705947 X $10^3 sec^{-1}$ and the apparent activation entropy was also found to be --38.343348759 e.u. by the solving equation.

$$\Delta S^{\neq} = 8.3143 logzh/kT$$

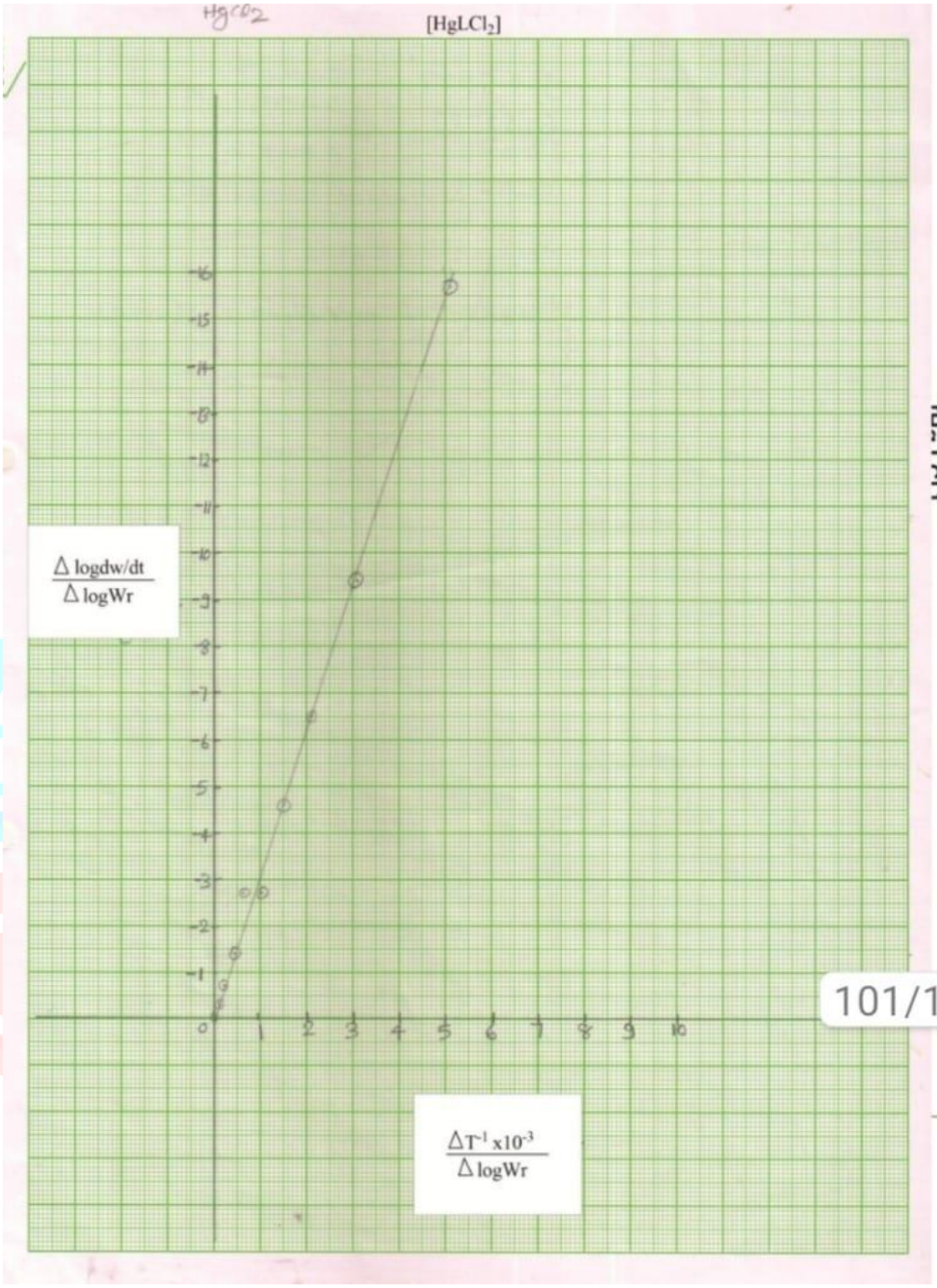
Table – VIII

SN.	Methods	Order of reaction	activation energy
1	Freeman and Carroll	1	23.45 Kcal/mole
2	J. Zsako	1	26 kcal/mole

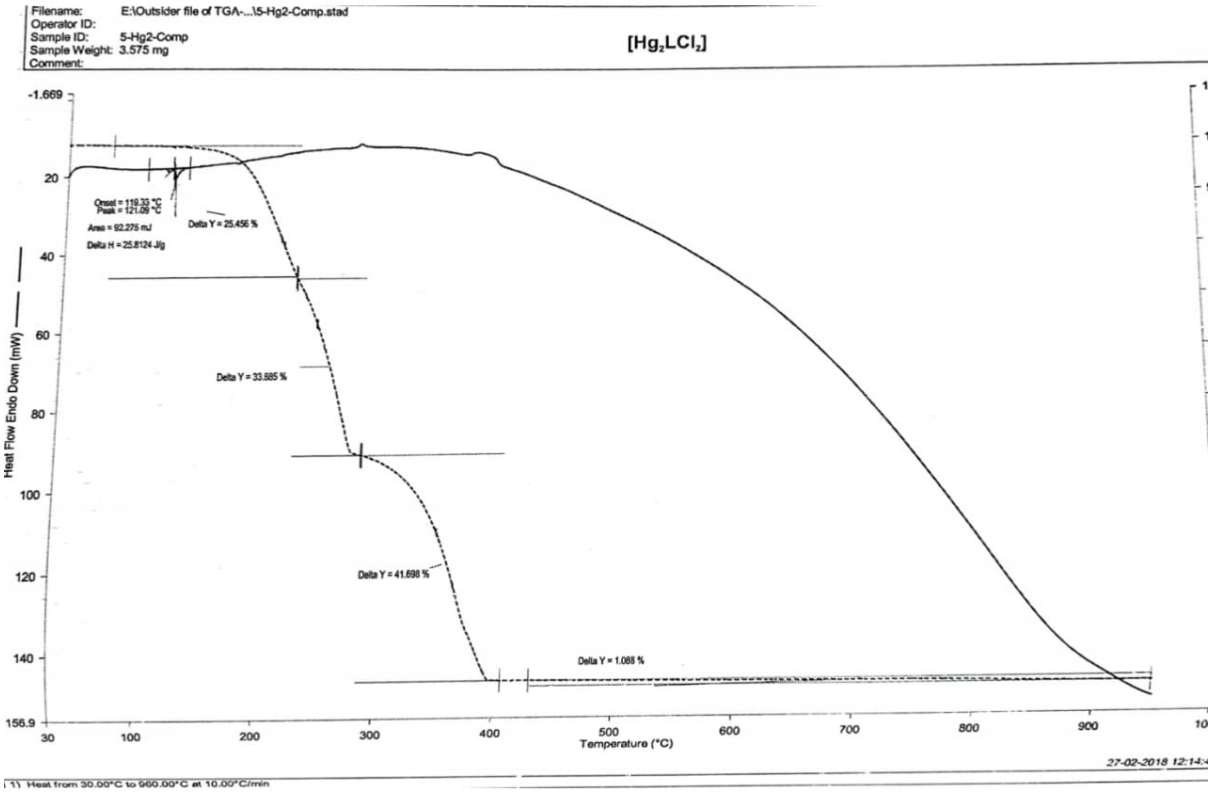
The value for absolute temperature T was taken as the temperature of which the weight loss was half of the total weight loss for the considered step i.e. 498 Kelvin.

The thermogram and plotted graph one shown in next page.

Freeman and carroll graph of $[Hg_2LCl_2]$



TG Curve of $[Hg_2LCl_2]$ Complex:



Future scope

1.NMR spectroscopy, UV- visible spectroscopy and infrared spectroscopy are commonly used to analyze electronic and vibrational properties of complexes.

2.Crystallegraphic techniques like X- ray diffraction provide detailed information about the three dimensional structure of the complexes

3.Transition metal complexes are widely used in the treatment of cancers.

Application

→This work may be used in the establishment of solid state mechanism of complex compounds.
→ Determination of kinetic parameters in non isothermal condition of complex compounds will help to determine the solid state reaction mechanism.

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