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Solid State Kinetics of Ni (II) Complex Derived from Schiff Base of 5-Amino1, 2, 3, 4 Thiatriazole with-Ortho-Ethoxybenzaldehyde $[NiL_2Cl_2].3H_2O$

Ajay Kumar, Akhilesh Prasad, Dhermendra Prasad and U. N.Verma*

University Department of Chemistry, Magadh University, Bodhgaya-824234, **INDIA**

Email: unverma.mu@gmail.com

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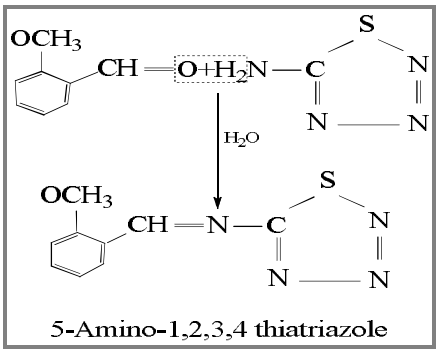
ABSTRACT

Ni(II) form 2:1 complex with Schiff base ligand of 5-amino 1, 2, 3, 4 thiatriazole and orthomethoxy-benzaldehyde. Kinetic parameters like order of reaction activation energy, apparent frequency factor and apparent entropy of activation of third stage of the decomposition of complex have been determined using graphical method of Freeman -Carroll and Doyl's method as modified by Zsako using non-isothermal TG curve.

Graphical Abstract



Preparation of Schiff base .

Keywords: Solid state kinetics, Thermogravimetric analysis, Schiff base.

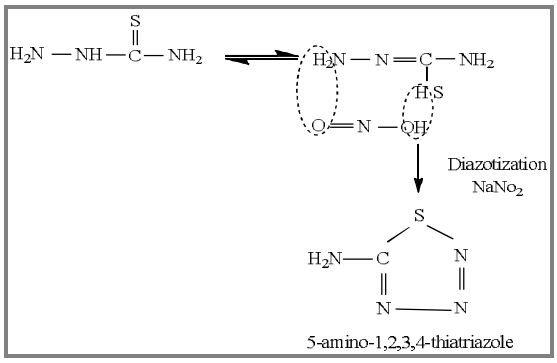
INTRODUCTION

Many organic compounds containing nitrogen-sulphur have proved their indispensability towards the chemotherapeutical treatment in human life [**1-3**]. Metal chelates of these ligands as nitrogen and sulphur donor have more sensational results in vivo [**4**]. The Schiff bases complexes have received considerable attention in view of their variable binding mode, structural diversity, promising pharmacological and biological implications [**5-10**]. Thiocarbohydrazones and their metal complexes are reported to exhibit anticancer [**11**], antitumor [**12, 13**], antibacterial [**14**], antiviral, antifungal and

other biological activities [**15, 16**]. These have also catalytic activities [**17**]. Thermal products of Schiff base have also been studied [**18-21**]. The thermal kinetics and decomposition products of the complex are apparently of significance in understanding the biochemistry of the complex [**22**]. However, the Ni(II) complex of Schiff base ligand(L) derived from 5-amino-1, 2, 3, 4-thiatrizole with o-methoxybenzaldehyde was not studied. In present communication, the solid state kinetics and decomposition product of complexes with ligand(L) are incorporated.

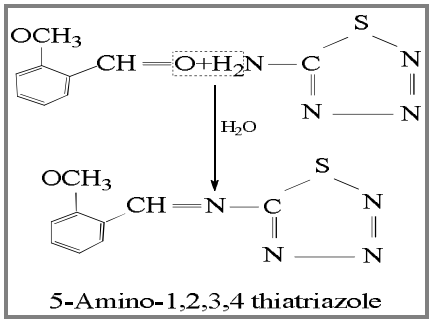
MATERIALS AND METHODS

An ice cold solution of 20 g of thiosemicarbazide in 95 cc of 2.2(N) HCl was added from a burette with stirring in a total of 14.7 g 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 returned to the reaction vessel. The crude product was vacuum dried and recrystallized from methanol yielded fine colorless needle which decomposition with a slight explosion of 136° in a capillary tube.



Schem 1. Structure of 5-Amino-1, 2, 3, 4-thiatriazole.

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. Light yellow solid Schiff base is filtered and recrystallized with ethanol.



Scheme 2. Preparation of Schiff base

Preparation of complex of Ni(II): 0.002 M of ligand in ethanolic solution was mixed with 0.001M Nickel(II) Chloride in ethanolic solution. The resulting solution was refluxed for half an hour on steam bath. Light grey colour precipitate was obtained. The precipitate was filtered off and washes with ethanol and dried in a desiccator over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

The result obtained by the usual elemental analysis and estimation of metal content are suggestive of the molecular formula $[NiL_2Cl_2].3H_2O$ and the molecular weight 623.693 to the complexes.

The basis of the calculation of kinetic parameter from a TG curve is based on the formal kinetic equation

$$-\frac{d\alpha}{dt} = k\alpha$$

Where α is the fraction of the initial compound undergoing reaction, n is the order of 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 four stages of the decomposition. Third 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 [23] and Doyle's method as modified [24] by Zsako [25].

The following table contains the data obtained by Freeman-Carroll method (Table 1).

Table 1. Data obtained by Freeman and Carroll method

S.No.	Temp °C	Weight(mg)	$\frac{\Delta \log dw/dt}{\Delta \log Wr}$	$\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log Wr}$
1	170	5.759295	-30.92248	11.39959
2	180	5.716470	0.47548	10.83647
3	190	5.674733	2.46938	10.52768
4	200	5.625170	-13.72871	8.39381
5	210	5.556043	-18.76995	5.68256
6	220	5.458004	-13.60143	3.76176
7	230	5.313881	-9.87803	2.37908
8	240	5.105412	-6.22918	1.50499
9	250	4.817165	-3.67433	0.97262
10	260	4.451965	-1.90508	0.66464
11	270	4.015463	-1.03653	0.46213
12	280	3.463968	-0.86359	0.28304
13	290	2.794869	-0.40807	0.15605
14	300	2.034687	-0.10946	0.06118

Initial weight at(150^0C): 5.833422mg, Final weight at (310^0C): 1.690573mg

Table 2. Data of log f(α) values for the complex $[NiL_2Cl_2].3H_2O$ calculated at different temperatures

S. No.	Temp °C	Weight (mg)	$\alpha = \frac{Wo-Wt}{Wo-Wf}$	Log α	$\text{Log}\left(ln\frac{1}{1-\alpha}\right)$	$\text{Log}\left(\frac{\alpha}{1-\alpha}\right)$
1	160	5.802336	0.00750353	-2.124734	-2.123100	-2.121463
2	170	5.759295	0.01789276	-1.747323	-1.743408	-1.739482
3	180	5.716470	0.02822985	-1.549291	-1.543088	-1.536855
4	190	5.674733	0.03830432	-1.416752	-1.408299	-1.399790
5	200	5.625170	0.05026782	-1.298710	-1.287559	-1.276311
6	210	5.556043	0.06695368	-1.174226	-1.159264	-1.144129
7	220	5.458004	0.09061832	-1.042784	-1.022320	-1.001530
8	230	5.313881	0.12540669	-0.901679	-0.872907	-0.843485
9	240	5.105412	0.17572690	-0.755162	-0.713873	-0.671233
10	250	4.817165	0.24530390	-0.610296	-0.550614	-0.488068
11	260	4.451965	0.33345579	-0.476962	-0.391850	-0.300791
12	270	4.015463	0.43881855	-0.357715	-0.238289	-0.106818
13	280	3.463968	0.571938	-0.242651	-0.071354	0.125843
14	290	2.794869	0.733445	-0.134632	0.121289	0.439581
15	300	2.034687	0.916938	-0.037660	0.395879	1.042937

Initial weight at(150°C): 5.833422mg, Final weight at (310°C): 1.690573mg

The plot $\left[\Delta log \frac{dw}{dt} / \Delta log Wr\right]$ versus $[\Delta T^{-1}]$ / $[\Delta \log Wr]$ with the value tabulated above gives a straight line with an intercept at 0 suggesting the order of reaction 0 and activation energy 14 kcalmol^{-1} as calculated from $Ea = 2.3030\ X$ slop.

Further the weights at different temperatures were used to calculate data using Doyle's method as modified by Zsako for the same steps of the reaction

Table 3. Calculation of β_0 for different activation energies and δ_0 values at different temperatures for $[NiL_2Cl_2].3H_2O$complex

S. No.	Temp °C	12 kcal	14 kcal	16 kcal
1	160	6.277265738	7.412265738	8.534265738
2	170	6.496677320	7.609677320	8.705677320
3	180	6.546708549	7.636708549	8.711708549
4	190	6.536247719	7.608247719	8.658247719
5	200	6.519290077	7.565290077	8.601290077
6	210	6.508774474	7.542774474	8.555774474
7	220	6.515215987	7.526215987	8.523215987
8	230	6.536320722	7.530320722	8.509320722
9	240	6.561838241	7.538838241	8.498838241
10	250	6.595704446	7.554704446	8.502704446
11	260	6.618038267	7.565038267	8.495038267
12	270	6.631284980	7.560284980	8.476284980
13	280	6.644349178	7.560349178	8.459349178
14	290	6.655367712	7.553367712	8.439367712
15	300	6.655339894	7.545339894	8.414339894
	Average($\overline{B_0}$)	*6.553228220*	*7.553961554*	*8.539028220*
	Standard deviation(δ_0)	*0.091606669*	*0.048349856*	*0.088600434*

Table 4. Calculation of β_1 for different activation energies and δ_1 values at different temperatures for $[NiL_2Cl_2].3H_2O$ complex

S. No.	Temp °C	14 kcal	16 kcal	18 kcal
1	160	7.413900227	8.535900227	9.641900227
2	170	7.613591965	8.709591965	9.798591965
3	180	7.642911933	8.717911933	9.784911933
4	190	7.616701282	8.666701282	9.709701282
5	200	7.576441367	8.612441367	9.635441367
6	210	7.557735971	8.570735971	9.571735971
7	220	7.546679619	8.543679619	9.526679619
8	230	7.559092789	8.538092789	9.504092789
9	240	7.580127073	8.540127073	9.494127073
10	250	7.614386010	8.562386010	9.493386010
11	260	7.650150212	8.580150212	9.493150212
12	270	7.679710629	8.595710629	9.496710629
13	280	7.731645667	8.630645667	9.518645667
14	290	7.809289167	8.695289167	9.571289167
15	300	7.978879351	8.847879351	9.708879351
	Average($\overline{B_1}$)	*7.638082884*	*8.623149551*	*9.596616217*
	Standard deviation(δ_1)	*0.125484177*	*0.086148688*	*0.105778764*

Table 5. Calculation of β_2 for different activation energies and δ_2 values at different temperatures for $[NiL_2Cl_2].3H_2O$complex

S.No.	Temp °C	16 kcal	18kcal	20 kcal
2	160	8.537536768	9.643536768	10.738536768
3	170	8.713518407	9.802518407	10.875518407
4	180	8.724144994	9.791144994	10.843144994
5	190	8.675210052	9.718210052	10.753210052
6	200	8.623688924	9.646688924	10.658688924
7	210	8.585871271	9.586871271	10.582871271
8	220	8.564469785	9.547469785	10.521469785
9	230	8.567514573	9.533514573	10.489514573
10	240	8.582767112	9.536767112	10.475767112
11	250	8.624932338	9.555932338	10.476932338
12	260	8.671209309	9.584209309	9.893209309
13	270	8.727181675	9.628181675	10.524181675
14	280	8.827842802	9.715842802	10.590842802
15	290	9.013581317	9.889581317	10.753581317
16	300	9.494936656	10.355936656	11.202936656
	Average($\overline{B_2}$)	*8.728960399*	*9.702427066*	*10.625360399*
	Standard deviation(δ_2)	*0.236292381*	*0.203516193*	*0.272426729*

A comparative value of δ along with their activation energies for the presumed order of reaction are given in table 6.

Table 6. A comparative value of δ along with their activation energies

b = 0		b = 1		b = 2	
Ea		***Ea***		***Ea***	
Kcal mol^{-1}	**δ_0**	**Kcal mol^{-1}**	**δ1**	**Kcal mol^{-1}**	**δ_2**
12	0.091606669	14	0.125484177	16	0.236292381
14	0.048349856	16	0.086148688	18	0.203516193
16	0.088600434	18	0.105778764	20	0.272426729

Obviously among all the δ minimum values given above δ_0=0.048349856 is the least one corresponding to the activation energy E*a*=14 Kcal mol^{-1} and the order of reaction b=0 for the stage of reaction consideration where $\overline{B}_0$=7.553961554.

Table 7. Order of reaction and activation energy

S. No.	Methods	Order of reaction	Activation energy
1	Freeman and Carroll	0M sec^{-1}	19.227 Kcal mol^{-1}
2	J. Zsako	0M sec^{-1}	14.000 Kcal mol^{-1}

The values of order of reaction and activation energy, evaluated by the two different methods are given above and are in good agreement within limit.

The frequency factor Z was calculated using the equation:

$$log\, z = \overline{B}_0 + logRq - log\, Ea$$

Where $\overline{B} = 7.553961554$, E*a*=14 *Kcal mol^{-1}*

Thus, the frequency factor for the thermolysis step under consideration was found to be Z = 5.1x 10^1 sec$^{-1.}$

The apparent entropy of activation was calculated about to be -94.432991138e.u from the equation.

$$\Delta S^{\#} = 8.3143 \log Zh/KT$$

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

APPLICATION

This work may be used in the establishment of solid state mechanism of complex compounds.

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