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Solid state kinetics of Cr(III) complex derived from Schiff base of 5-amino1,2,3,4 thiatriazole with-ortho-methoxybenzaldehyde.

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Abstract:

Cr(III) form 2 : 1 complex with Schiff base ligand of 5-amino 1,2,3,4 thiatriazole and ortho-methoxybenzaldehyde. Kinetic parameters like order of reaction activation energy, apparent frequency factor and apparent entropy of activation of second 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.

Key Word : - Solid State kinetics , Thermogravimetric analysis, Schiff base. T.G. curve, activation energy, order of reaction, entropy of activation and frequency factors.

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 Cr(III)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 Zsako[17, 17, 19].

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.

Preparation of complex of Cr(III)

0.002 M of ligand in ethanolic solution was mixed with 0.001M Cr(III) Chloride in ethanolic solution. The resulting solution was refluxed for half hour on steam bath. Greenish White 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 **[(CrL_2Cl_2) Cl]** and the molecular weight 598.355 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[20] and Doyle's method as modified[21] by Zsako[22].

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

Table – I

Data obtained by Freeman and Carroll method.

S.No.	Temp(^{0}C)	Weight (mg)	$\frac{\Delta \log dw/dt}{\Delta \log Wr}$	$\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log Wr}$
1	180	4.153935	4.40375	3.11257
2	190	4.102416	7.14706	3.58391
3	200	4.060244	7.76173	4.07643
4	210	3.999377	-9.54563	1.93235
5	220	3.912207	-6.21833	1.37416
6	230	3.770692	-4.77326	0.91470
7	240	3.624830	-0.25931	0.76481
8	250	3.424622	-1.70116	0.46100
9	260	3.163112	-0.85894	0.26561
10	270	2.834432	-0.37273	0.12971

Initial Weight at 160^{0}C = 4.293494mg.

Final Weight at 280^{0}C = 2.446189mg.

Plotting graph between $\left[\Delta log \frac{dw}{dt} / \Delta log Wr\right]$ versus $[\Delta T^{-1}] / [\Delta \log Wr]$. A straight line is obtained by the line intercept at 0.8 and slope 4.8 Applying

Ea = 2.300 X slope gave the activation energy equal to 22.10 Kcal/mole and order of reaction is 0.8M/sec.

The value of mass obtained of different temperature as in graphical method and utilised to calculate different formation using Doyle's method as modified by Zsako.

Firstly $\alpha, log\alpha, \log\left(ln\frac{1}{1-\alpha}\right) and\ log\left(\frac{\alpha}{1-\alpha}\right)$ have been calculated using the following Table II.

Table – II

Data of log f(α) values for the complex *[CrL₂Cl₂]Cl* calculated at different temperatures.

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	170	4.218063	0.040833	-1.388989	-1.379967	-1.370883
2	180	4.153935	0.075547	-1.121781	-1.104835	-1.087665
3	190	4.102416	0.103436	-0.985328	-0.961834	-0.937909
4	200	4.060244	0.126265	-0.898717	-0.869736	-0.840097
5	210	3.999377	0.159214	-0.798018	-0.760905	-0.722704
6	220	3.912207	0.206402	-0.685287	-0.636054	-0.584887
7	230	3.770692	0.283008	-0.548201	-0.477960	-0.403716
8	240	3.624830	0.361967	-0.441331	-0.347400	-0.246174
9	250	3.424622	0.470346	-0.327583	-0.196863	-0.051575
10	260	3.163112	0.611909	-0.213313	-0.023873	0.197753
11	270	2.834432	0.789833	-0.102465	0.193083	0.574970

Initial weight at 160 ^{0} = 4.293494mg

Final weight at 280 ^{0} = 2.446189mg

The values obtained above have been utilized to calculate B_0&δ_0 , B_1& δ_1, B_2& δ_2, using standard deviation method.

Table III

Calculation of B_0 for different activation energies and δ_0 values at different temperature for *[CrL₂Cl₂]Cl complex*

S.No.	Temp(^{0}C)	20 kcal	22 kcal	24 kcal
1	170	11.226011260	12.292011260	13.351011260
2	180	11.258219243	12.301219243	13.339219243
3	190	11.167672081	12.189672081	13.204672081
4	200	11.036283047	12.041283047	13.035283047
5	210	10.928981522	11.910981522	12.892981522
6	220	10.837713393	11.807713393	12.765713393
7	230	10.784798635	11.732798635	12.673798635
8	240	10.705669336	11.635669336	12.559669336
9	250	10.637417196	11.555417196	12.461417196
10	260	9.980686628	11.479686628	12.373686628
11	270	10.528535141	11.470535141	12.285535141
	Average($\overline{B}_0$)	*10.826544316*	*11.856089771*	*12.812998862*
	Standard deviation(δ_0)	*0.353334882*	*0.299031231*	*0.363842121*

Table- IV

Calculation of B_1 for different activation energies and δ_1 values at different temperature for *[CrL₂Cl₂]Cl* complex

S.No.	Temp(^{0}C)	12kcal	14kcal	16kcal
1	300	6.864032694	7.977032694	9.078032694
2	310	6.991165252	8.081165252	9.156165252
3	320	6.991165748	8.063165748	9.113165748
4	330	6.948263549	7.994263549	9.030263549
5	340	6.922094743	7.956094743	8.969094743
6	350	6.921946387	7.932946387	8.929946387
7	360	6.960040433	7.954040433	8.933040433
8	370	6.969599959	7.946599959	8.906599959
9	380	7.009136594	7.968136594	8.916136594
10	390	7.071127343	8.018127343	8.948127343
11	400	7.182083301	8.111083301	9.027083301
	AVERAGE($\overline{B_1}$)	*6.984605091*	*8.000241455*	*9.000696000*
	Standard deviation(δ_1)	*0.0807309*	*0.057373224*	*0.081865117*

Table- V

Calculation of B_2 for different activation energies and δ_2 values at different temperature for *[CrL₂Cl₂]Cl* complex

S No	Temp(^{0}C)	16kcal	18kcal	20kcal
1	300	9.087117030	10.171117030	11.244117030
2	310	9.173334572	10.240334572	11.292334572
3	320	9.137090827	10.180090827	11.215090827
4	330	9.059903323	10.082903323	11.094903323
5	340	9.007296101	10.008296101	11.004296101
6	350	8.981112696	9.964112696	10.938112696
7	360	9.007284294	9.973284294	10.929284294
8	370	9.007826398	9.961826398	10.900826398
9	380	9.061424710	9.992424710	10.913424710
10	390	9.169752720	10.082752720	10.391752720
11	400	9.408970113	10.309970113	11.205970113
	AVERAGE($\overline{B_2}$)	*9.100101162*	*10.087919344*	*11.011828435*
	Standard deviation(δ_2)	*0.116838543*	*0.115928675*	*0.240709676*

Table – VI					
b = 0		**b = 1**		**b = 2**	
Ea		*Ea*		*Ea*	
k cal /mol	δ_0	k cal /mol	δ1	k cal /mol	δ_2
20	*0.353334882*	12	*0.0807309*	16	*0.116838543*
22	*0.299031231*	14	*0.057373224*	18	*0.115928675*
24	*0.363842121*	16	*0.081865117*	20	*0.240709676*

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.

The minimum value for B_1 is 0.057373224 and here order of reaction is 1M/sec and activation energy 14 kcal/mole.

The apparent frequency factor Z = 1.429 X $10^2 sec^{-1}$ and apparent entropy of activation.

where calculated using the equation

$$\log z = \bar{B} + \log Rq - logEa$$

Where R is the gas constant and a is the heating rate. The frequency factor was calculated to be 1.429 X $10^2 sec^{-1}$ and the apparent activation entropy was also found to be -90.515350646 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	0.8M/sec	22.10 kal/mol
2	J. Zsako	1M/sec	14.000 kal/mol

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. 525 Kelvin.

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