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Solid State Kinetics Of Cu(Ii) Complex Derived From Acetone Thiocarbohydrazone

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ABSTRACT

Cu(II) chloride form 1:1 complex with ligand acetone thiocarbohydrazone. It undergoes from steps decomposition, kinetic parameters like apparent activation energy, frequency factor, activation entropy and order of reaction have been determined employing the graphical method of Freeman-Carroll and Doyle method as modified by Zsako using TG curve. First stage of decomposition have been selected for the determination of kinetic parameters.

Key word: Solid state kinetic, thermogravimetric analysis, acetone thiocarbahydrazone.

INTRODUCTION

Many Organic compounds containing nitrogen-sulphur have proved their indispensability towards the chemotherapeutic treatment in human life[1-3]. Metal chelates of these ligands as nitrogen and sulphur donor have more sensational result 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], catalytic activities[17].

The kinetics and decomposition products of the complexes formed from nitrogen sulphur ligands are apparently of significance in understanding the biochemistry of the compound[17]. This paper deals the solid state kinetics of Ni(II) complex with 1-(o-hydroxyacetophenone)-5-(salicylidine)thiocarbahydrazone and calculation of kinetic parameters i.e. order of reaction, activation energy, entropy of activation and frequency factor using Freeman-Carroll[18] as well as Doyles[19] method as modified by Zsako[20].

EXPERIMENTAL

Ligand(L) acetone thiocarbahydrazone was prepared by condensation of thiocabohydrazide with acetone. Carbon disulphide (15ml) was added drop wise with continuous stirring over a period of one hour to warm (nearly to 50^0C) solution of hydrazine hydrate (50ml) in water (150ml). The mixture was refluxed on steam bath at 90^0C for further one hour and rapidly cooled in ice bath with continuous shaking. The colourless crystal which separated out was filtered, and recrystallizes from hot water.

The crystal were dried over anhydrous $CaCl_2$ in a desiccator and used for the next step of the reaction.

Preparation of complex of Cu(II):- An alcoholic solution of copper(II) chloride (0.01M) in 50 ml ethanol was slowly added to a hot alcoholic dioxane solution of the ligand (0.01M in 70ml 50% ethanol) and reflux on a steam bath for one hour.

The blackish brown precipitate separated out gradually. The product was filtered, washed thoroughly with hot water, ethanol and finally with ether and the dried in desiccator over anhydrous $CaCl_2$.

The analysis of carbon, hydrogen and nitrogen contents present in the ligand and mental complex were carried out at CDRI Lucknow.

RESULT AND DISCUSSION

The result obtained by the used elemental analysis and estimation of metal content are suggestive of molecular formula $[Cu(atcz)Cl_2]$ and the molecular weight 280.5

The first stage of decomposition was selected to study the chemical kinetics. The kinetic parameters, such as order of reaction, activation energy etc. was primarily evaluated by Freeman and Carroll method and was compared by the values obtained by Doyl's method as modified by Zsako.

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

TABLE –I

DATA OBTAINED BY FREEMAN AND CARROL METHOD:

Temp.	Wt of comp (mg)	$w_r=w_c-w$	$\frac{\Delta log\frac{dW}{dt}}{\Delta log W_r}$	$\frac{\Delta T^{-1}\times 10^{-3}}{\Delta log W_r}$
270	5.70			
280	5.67	0.63		
290	5.61	0.59	3.40154	1.12741
300	5.55	0.53	-3.78059	0.46530
310	5.48	0.46	-1.08810	0.28667
320	5.45	0.43	12.56299	0.98736
330	5.40	0.34	-4.13263	0.52105
340	5.34	0.32	-2.46095	0.36240

350	5.29	0.27	1.07332	0.05497
360	5.21	0.19	-1.33752	0.16617
370	5.14	0.12	0.29057	0.12306

Initial weight at 260^0C=5.70mg

Final weight at 380^0C=5.02mg

$Wc=W_0 - W_f = 5.70 - 5.02 = 0.68$mg

The plot of $\frac{\Delta log\frac{dW}{dt}}{\Delta log W_r}$ verses $\frac{\Delta T^{-1}\times 10^{-3}}{\Delta log W_r}$ gave a straight line with an intercept at 1.8 suggesting the order of reaction as 1.8 and applying E=2.303R slope, gave the value of activation energy to be equal to 31.0101 kcal/mole.

The same value for different weights taken at different temperatures were further subjected to the Zsako method to evaluate the data given in the table-II

TABLE –II

THE DATA OF LOG f(α) VALUES FOR THE COPLEX CALCULATED AT DIFFERENT TEMPERTURE

Tem.	Weight (in mg)	$\alpha = \frac{W_0 - W_t}{W_0 - W_f}$	logα	$\log\left(ln\frac{1}{1-\alpha}\right)$	$\log\frac{\alpha}{1-\alpha}$
280	5.67	0.07352	-1.13353	-1.11706	-1.10037
290	5.61	0.13235	-0.87826	-0.84780	-0.81660
300	5.55	0.22058	-0.65641	-0.60342	-0.54818
310	5.48	0.32352	-0.49009	-0.40949	-0.32033
320	5.45	0.36764	-0.43456	-0.33884	-0.23552
330	5.40	0.44117	-0.35538	-0.23513	-0.10266
340	5.34	0.52941	-0.27620	-0.12276	0.05115
350	5.29	0.60294	-0.21972	-0.03448	0.18142
360	5.21	0.72058	-0.14231	0.10553	0.41144
370	5.14	0.82352	0.08432	0.23919	0.66900

Initial weight at 260^0C= 5.70mg

Final weight at 290^0C=5,02 mg

The value of logF(α) were used to evaluate the values B_0, B_1 and B_2 at different activation energies at all temperatures. The calculated values of $\bar{B}$ were ultimately used to get the δ_{min} values for all three presumed order of reactions.

TABLE-III

CALCULATION OF $B_0 = log\alpha - logP(x)$ FOR DIFFERENT ACTIVATION ENERGIES AND δ_0 VALUES AT DIFFERNT TEMPERATURE.

Tem.	E=12 kcal	E=14 kcal	E=16 kcal
280	5.75347	6.66947	7.56847
290	5.91174	6.80974	7.69574
300	6.03659	6.92659	7.79559
310	6.11091	6.98291	7.84291
320	6.07444	6.93744	7.78544
330	6.06662	6.91562	7.55062
340		6.89880	7.72080
350		6.86528	7.67328
360		6.85369	7.65069
370		6.82368	7.60868
$\bar{B}_0$	5.99229	6.86832	7.68922
δ_0	0.12371	0.08346	0.09340

TABLE –IV

CALCULATION OF $B_1 = \log\left(ln\frac{1}{1-\alpha}\right) - logP(x)$ FOR DIFFRENT ACTIVATION ENERGIES AND δ_1 VALUES AT DIFFERENT TEMPERATURE.

Tem.	E=18 kcal	E=20 kcal	E=22 kcal
280	8.47294	9.35094	10.21994
290	8.60220	9.46620	10.31820
300	8.70958	9.55658	10.40058
310	8.77303	9.60703	10.43803
320	8.71616	9.53616	10.35416
330	8.69287	9.50487	10.30887
340	8.68724	9.48624	10.27824
350	8.65752	9.44852	10.22652
360	8.68453	9.46253	10.23153
370	8.71019	9.47419	10.23519
$\overline{B_1}$	8.67062	9.48932	10.30112
δ_1	0.07780	0.06566	0.07325

TABLE –V

CALCULATION OF $B_2 = \log\left(\frac{\alpha}{1-\alpha}\right) - log\ p(x)$

Tem.	E=24 kcal	E=26 kcal	E=28 kcal
280	11.09963	11.95663	12.80963
290	11.19940	12.04340	12.88340
300	11.29282	12.11882	12.94582
310	11.34967	12.16267	12.97667
320	11.26848	12.06848	12.86848
330	11.23934	12.03134	12.81834
340	11.23615	12.01415	12.79315
350	11.21842	11.98442	12.74942
360	11.30044	12.05744	12.80944
370	11.41500	12.16300	12.90200
$\overline{B_1}$	11.26193	12.06003	12.85563
δ_1	0.81809	0.06454	0.06833

A comparison of the δ_{min} value for different presumed order incorporated in the previous tables are given in table VI showing δ_2= 0.06454 is the minimum value which corresponds to the order of reaction b=2 activation energy E=26kcal/mole and $\overline{B_2}$ =12.06003

TABLE-VI

b=0		b=1		b=2	
E kcal/mol	δ_0	E kcal/mol	δ_1	E kcal/mol	δ_2
12	0.12371	18	0.07780	24	0.81809
14	0.08346	20	0.06566	28	0.06454
16	0.09340	22	0.07325	30	0.06833

The values obtained for the order of reaction and the activation energy for the step under consideration by different method, obviously, seem to be good agreement with each other.

From the $\bar{B}$ value obtained above and using equation.

logZ=$\bar{B} + logRq - logE$

Where R is the gas constant and q is the heating rate, the apparent frequency Z was calculated to be $8.83256 \times 10^8\ S^{-1}$

The apparent activation entropy ΔS^* was also found to be -32.2799 e.u.,on solving the equation $\Delta S^* = 8.3143 log \frac{Zh}{KT}$

The values for absolute temperature T (340 K) was taken as the temperature T_2 at which the weight loss was half of the total loss for the considered step.

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