

Solid State Kinetics Of Ni(II) Complex With 1-(O-Hydroxy Acetophenone)-5-(Salicylidine) Thiocarbazone

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Abstract: Ni(II) chloride form 1:1 complex with 1-(o-hydroxyacetophenone)-5-(salicylidine) thiocarbazone. 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. This stage of decomposition have been selected for the determination of kinetic parameters.

Keywords: Solid state kinetic, thermogravimetric analysis, 1-(o-hydroxyacetophenone)- 5-(salicylidine), thiocarbazone.

INTRODUCTION

Organic compound containing nitrogen-sulphur recently proved their indispensability towards the chemotherapeutic treatment in human life¹⁻³. The Schiff bases complexes have received considerable attention in view of their variable binding mode, structural diversity, promising pharmacological and biological implications⁴⁻⁹. Thiocarbazones and their metal complexes are reported to exhibit anticancer¹⁰, antitumor¹¹⁻¹², antibacterial¹³, antiviral, antifungal and other biological activities^{14,15}, catalytic activities¹⁶. The kinetics and decomposition products of the complexes formed from nitrogen sulphur ligands are apparently of significance in understanding the biochemistry of the compound¹⁷. This paper deals the solid state kinetics of Ni(II) complex with 1-(o-hydroxyacetophenone)-5-(salicylidine)thiocarbazone and calculation of kinetic parameters i.e. order of reaction, activation energy, entropy of activation and frequency factor using Freeman-Carroll¹⁸ as well as Doyles¹⁹ method as modified by Zsako²⁰.

EXPERIMENTAL

Ligand 1-(o-hydroxyacetophenone)-5-(salicylidine)thiocarbazone was prepared by adding drop wise alcoholic solution of salicylaldehyde (10.5ml; 0.1M) to the hot alcoholic suspension of mono-(o-hydroxyacetophenone) thiocarbazone. The mixture was refluxed on steam bath for half an hour. After cooling at room temperature yellowish colour precipitate was filtered, washed with alcohol and recrystallized from acetone.

An aqueous ethanolic solution of hydrated nickel(II) chloride (0.01M) was slowly added to ligand (0.01M)solution in ethanolic pyridine (50ml of 20% pyridine) the resulting solution was refluxed for half an hours on a steam bath when orange red coloured solution obtained. The resulting solution on diluted with about 200ml of water yielded a yellowish precipitate. The precipitate was digested on a steam bath for further one hour and filtered. The precipitate was washed with excess of water and finely with acetone – alcohol mixture and dried in a desiccators over anhydrous CaCl₂

RESULT AND DISCUSSION

The result obtained by the usual elemental analysis and estimation of metal content are suggestive of the molecular formula [Ni(hastcz)].H₂O and the molecular mass 404.69 to the complex

The second 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. (°C)	Wt. of comp(mg)	$\Delta \log dw/dT$	$w_r = w_c - w$	$\frac{\Delta \log \frac{dW}{dt}}{\Delta \log W_r}$	$\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log W_r}$
320	3.44005	-0.03000695	0.93213	-0.85935526	0.3906500
330	3.3594	-0.01428711	0.85148	-0.3635209	0.7112055
340	3.27397	-0.02500603	0.76605	-0.54458811	0.35067800
350	3.18485	-0.01836477	0.67693	-0.34190326	0.31235600
360	3.05728	-0.15577338	0.54936	-1.71770867	0.50345600
370	2.97355	0.182867464	0.46563	2.546330326	0.34194749
380	2.93399	0.325624808	0.42607	8.444627329	0.61735902
390	2.85334	-0.30934809	0.34542	-3.39445066	0.25333626
400	2.78052	0.044353697	0.2726	0.431365442	0.21786722
410	2.71552	0.049337318	0.2076	0.417057841	0.18382003
420	2.65618	0.039565815	0.14826	0.2706218	0.20345000
430	2.60705	0.082000778	0.09913	1.27562000	0.11736441
440	2.55727	-0.00570813	0.04935	-0.01884381	0.26583338

Initial weight at 300°C=3.59092mg

Final weight at 450°C=2.50792mg

$W_c = W_0 - W_f = 3.59092 - 2.50792 = 1.083\text{mg}$

The plot of $\frac{\Delta \log \frac{dW}{dt}}{\Delta \log W_r}$ versus $\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log W_r}$ gave a straight line with an intercept at 2.2 suggesting the order of reaction as 2.2 and applying $E = 2.303R$ slope, gave the value of activation energy to be equal to 28.95 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 TEMPERATURE

Tem. (°C)	Weight (in mg)	$\alpha = \frac{W_0 - W_t}{W_0 - W_f}$	Log α	$\log \left(\ln \frac{1}{1-\alpha} \right)$	$\frac{\alpha}{\log 1-\alpha}$
310	3.51809	0.067248	-1.17232	-1.15729	-1.14208
320	3.44005	0.139307	-0.85603	-0.82386	-0.79087
330	3.3594	0.213777	-0.67004	-0.61886	-0.56559
340	3.27397	0.292659	-0.53364	-0.46062	-0.38327
350	3.18485	0.374949	-0.42603	-0.32797	-0.22194
360	3.05728	0.492742	-0.30738	-0.1683	-0.01261
370	2.97355	0.570055	-0.24408	-0.07361	0.122505
380	2.93399	0.606584	-0.21711	-0.03017	0.188038
390	2.85334	0.681053	-0.16682	0.057943	0.329462
400	2.78052	0.748292	-0.12593	0.139717	0.473174
410	2.71552	0.80831	-0.09242	0.217978	0.624979
420	2.65618	0.863102	-0.06394	0.298531	0.799667
430	2.60705	0.908467	-0.04169	0.37859	0.996733
440	2.55727	0.954432	-0.02025	0.489755	1.321086

Initial weight at 300°C= 3.59092mg

Final weight at 450°C=2.50792 mg

The value of logF(α) were used to evaluate the values B₀, B₁ and B₂ 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 $B_0 = \log \alpha - \log P(x)$ for different activation energies and δ_0 values at different temperature.

Temp. (°C)	E=14 kcal	E=16 kcal	E=18 kcal
310	6.30068	7.16068	8.00868
320	6.51597	7.36397	8.19897
330	6.60096	7.43596	8.25796
340	6.64136	7.46336	8.27636
350	6.65897	7.46697	8.26597
360	6.68862	7.48562	8.27162
370	6.66392	7.44892	8.22692
380	6.60389	7.37589	8.14589
390	6.57218	7.33618	8.09218
400	6.53107	7.28707	8.03407
410	6.48858	7.23458	7.96858
420	6.44006	7.17706	7.90406
430	6.38531	7.11331	7.83131
\bar{B}_0	6.545505	7.334582	8.114044
δ_0	0.117191	0.128815	0.152508

Table -IV

Calculation of $B_1 = \log \left(\ln \frac{1}{1-\alpha} \right) - \log P(x)$ for different activation energies and δ_1 values at different temperature.

Temp. (°C)	$\log \left(\ln \frac{1}{1-\alpha} \right)$	E=18 kcal	E=20 kcal	E=22 kcal
310	-1.15729	8.023710	8.857710	9.688710
320	-0.82386	8.231140	9.051140	9.869140
330	-0.61886	8.309140	9.121140	9.925140
340	-0.46062	8.349380	9.148380	9.940380
350	-0.32797	8.364030	9.155030	9.933030
360	-0.1683	8.410700	9.188700	9.957700
370	-0.07361	8.397390	9.161390	9.922390
380	-0.03017	8.332830	9.087830	9.835830
390	0.057943	8.316943	9.063943	9.802943
400	0.139717	8.299717	9.032717	9.763717
410	0.217978	8.278978	9.007978	9.725978
420	0.298531	8.263531	8.980531	9.693531
430	0.37859	8.25159	8.96259	9.66259
	\bar{B}_1	8.294545	9.063006	9.824698
	δ_1	0.097695	0.095022	0.108187

TABLE -V

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

Temp. (°C)	$\log \left(\frac{\alpha}{1-\alpha} \right)$	E=26 kcal	E=28 kcal	E=30 kcal
310	-1.14208	12.483	12.15492	12.96392
320	-0.79087	12.304	12.31313	13.11013
330	-0.56559	12.134	12.35541	13.13941
340	-0.38327	11.963	12.35873	13.12873
350	-0.22194	11.803	12.34606	13.10306
360	-0.01261	11.646	12.38539	13.13439
370	0.122505	11.494	12.35551	13.09551
380	0.188038	11.347	12.26504	12.99104

390	0.329462	11.199	12.25046	12.96846
400	0.473174	11.061	12.24717	12.95217
410	0.624979	10.927	12.25198	12.94798
420	0.799667	10.793	12.28467	12.97067
430	0.996733	10.664	12.33873	13.02173
	\bar{B}_2	11.52446	12.30055	13.04055
	δ_2	0.589365	0.065024	0.078135

A comparison of the δ_{\min} value for different presumed order incorporated in the previous tables are given in table VI showing $\delta_2=0.065024$ is the minimum value which corresponds to the order of reaction $b=2$ activation energy $E=28\text{kcal/mole}$ and $\bar{B}_2=12.30055$

TABLE-VI

b=0		b=1		b=2	
E		E		E	
kcal/mol	δ_0	kcal/mol	δ_1	kcal/mol	δ_2
14	0.117191	18	0.097695	26	0.589365
16	0.128815	20	0.095022	28	0.065024
18	0.152508	22	0.108187	30	0.078135

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.

$$\log Z = \bar{B} + \log Rq - \log E$$

Where R is the gas constant and q is the heating rate, the apparent frequency Z was calculated to be $2.379 \times 10^7 \text{ s}^{-1}$

The apparent activation entropy ΔS^* was also found to be -47.7565076 e.u. , on solving the equation $\Delta S^* = 8.3143 \log \frac{Zh}{KT}$

The values for absolute temperature T (633 K) was taken

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