



Solid State Kinetics Of Ni(II) Complex Derived From 1-(Ohydroxyacetophenone)-5-(Salicylidine)Thiocarbohydrazone And B-Picoline.

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Abstract: Ni(II) form 1:1 complex with ligands ie. 1-(O-hydroxy acetophenone)-5-(salicylidine)thiocarbohydrazone and β -picoline. Kinetic parameters like order of reaction, activation energy, apparent frequency factor and apparent entropy of activation of first stage of the decomposition of complex have been determine using graphical method of Freeman and Carroll ; and Doyle's method as modified by Zsako using non isothermal TG curve.

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 life¹⁻³ Metal chelates of these ligands as nitrogen and sulphur donor have more sensational results in vivo⁴. The Schiff bases complexes have received considerable attention in view of their variable binding mode, structural diversity, promising pharmacological and biological implications⁵⁻¹⁰. Thiocarbohydrazones and their metal complexes are reported to exhibit anticancer¹¹, antitumor¹²⁻¹³, antibacterial¹⁴, antiviral, antifungal and other biological activities^{15,16}, catalytic activities¹⁷. Thermal products of Schiff base have also been studied¹⁸⁻²¹. The thermal kinetics and decomposition products of the complex are apparently of significance in understanding the biochemistry of the complex²². However, the Ni(III) complex of Schiff base ligand (L) derived from 1-(o-hydroxyacetophenone)-5-(salicylidine)-thiocarbohydrazone and β -picoline was not examined. In present communication, the solid state kinetics and decomposition product of complex with ligand(L) are incorporated.

Experimental

Ligand (L) 1-(o-hydroxy acetophenone)-5-(salicylidine) thiocarbohydrazene was prepared by adding drop wise hot alcoholic suspension of 1-(o-hydroxyacetophenone)thiocarbonylhydrazide (0.1M) to alcoholic solution of salicylaldehyde (0.1M). The reaction mixture was refluxed on a steam bath for half an hour to begin reaction with dissolution of solid compound and then allowed to cool at room temperature.

The yellowish coloured precipitate was filtered, washed with alcohol, recrystallised from acetone as faint yellow plates and dried in a desiccator over anhydrous CaCl_2

Preparation of complex of Ni(II)

Nickel(II) acetate dissolved in β -picoline methanol mixture(0.01M) was filtered and the filtrate was treated with β -picoline solution of the ligand in 1:1 molar proportion. The resulting deep orange solution was refluxed on a steam bath for a few minutes while desired complex was separated out by diluting the solution with a large volume of water. The product was filtered, washed with aqueous β -picoline and dried over KOH in atmosphere of β -picoline.

The colours, analytical results, magnetic moment value and molar conductance data at room temperature (30°C) of the complex are recorded in.

RESULT AND DISCUSSION

The result obtained by the usual elemental analysis and estimation of metal content are suggestive of the molecular formula $[\text{Ni}(\text{hacz})(\beta\text{-pico})]$ and the molecular mass 479.82 to the complex.

The basis of the calculation of kinetic parameter from a TG curve is based on the formal kinetic equation. $-\frac{d\alpha}{dt} = k\alpha^n$ 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 depend 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 thermogram of the complex shows five 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 and Carroll²³ and Doyle's method²⁴ as modified by Zsako²⁵.

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

TABLE-1

DATA OBTAINED BY FREEMAN AND CARROLL METHOD

Temp. ^o C	Wt of comp. (mg)	$W_r = W_c - w$	$\frac{\Delta \log \frac{dW}{dt}}{\Delta \log W_r}$	$\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log W_r}$
240	4.61608	1.22711	-0.88442329	0.72581503
250	4.45326	1.06429	-0.10387903	0.60252595
260	4.26653	0.87756	-0.71024231	0.42792495
270	4.01524	0.62627	-0.88018922	0.23569376
280	3.71113	0.32216	-0.28700508	0.1152937
290	3.54135	0.15238	0.778561027	0.09873195
300	3.46809	0.07912	1.282382823	0.10884516
310	3.42418	0.03521	0.632226031	0.08508981

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 1.1 suggesting the order of reaction as 1.1 and applying $E=2.303$ slope, gave the value of activation energy to be equal to 17.18 Kcal/mol.

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 $f(\alpha)$ VALUES FOR THE COMPLEX CALCULATED AT DIFFERENT TEMPERATURE

Tem.	Wt (mg)	α $= \frac{W_0 - W_t}{W_0 - W_f}$	Log α	$\log(\ln \frac{1}{1-\alpha})$	$\log \frac{1}{1-\alpha}$
230	4.77651	0.09397	-1.02701	-1.00576	0.042857
240	4.61608	0.198727	-0.70174	-0.65452	0.096219
250	4.45326	0.305044	-0.51564	-0.43901	0.158043
260	4.26653	0.426974	-0.3696	-0.25428	0.241826
270	4.01524	0.591061	-0.22837	-0.04857	0.388341
280	3.71113	0.789637	-0.10257	0.192824	0.677031
290	3.54135	0.9005	-0.04552	0.363159	1.002175
300	3.46809	0.948337	-0.02304	0.471732	1.286817
310	3.42418	0.977009	-0.0101	0.576645	1.638437

320	3.38897	1	0		
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Initial weight at 220⁰C=4.92042mg, Final weight at 320⁰C=3.38897mg

TABLE-III

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

Tem.	E=12 kcal	E=14 kcal	E=16 kcal
220	6.530988	7.541988	8.538988
230	6.736256	7.730256	8.709256
240	6.801363	7.778363	8.743363
250	6.836402	7.795402	8.743402
260	6.866632	7.813632	8.743632
270	6.886428	7.815428	8.431428
280	6.841483	7.757483	8.656483
290	6.766962	7.664962	8.550962
300	6.682898	7.572898	8.441898
\bar{B}_0	7.294941	7.718935	8.617713
δ_0	0.111364	0.102969	0.129224

TABLE-IV

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

Tem.	E=24 kcal	E=26 kcal	E=28 kcal
230	12.21624	13.15224	14.08324
240	12.34648	13.26448	14.18348
250	12.34999	13.25599	14.15199
260	12.53472	13.22072	14.10372
270	12.33943	13.24543	14.08143
280	12.39282	13.24982	14.10282
290	12.37916	13.22316	14.06316
300	12.31273	13.13873	13.96573
310	12.24665	13.05965	13.87365
\bar{B}_1	12.34647	13.20114	14.06769

δ_1	0.091365	0.069397	0.094569
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TABLE -V

$$\text{CALCULATION OF } \bar{B}_2 = \log\left(\frac{1}{1-\alpha}\right) - \log P(x)$$

Tem.	$\log\left(\frac{1}{1-\alpha}\right)$	E=24kcal	E=26kcal	E=28kcal
230	2.361728	15.58373	16.51973	17.45073
240	2.380211	15.38121	16.29921	17.21821
250	2.39794	15.18694	16.09294	16.98894
260	2.414973	15.00197	15.88997	16.77297
270	2.431364	14.81936	15.72536	16.56136
280	2.447158	14.64716	15.50416	16.35716
290	2.462398	14.4784	15.3224	16.1624
300	2.477121	13.48112	15.14412	15.97112
310	2.491362	13.33736	14.97436	15.78836
320	\bar{B}_2	2.429362	15.71914	16.5857
	δ_2	0.787848	0.528599	0.569153

A comparison of the δ_{\min} value for different presumed order incorporated in the previous tables are given in table VI showing $\delta_2=0.69397$ is the minimum value which corresponds to the order of reaction $b=1$ activation energy $E=26\text{Kcal/mole}$ and $\bar{B}_1=13.20114$

TABLE-VI

b=0		b=1		b=2	
E		E		E	
Kcal/mol	δ_0	Kcal/mol	δ_1	Kcal/mol	δ_2
12	0.111364	24	0.091365	24	0.787848
14	0.102969	26	0.069397	26	0.528599
16	0.129224	28	0.094569	28	0.569153

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 $2.037 \times 10^8 \text{ S}^{-1}$

The apparent activation entropy ΔS^* was also found to be -40.0295242 e.u., on solving the equation $\Delta S^* = 8.3143 \log \frac{zh}{KT}$

The values for absolute temperature T (638K) Was taken at the decomposition of half of the reactant in the considered step.

The value obtained for the kinetic parameter by different methods are in good agreement with each other and reliable.

References:

- 1.Scovill J P, Klayman D L, Franchino C F, J Med Chem,25, 126-64, (1982).
2. Hossain MN, Alam MN, Begum J, Inorganic Chim Acta, 249, 207-13,(1996).
- 3.West D X, Padhy S B Sonawane P B, Chikte R C, Strct. Bond, 76, 1-50,(1991).
4. Bhowan MG, Saina J, Lanlloo RT, 26, 329-332, (2001).
5. Khander A.A,Hosseini-Yazdi S.A., Zarei S.A. and Rebie U.M. Inorg. Chem., Acta, 358(II), 3211(2005)
6. Yousef J.M. and Saddiq A.A. Inter, J. Microbio. Res., 1(1): 01-13, (2010).
7. Shabani F., Saghatforoush L.A. and Ghammamy S. Bull Chem., Soc., 24, 2, :193,(2010).
8. Sathisa M.P, Revankar V.K. and Pai K.S.R., 2008 (ID 362105)01-11, (2008).
9. Badwaik V.B, Deshmukh R.d. and Aswar A. J. Coord. Chem., 62(12)2037,(2009).
10. Chandra S. And Sharma A.K. J. Coord.Chem., 62(22),3688,(2009)
11. Yousef J.M. and Saddiq A.A. Inter, J.Microbio.Res., 1(1):01-13,(2010) .
12. Shabani F., Saghatforoush L.A. and Ghammamy S. Bull. Chem.,Sco.,24,(2),193,(2010).
- 13.Sathisa M.P.,Revankar V.K. and Pai K.S.R. (ID 362105), 01-11, (2008).
14. Badwaik V.B., Deshmukh R.D. and Aswar A. J.Coord. Chem.,62(12), 2037,(2009).
15. Chandra S. And Sharma A.K. J. Coord.Chem., 62(22),3688,(2009)
16. Patil M.V. and Malve S.P. (2004). J. Indian Chem., Soc., 81(8), 683-686,(2009).
17. Deshun Huang, Pengxiang Zhao, Dideer Astrac . Coordination Chemistry Reviews- Vol. 2772:145-165 doi 10.1016,(2014).
- 18.Verma U.N., Bharti and Mukhopadhyay K Asian J. of Chem. 23,2,773-776, (2011).
19. Verma U.N., Bharti and Mukhopadhyay K. J.Therm Anal Calorim 104,1071-1075,(2011).
20. Ahmed J.M. et.al. Journal of king sand University Science vol. 24(1)25-31, (2012).
21. Zheng-jun L, et al. Taylor and francis on line- Vol 46, Issues, 529-533 published online 31 jul 2015, (2016).
22. M. Ravelingien.S.Mullens.J.Luyten.V.Meynen.E. Vinick.C.Vervaet and J.P.Remon. Apple.Surf.Sci, 255,9539(2009)
23. E.S. Freeman and Carrol, J.Phyc. Chem. 62,394(1958)
24. CD. Dogle,J.Appl.Polyno.Sci 5,285(1961)
25. J.Zsako,J.Phys.Chem. 72,2406(1968)