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Solid State Kinetics of Hg(II) Complex Derived from Schiff base of 5-amino-1, 2, 3, 4 thiatriazole with Ortho-methoxybenzaldehyde

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ABSTRACT

Hg(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.

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

INTRODUCTION

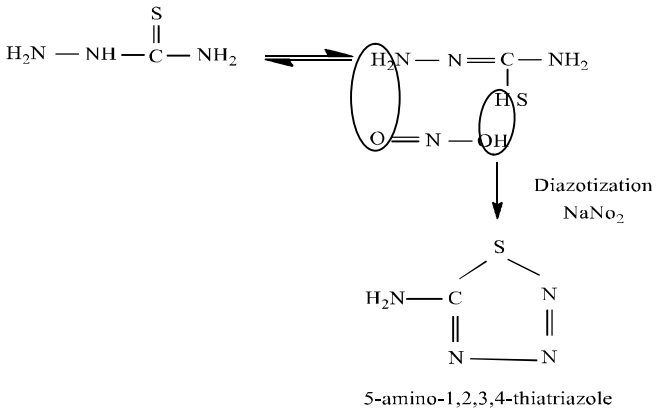
A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g., their ability to reversibly bind oxygen [1], catalytic activity in hydrogenation of olefins [2] and transfer of an amino group [3] photochromic properties [4], and complexing ability towards some toxic metals [5]. Schiff bases are most widely used as chelating ligands in coordination chemistry [6]. They are also useful in catalysis and in medicine as antibiotics, antiallergic and antitumor agents [7]. The metal complexes of Schiff bases derived from heterocyclic compounds have been the centre of attraction for many workers in recent years [8-12]. Thermal analysis is a technique in which a physical property of a substance and its reaction products is measured as a function of temperature. Thermal analysis can measure weight loss on heating, melting points, heat and energy transitions and change in the substance from. Thermal analysis techniques are widely used in the pharmaceutical science for the characterization and quality control of drugs, stability, drug-excipient interactions and purity studies of raw material and pharmaceutical products [13-17]. The coordination chemistry of transition metals with Schiff base has been studied extensively due to their structural diversities, versatile properties and application [18-20]. These complexes can also exhibit biological activity as antifungal, antibacterial, antimalarial, antitumor, antiproliferative, anti-inflammatory, antiviral, antioxidant agent [21, 22]. Thermal products of Schiff base have also been studied [23-26].

However, the Hg (II) complex of Schiff base ligand (L) derived from 5-amino-1, 2, 3, 4-thiatriazole with o-methoxy-benzaldehyde was not studied. In present communication, the solid state kinetics and decomposition product of complexes with ligand (L) are in incorporated.

MATERIALS AND METHODS

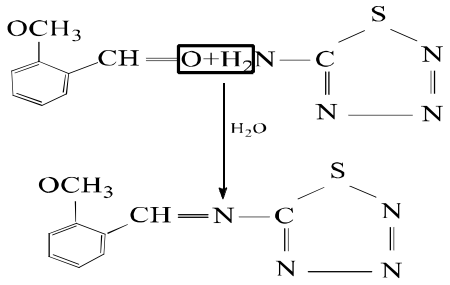
An ice cold solution of 20 g of thiosemicarbazide in 95cc of 2.2(N) HCl was added from a burette with stirring in a total of 14.7 g of $NaNO_2$ in 150 mL water. After each 50 mL was added, the product was collected and washed with 10 mL of ice water. The filtrate returned to the reaction vessel. The 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.

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



5-amino-1,2,3,4-thiatriazole

Preparation of Schiff base: 1:1 molar solution of o-methoxybenzaldehyde and 5-amino1, 2, 3, 4 thiatrizole in ethanol are mixed and condensed in acidic medium. Light yellow solid Schiff base is filtered and recrystallized with ethanol.



Schiff Base

The Preparation of complex of Hg(II): 0.002 M of ligand in ethanolic solution was mixed with 0.001M Hg(II) Chloride in ethanolic solution. The resulting solution was refluxed for half 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 **[**$HgLCl_2$**]** and the molecular weight 491.59 mg to the complexes.

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

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

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 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 thermo-gram of the complex shows three stages of the decomposition. First 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 [27] and Doyle's method as modified [28] by Zsako [29]. The following table contains the data obtained by Freeman-Carroll method.

Table 1. Data obtained by Freeman and Carroll method

S.No.	Temp (°C)	Weight (mg)	$\frac{\Delta log dw/dt}{\Delta log Wr}$	$\frac{\Delta T^{-1} X 10^{-3}}{\Delta log Wr}$
1	150	4.270017	7.69194	46.17327
2	160	4.257191	-72.19997	33.47822
3	170	4.240236	-56.01676	24.07703
4	180	4.215019	-53.23804	15.37812
5	190	4.178065	-34.65290	9.94836
6	200	4.127197	-20.77476	6.83091
7	210	4.053940	-16.15565	5.12467
8	220	3.955684	-9.43937	3.10697
9	230	3.825907	-6.52787	2.17715
10	240	3.654611	-4.68924	1.50659
11	250	3.442012	-2.74471	1.08983
12	260	3.146374	-2.72761	0.68291
13	270	2.762044	-1.43546	0.43504
14	280	2.28511	-0.75436	0.26781
15	290	1.727962	-0.31760	0.15102
16	300	1.104948	-0.09125	0.05826

Initial weight at (150°C): 4.289798 mg, Final weight at (310°C): 0.845612 mg

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 kcal mol^{-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 2. Data of log f(α) values for the complex $[HgLCl_2]$ calculated at different temperatures

S.No.	Temp (°C)	Weight (mg)	$\alpha = \frac{W_0 - W_t}{W_0 - W_f}$	$log\alpha$	$log\left(ln\frac{1}{1-\alpha}\right)$	$log\left(\frac{1}{1-\alpha}\right)$
1	140	4.279799	0.002903153	-2.537130029	-2.536498853	-2.535867372
2	150	4.270017	0.005743302	-2.240838354	-2.239588217	-2.238336880
3	160	4.257191	0.009467259	-2.023775754	-2.021711809	-2.019644589
4	170	4.240236	0.014390047	-1.841937774	-1.838794116	-1.835642854
5	180	4.215019	0.021711661	-1.663306944	-1.658549101	-1.653773821
6	190	4.178065	0.032441047	-1.488905137	-1.481763536	-1.474582573
7	200	4.127197	0.047210284	-1.325963385	-1.315504236	-1.304960446
8	210	4.053940	0.068480041	-1.164435986	-1.149123124	-1.133628150
9	220	3.955684	0.097008117	-1.013191923	-0.991222251	-0.968875770
10	230	3.825907	0.134688138	-0.870670650	-0.839635618	-0.807843307
11	240	3.654611	0.184422967	-0.734184996	-0.690669258	-0.645649984
12	250	3.442012	0.246149889	-0.608800357	-0.548886672	-0.486085360
13	260	3.146374	0.331986716	-0.478879293	-0.394213273	-0.303664392
14	270	2.762044	0.443574766	-0.353033168	-0.231937540	-0.098439984
15	280	2.28511	0.582049866	-0.235039806	-0.059287753	0.143835725
16	290	1.727962	0.743814649	-0.128535273	0.134130573	0.462910434
17	300	1.104948	0.924703254	-0.033997614	0.412681982	1.089226175

Table 3. Calculation of B_0 for different activation energies and δ_0 values at different temperatures for $[HgLCl_2]$ complex

S.No.	Temp(^{0}C)	12 kcal	14 kcal	16 kcal
1	140	6.193869971	7.379869971	8.512869971
2	150	6.324161646	7.484161646	8.624161646
3	160	6.378224246	7.513224246	8.635224246
4	170	6.402062226	7.515062226	8.611062226
5	180	6.432693056	7.522693056	8.597693056
6	190	6.464094863	7.536094863	8.586094863
7	200	6.492036615	7.538036615	8.574036615
8	210	6.518564014	7.552564014	8.565564014
9	220	6.544808077	7.555808077	8.552808077
10	230	6.567329350	7.561329350	8.540329350
11	240	6.582815004	7.559815004	8.518815004
12	250	6.597199643	7.556199643	8.504199643
13	260	6.616120707	7.563120707	8.493120707
14	270	6.635966832	7.564966832	8.480966832
15	280	6.651960194	7.567960194	8.466960194
16	290	6.661464727	7.559464727	8.445464727
17	300	6.659002386	7.549002386	8.418002386
	Average($\overline{B_0}$)	6.513080797	7.534080797	8.536904327
	Standard deviation(δ_0)	0.128712424	0.044549208	0.062200528

Table 4. Calculation of B_1 for different activation energies and δ_1 values at different temperatures for $[HgLCl_2]$ complex

S.No.	Temp(°C)	14 kcal	16 kcal	18 kcal
1	140	7.380501147	8.513501147	9.706501147
2	150	7.485411783	8.625411783	9.757411783
3	160	7.515288191	8.637288191	9.743288191
4	170	7.518205884	8.614205884	9.703205884
5	180	7.527450899	8.602450899	9.669450899
6	190	7.543236464	8.593236464	9.636236464
7	200	7.548495764	8.584495764	9.607495764
8	210	7.567876876	8.580876876	9.581876876
9	220	7.577777749	8.574777749	9.557777749
10	230	7.592364382	8.571364382	9.537364382
11	240	7.603330742	8.562330742	9.517330742
12	250	7.616113328	8.564113328	9.495113328
13	260	7.647786727	8.577786727	9.490786727
14	270	7.686062460	8.602062460	9.503062460
15	280	7.743712247	8.642712247	9.530712247
16	290	7.822130573	8.708130573	9.584130573
17	300	7.995681982	8.864681982	9.725681982
	Average($\overline{B_1}$)	7.610083953	8.612907482	9.608672188
	Standard deviation(δ_1)	0.137774448	0.075060517	0.090183123

Table 5. Calculation of B_2 for different activation energies and δ_2 values at different temperatures for $[HgLCl_2]$ complex

S.No.	Temp(°C)	18 kcal	20 kcal	22kcal
1	140	9.707132628	10.855132628	11.994132628
2	150	9.758663120	10.879663120	11.993663120
3	160	9.745355411	10.840355411	11.932355411
4	170	9.706357146	10.779357146	11.845357146
5	180	9.674226179	10.726226179	11.769226179
6	190	9.643417427	10.678417427	11.700417427
7	200	9.618039554	10.630039554	11.635039554
8	210	9.597371850	10.593371850	11.575371850
9	220	9.580124230	10.554124230	11.524124230
10	230	9.569156693	10.525156693	11.473156693
11	240	9.562350016	10.501350016	11.431350016
12	250	9.557914640	10.478914640	11.396914640
13	260	9.581335608	10.490335608	11.389335608
14	270	9.636560016	10.532560016	11.474560016
15	280	9.733835725	10.608835725	11.480835725
16	290	9.912910434	10.776910434	11.628910434
17	300	10.402226175	11.249226175	12.093226175
	Average($\overline{B_2}$)	9.705116285	10.688233933	11.666939815
	Standard deviation(δ_2)	0.196227631	0.191812966	0.224303688

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

Table 6. Comparison of δ_o values

b = 0		b = 1		b = 2	
Ea		***Ea***		***Ea***	
k cal mol $^{-1}$	**δ0**	**k cal mol $^{-1}$**	**δ1**	**k cal mol^{-1}**	**δ2**
12	0.128712424	14	0.137774448	18	0.196227631
14	0.044549208	16	0.075060517	20	0.191812966
16	0.062200528	18	0.090183123	22	0.224303688

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

Table 7. Comparison of Parameters

S No.	Methods	Order of reaction	activation energy
1	Freeman and Carroll	0M sec^{-1}	14.422 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:-

$$logz = \bar{B}_0 + logRq - logEa$$

Where $\bar{B}$ =7.534080797, Ea = 14 $Kcal\ mol^{-1}$

Thus, the frequency factor for the thermolysis step under consideration was found to be $Z = 4.8 \times 10^{1} sec^{-1}$

The apparent entropy of activation was calculated about to be -94.580005081e.u. from the equation.

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

Where T stands for the absolute temperature547 K at which the step under consideration was half complete.

APPLICATION

Determination of kinetic parameters in non isothermal condition of complex compounds will help to determine the solid state reaction mechanism.

REFERENCES

[1]. R. D Jones, D. A. Summerville, F. Basolo, C*hem. Rev.*, 1979, 79, 139.
[2]. G. H. Olie and S. Olive, The chemistry of the catalyzes Hydrogenation of carbon monoxide, P.152, Springer, Berlin, **1984**.
[3]. H. Dugas, C. Penney, Bioorganic chemistry, P, 435, Springer, New York, **1981**.
[4]. J. D. Margerum, L. J. Mller, Photochromism, P. 569, Wiley Interscience, NewYork, **1971**.
[5]. W .J. Sawodny, M. Riederer, *Angew. Chem. Int. Edn. Engl*., **1977**, 16, 859.
[6]. Y. Schibuya, K. Nabari, M. Kondo. S. Yasue, K. Maeeda, F. Uchida, H. Kawaguchi, *Chem. Lett.*, **2008**, 37, 78.
[7]. B. J. Gangani, P. H. Parsania, *Spectrosc. Lett*., **2007**, 40, 97.
[8]. B. Sindhu Kumari, G. Rijuulal, K. Mohanan, Synth. React. Inorg., *Met. Org. Nano- Met. Chem.*, **2009**, 39, 24.
[9]. M. Thankamony, K. Mohanan, *Indian J. Chem*., **2007**, 46A, 47.
[10]. N. Raman, J. Dhaveethu Raju, A. Sakthivel, *J. Chem. Sci*., **2007**, 119, 303.
[11]. W. Danghul, Y. Yixing, Y. Yixin, Z. Tiancheng, W. Xing, W. Shaokang, H. Yao, C. Wei-Zong, Chin. Sci. Bull., **2006,** 51, 785.
[12]. K. Shivakumar, Shashidhar, M. B. Halli, Russ, *J. Phys. Chem.*, **2008**, 82, 2269.
[13]. T. T. Al-Nahary, M. A. El-Ries, M. Sultan, Y. N. Mabkhot, A. M. Al-Hussam. Thermal stability of anti-rheumatic pharmaceutical drugs parecoxib sodium and valdecoxib, *J Saudi Chem Soc*., **2012**, 16(2), 177-82.
[14]. I. M. Kenawi, B.N. Barsoum, M. A. Youssef. Drug-drug interaction between diclofenac, cetirizine and ranitidine, *J. Pharm Biomed Anal*., **2005**, 37(4), 655-61.
[15]. Radha S, Gutch PK, Ganesan K, Vijayraghavan R, Suman J, Subodh D, Thermal analysis of interactions between and oxime and excipients in some binary mixtures by differential scanning calorimetry and thermalgravimetric analysis, *J. Pharm Res*., **2010**, 3(3), 590-5.
[16]. M. Abou-Sekkima, M. A. El- Ries, A. Molokhia, N. Rabie, A. Y. Wassel, Induced thermal stability and thermal studies on timolol β-Blocker, *J. Therm Anal Calorim*., **2002**, 68(3), 1017-23.
[17]. Y. Haung, Y. Cheng, K. Alexander, D. Dalimore, Thermal analysis study of the drug captopril, *Thermochim Acta*., **2001**, 367-8, 43-58.
[18]. A. Bartyzel Synthesis, thermal study and some properties of N_2O_4-donor Schiff base and its Mn(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes, *J. Therm anal Calorim.*, **2017**, 127, 2133-2147.
[19]. B. Cristo′vãao, B. Miroslaw. Propeller- like hetrotrinuclear Cu^{11}-Ln^{III}-Cu^{II} compounds-physico chemical properties, *Inorg chim Acta.*, **2013**, 401, 50-57.

[20]. B. Shafaatian, S. S. Mousavi, S. Afshari, Synthesis, characterization, spectroscopic and the oretical studies of new Zinc(II) , Copper(II) and Nickel(II) complexes based on imine ligand containing 2-amino thiophenol moiety, *J Mol struc*., **2016**, 1123, 191-8.
[21]. S. Kumar, D. N. Dhar, P. N. Saxena, Applications of metal complexes of Schiff bases-a review, *J. Sci. Ind Res.*, **2009**, 68, 181-187.
[22]. A. Bartyzel, E. M. Cukrowska, Solid phase extraction method for the separation and determination of chromium(III) in the presence of chromium(VI) using silica gel modified by N,N'-bis-(alpha-methyl salicylidene-2-2-dimethyl-1,3-propane diimine, *Anal chim Acta*, **2011**, 707, 204-9.
[23]. U.N. Verma, Bharti, K. Mukhopadhyay *Asian J. of Chem.*, **2011**, 23(2) 773.
[24]. U.N. Verma, Bharti. K. Mukhopadhyay, *J. Therm Anal Clorim*., **2011**, 104, 107.
[25]. J. M. Ahmed Journal of king sand University Science, **2012**, 24(1) 25.
[26]. Zheng-jun L, Taylor and francis on line- 46, 529-533 published online 31 July, 2015.
[27]. E.S. Freeman, Carrol, *J. Phyc. Chem*., **1958**, 62, 394.
[28]. C. D. Dogle, *J. Appl.Polyno. Sci*., **1961**, 5, 285.
[29]. J. Zsako, *J. Phys. Chem.*, **1968**, 72, 2406.