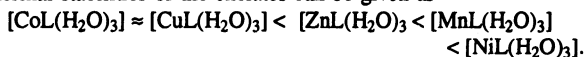


## Kinetics and Mechanism of the Thermal Decomposition of *o*-Vanillin-L-Histidine Complexes of Transition Metal Ions

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*o*-Vanillin-L-histidine forms 1 : 1 complexes with the transition metals like manganese, cobalt, nickel, copper and zinc. All the complexes are found to be non-electrolytes in distilled water and octahedral structures are assigned to them based on electronic, ESR and room-temperature magnetic measurements. IR studies reveal that the *o*-vanillin-L-histidine can act as a tridentate ligand towards the transition metals. The thermal decomposition of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelates of *o*-vanillin-L-histidine was studied by thermogravimetry. Thermal studies indicate that the decomposition takes place in two stages. The kinetic parameters, namely activation energy E, pre-exponential factor A and entropy of activation  $\Delta S$  were also calculated from the thermogravimetric curves using mechanistic and non-mechanistic (Coats-Redfern) equations. The mechanism of the decomposition has been established from thermogravimetric data. On the basis of our findings the relative thermal stabilities of the chelates can be given as



**Key Words:** Kinetics, Thermal decomposition, *o*-Vanillin-L-Histidine, Mn(II), Co(II), Ni(II), Cu(II), Zn(II) complexes.

### INTRODUCTION

Recently much interest has been shown in the synthesis of metal chelates with O/S containing ligands, as these possess antitumour or antibacterial activity. The marked biological activity of transition metal complexes of histidine Schiff bases as antifungal/antibacterial agents and their role in the biosystems prompted us to study the thermal decomposition and dehydration reactions of transition metal complexes of *o*-vanillin-L-histidine.

Comparatively less have been reported showing the relationship between the thermal stability of metal chelates and the structure of the chelating reagents<sup>1</sup>. Wendlandt and coworkers<sup>2-5</sup> and Hill and co-workers<sup>6,7</sup> studied the thermal properties of metal chelates with different types of complexing ligands. Such studies on thermal decomposition and kinetics of metal chelates with azomethine ligands have been carried out by a few workers<sup>8-11</sup>. In continuation of our work<sup>12-14</sup> on thermal decomposition kinetics of metal chelates, we report in this paper the preparation, characterization and thermoanalytical data for five transition metal complexes of a novel Schiff base, *o*-vanillin-L-histidine.

Non-isothermal methods have been widely used to study the kinetics and mechanism of thermal decomposition of solids<sup>15-17</sup>. This study therefore attempts to determine the mechanism of decomposition of  $[\text{MnL}(\text{H}_2\text{O})_3]$ ,  $[\text{CoL}(\text{H}_2\text{O})_3]$ ,  $[\text{NiL}(\text{H}_2\text{O})_3]$ ,  $[\text{CuL}(\text{H}_2\text{O})_3]$  and  $[\text{ZnL}(\text{H}_2\text{O})_3]$  from TG experiments.

### EXPERIMENTAL

The ligand was prepared from *o*-vanillin and L-histidine following the procedure reported by Schiff. Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelates of *o*-vanillin-L-histidine were prepared by adding an ethanolic solution of the ligand to the metallic salt solution in a 2 : 1 ratio. Cu(II) and Zn(II) complexes were separated immediately after mixing while Mn(II) and Ni(II) complexes were separated after refluxing for 2 h. Co(II) complex was formed by adding the refluxed solution dropwise to distilled water taken in a beaker with constant stirring. The separated complexes were filtered, washed and dried in a vacuum desiccator.

The IR spectra were recorded using Shimadzu FTIR-8101 spectrophotometer. Thermal analysis was carried out using a Perkin-Elmer 7 series thermal analysis system. A constant heating rate of  $10^\circ\text{C min}^{-1}$  and a sample mass of *ca.* 5 mg were employed for the entire study. The atmosphere was static air. The fractional decomposition  $\alpha$  was determined directly from the TG curves. Computational work was performed with a Horizon III mini-computer using the programming language Fortran.

The complexes were characterized on the basis of elemental analysis, spectral and thermal studies. The infrared spectra of chelate indicate that  $-\text{COOH}$ ,  $-\text{OH}$  and  $\text{C}=\text{N}$  are involved in coordination. Characteristic bands of  $\text{H}_2\text{O}$  are present in the spectra of all the above complexes. On steric principles, one can assign octahedral structures for the complexes (Fig. 1).

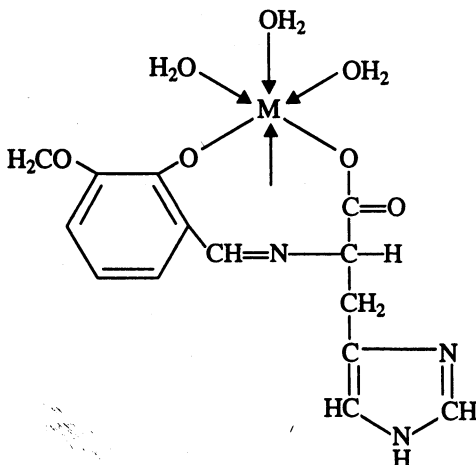


Fig. 1

### Mathematical analysis of data

The TG curves of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelates show a two-stage decomposition. Mass loss considerations from TG curves indicate that the first step of decomposition consists of the water molecules. The loss of ligand moiety takes place in the second step and X-ray diffraction data confirmed the products to be the corresponding oxides.

Evaluation of the mechanism of the reactions from non-isothermal methods has been discussed by Sestak and Berggren<sup>18</sup> and Satava<sup>19</sup>. The procedure is based on the assumption that the non-isothermal reaction proceeds isothermally in an infinitesimal time interval, so that the rate can be expressed by an Arrhenius-type equation:

$$\frac{d\alpha}{dt} = A e^{-E/Rt} f(\alpha) \quad (1)$$

where A is the pre-exponential factor, t is the time and f( $\alpha$ ) depends on the mechanism of the process. For a linear rate,  $\phi, dT/dt = \phi$  and substitution into eqn. (1) gives

$$\frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\phi} e^{-E/Rt} dT \quad (2)$$

Integration of the left hand side of eqn. (2) gives

$$\int_0^\infty \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_0^T \frac{A}{\phi} e^{-E/Rt} dT \quad (3)$$

where g( $\alpha$ ) is the integrated form of f( $\alpha$ ). A series of f( $\alpha$ ) is proposed and the mechanism is obtained from that which gives the best representation of the experimental data. Nine probable reaction mechanisms given by Satava<sup>19</sup> are shown in Table-1. For evaluating the kinetic parameters from the mechanistic equations, the right hand side of eqn. (3), the temperature integral which is an incomplete gamma function, was used in the form given by Coats and Redfern<sup>20</sup>, which produces one of the best solutions and is recommended by several authors<sup>21, 22</sup>.

TABLE 1  
KINETIC EQUATIONS

Function	Equation	Rate-Controlling Process
D <sub>1</sub>	$\alpha^2 = kt$	One-dimensional diffusion
D <sub>2</sub>	$(1 - \alpha) \ln(1 - \alpha) + \alpha = kt$	Two-dimensional diffusion, cylindrical symmetry
D <sub>3</sub>	$1 - (1 - \alpha)^{1/3} = kt$	Three-dimensional diffusion, spherical symmetry, Jander equation
D <sub>4</sub>	$(1 - 3/5\alpha) - (1 - \alpha)^{2/3} = kt$	Three-dimensional diffusion, spherical symmetry, Ginstling-Brownshtein equation
F <sub>1</sub>	$-\ln(1 - \alpha) = kt$	Random nucleation, one nucleus on each particle, Mampel equation
A <sub>2</sub>	$-\ln(1 - \alpha)^{1/2} = kt$	Random nucleation, Avrami equation I
A <sub>3</sub>	$-\ln(1 - \alpha)^{1/3} = kt$	Random nucleation, Avrami equation II
R <sub>2</sub>	$1 - (1 - \alpha)^{1/2} = kt$	Phase boundary reaction, cylindrical symmetry
R <sub>3</sub>	$1 - (1 - \alpha)^{1/3} = kt$	Phase boundary reaction, spherical symmetry.

The general form of the equation used is

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\phi E} - \frac{E}{RT} \quad (4)$$

Along with the mechanistic equations, the non-mechanistic method suggested by Coats and Redfern<sup>20</sup> was also used for comparison. The reaction order can easily be estimated by comparing the  $\gamma$  values using  $n = 0.33, 0.5, 0.66$  and  $1$  in the equations

$$1 - (1 - \alpha)^{1-n}/(1-n)T^2 \text{ vs. } 1/T \text{ for } n \neq 1 \quad (5)$$

$$\log [-\log (1 - \alpha)]/T^2 \text{ vs. } 1/T \text{ for } n = 1 \quad (6)$$

## RESULTS AND DISCUSSION

The temperature ranges of thermal decomposition for the metal chelates are given in Table-2.

TABLE-2  
THERMAL DECOMPOSITION DATA OF Mn(II), Co(II), Ni(II), Cu(II) AND Zn(II)  
COMPLEXES OF *o*-VANILLIN-L-HISTIDINE

Complex	Stage	Temp. range in TG (°C)	Peak temp. in TG (°C)	Loss of mass (%)			Probable assignments
				From TG	Theoretical	From pyrolysis	
[MnL(H <sub>2</sub> O) <sub>3</sub> ]	I	60-240	180	11.00	13.60	—	Loss of 3H <sub>2</sub> O
	II	240-470	390	71.00	67.00	—	Loss of ligand part
				82.00	80.60	81.20	
[CoL(H <sub>2</sub> O) <sub>3</sub> ]	I	40-110	105	5.00	5.00	—	Loss of 1H <sub>2</sub> O
	II	120-380	370	80.00	75.00	—	Loss of 2H <sub>2</sub> O + ligand part
				85.00	80.00	81.50	
[NiL(H <sub>2</sub> O) <sub>3</sub> ]	I	140-160	160	5.00	4.50	—	Loss of 1H <sub>2</sub> O
	II	160-390	390	80.00	80.80	—	Loss of 2H <sub>2</sub> O + ligand part
				85.00	85.30	83.30	
[CuL(H <sub>2</sub> O) <sub>3</sub> ]	I	40-140	120	5.00	5.00	—	Loss of 1H <sub>2</sub> O
	II	250-350	320	75.00	75.00	—	Loss of 2H <sub>2</sub> O + ligand part
				80.00	80.00	80.80	
ZnL(H <sub>2</sub> O) <sub>3</sub> ]	I	50-190	180	9.00	8.80	—	Loss of 2H <sub>2</sub> O
	II	200-510	330	74.00	71.00	—	Loss of 1H <sub>2</sub> O + ligand part
				83.00	79.80	79.30	

TABLE-3  
 KINETIC PARAMETERS FOR THE DECOMPOSITION OF Mn(II), Co(II), Ni(II) AND Zn(II) COMPLEXES OF *o*-VANILLIN-L-HISTIDINE (LH<sub>2</sub>)  
 FROM TG USING MECHANISTIC EQUATIONS

Complex	Parameter	Mechanistic equations									
		1	2	3	4	5	6	7	8	9	
<b>[MnL(H<sub>2</sub>O)<sub>3</sub>]</b>											
I Stage	Weight loss is too small to carry out the kinetic study										
II Stage	E	55.2837	60.3165	66.4674	61.9758	30.9831	30.9806	31.0224	26.6761	28.0751	
	A	$2.8905 \times 10^1$	$5.0699 \times 10^1$	$5.0210 \times 10^1$	$1.7120 \times 10^2$	$4.1960 \times 10^{-1}$	$2.0970 \times 10^{-1}$	$1.3980 \times 10^{-1}$	$6.6960 \times 10^{-1}$	$6.4801 \times 10^{-1}$	
	ΔS	-11.9422	-7.2686	-7.3489	-16.2986	-47.1452	-52.9156	-56.2883	-62.409	-62.6803	
	γ	0.9926	0.9944	0.9953	0.9950	0.9958	0.9958	0.9958	0.9929	0.9940	
<b>[CoL(H<sub>2</sub>O)<sub>3</sub>]</b>											
I Stage	Weight loss is too small to carry out the kinetic study										
II Stage	E	65.3221	73.9185	84.9298	77.4791	43.6164	43.5997	43.1158	34.9355	37.6480	
	A	$4.7763 \times 10^2$	$1.9592 \times 10^3$	$6.1452 \times 10^3$	$1.0295 \times 10^{29}$	$1.2271 \times 10^1$	6.1120	3.6587	1.4661	$1.2272 \times 10^1$	
	ΔS	-391.6003	-126.0823	-370.3773	-385.2376	-422.0744	-427.8511	-432.1208	-439.7393	-443.7235	
	γ	0.9930	0.9914	0.9842	0.9895	0.9676	0.9675	0.9969	0.9848	0.9803	

Complex	Mechanistic equations								
	1	2	3	4	5	6	7	8	9
<b>[NiL(H<sub>2</sub>O)<sub>3</sub>]</b>									
I Stage	Weight loss is too small to carry out the kinetic study								
E	367.6346	397.8550	432.0768	408.7909	228.3625	228.3974	228.3806	202.2420	210.6851
A	$1.6900 \times 10^{27}$	$3.0660 \times 10^{29}$	$5.2900 \times 10^{31}$	$5.7300 \times 10^{29}$	$1.8311 \times 10^{16}$	$9.2158 \times 10^5$	$6.1200 \times 10^{15}$	$5.3700 \times 10^{13}$	$1.8870 \times 10^{14}$
ΔS	78.2782	121.5614	164.3842	126.7521	-131.7334	-137.4264	-140.8170	180.2492	169.7842
γ	0.9566	0.9602	0.9641	0.9616	0.9660	0.9660	0.9660	0.9604	0.9623
<b>[ZnL(H<sub>2</sub>O)<sub>3</sub>]</b>									
I Stage	Weight loss is too small to carry out the kinetic study								
E	39.8984	46.9983	56.7153	50.1918	28.4518	28.3505	28.3497	20.6458	23.0389
A	$7.3880 \times 10^{-1}$	$1.5001 \times 10^{-2}$	$5.1300 \times 10^{-2}$	$2.0570 \times 10^{-2}$	$2.0570 \times 10^{-1}$	$1.0070 \times 10^{-1}$	$6.7101 \times 10^{-1}$	$1.3600 \times 10^{-2}$	$1.7100 \times 10^{-1}$
ΔS	-445.3067	-477.7289	-467.5013	-455.9517	-455.9517	-461.8941	-465.2672	-478.5389	-476.6464
γ	0.9896	0.9962	0.9974	0.9975	0.9895	0.9890	0.9890	0.9962	0.9963

E in kJ mol<sup>-1</sup>, ΔS in J mol<sup>-1</sup> K<sup>-1</sup>.

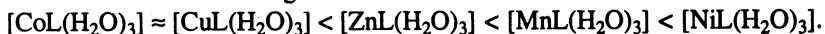
Data from independent pyrolytic experiments are also included in this table. The values of  $E$ ,  $A$ ,  $\Delta S$  and  $\gamma$  from non-mechanistic equation, Coats-Redfern<sup>20</sup> and the comparable values obtained from nine mechanistic equations are given in Tables 3 and 4. For Cu(II) complex, the first stage of decomposition involves a very small loss and the second stage is very steep. So these could not be subjected to kinetic analysis.

TABLE-4  
KINETIC PARAMETERS FOR THE DECOMPOSITION OF Mn(II), Co(II), Ni(II) AND Zn(II) COMPLEXES OF *o*-VANILLIN-L-HISTIDINE (LH<sub>2</sub>) FROM TG USING COATS-REDFERN EQUATION AND ACCEPTED MECHANISTIC EQUATION

Complex	Parameter	From Coats-Redfern equation	From mechanistic equation	Reaction mechanism	Order of reaction
<b>[MnL(H<sub>2</sub>O)<sub>3</sub>]</b>					
I Stage	Weight loss is too small to carry out the kinetic study				
II Stage	E	28.0759	30.9806	Equation VI	2/3
	A	$1.9468 \times 10^{-1}$	$2.0970 \times 10^{-1}$	A <sub>2</sub> mechanism	
	$\Delta S$	-53.5335	-52.9156	Random nucleation	
	$\gamma$	0.9941	0.9958	Avrami equation	
<b>[CoL(H<sub>2</sub>O)<sub>3</sub>]</b>					
I Stage	Weight loss is too small to carry out the kinetic study				
II Stage	E	37.6489	37.6480	Equation IX	2/3
	A	$1.0042 \times 10^1$	$1.2272 \times 10^1$	R <sub>3</sub> mechanism	
	$\Delta S$	-442.8930	-443.7235	Phase boundary reaction	
	$\gamma$	0.9803	0.9803	Spherical symmetry	
<b>[NiL(H<sub>2</sub>O)<sub>3</sub>]</b>					
I Stage	Weight loss is too small to carry out the kinetic study				
II Stage	E	228.3625	228.3625	Equation V	1
	A	$1.8311 \times 10^{16}$	$1.8311 \times 10^{16}$	F <sub>1</sub> mechanism	
	$\Delta S$	-131.7334	-131.7334	Random nucleation	
	$\gamma$	0.9660	0.9660	Mampel equation	
<b>[ZnL(H<sub>2</sub>O)<sub>3</sub>]</b>					
I Stage	Weight loss is too small to carry out the kinetic study				
II Stage	E	18.4544	20.6458	Equation VIII	1/3
	A	$1.5001 \times 10^{-2}$	$1.3600 \times 10^{-2}$	R <sub>2</sub> mechanism	
	$\Delta S$	-477.7202	-478.5389	Phase boundary reaction	
	$\gamma$	0.9933	0.9962	Cylindrical symmetry	

$E$  in  $\text{kJ mol}^{-1}$ ,  $A$  in  $\text{sec}^{-1}$ ,  $\Delta S$  in  $\text{J mol}^{-1} \text{K}^{-1}$ .

The activation energies obtained in the present complexes are comparable to those of the coordination compounds of 3d transition metals having similar structure. In all the complexes H<sub>2</sub>O molecules are lost around 130–150°C. According to Nikolaev *et al.*<sup>23</sup> water eliminated at this temperature has been used to determine the thermal stability of metal chelates. In the present course of studies, based on observations made by earlier workers<sup>24,25</sup>, the relative thermal stabilities of the metal chelates can be given as



### Decomposition kinetics

From Tables 3 and 4 it can be seen that one equation gives a good linear curve with a high value of correlation coefficient, so that it may become difficult to assign the reaction mechanisms unequivocally from the linearity of the curve alone. In such cases, some authors have chosen the function  $g(\alpha)$  which gives kinetic parameters in agreement with those obtained by the numerical method.

In the present case, it is observed that the kinetic parameter calculated for the second stage of decomposition of Zn(II) complex, from the Coats-Redfern equation with  $n = 1/3$  are in good agreement with those obtained for the R<sub>2</sub> mechanism based on phase boundary reaction with cylindrical symmetry.

The second stage decomposition of Co(II) complex gives good correlation with R<sub>3</sub> mechanism based on phase boundary reaction, spherical symmetry. A<sub>2</sub> mechanism based on Avrami equation I with random nucleation gives the maximum correlation for the second stage of decomposition of Mn(II) complex. In both cases order of the reaction is found to be 2/3.

For the second stage of decomposition of Ni(II) complex, good agreement is resulted between the kinetic parameters obtained from Coats-Redfern method with  $n = 1$  and F<sub>1</sub> mechanism (Mampel equation) which is based on random nucleation. We can thus infer that the rate controlling process for the reaction is random nucleation with the formation of one nucleus on each particle and is independent of the thermal technique used.

All these mechanisms are proposed since the values of E, A and  $\Delta S$  computed from the mechanistic equation agree well with those from the non-mechanistic equation (Coats-Redfern) having maximum correlation coefficient. These values of E, A and  $\Delta S$  obtained for these complexes are comparable. The negative values for entropy of activation indicate that the activated complexes have more ordered structure than the reactants and the reactions are slower than normal.

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