



## Thermal Decomposition Kinetics of Mn(III) Complexes of Hydrazone Schiff Bases

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**Abstract:** The thermal decomposition study of a series of Mn(III) complexes of hydrazone Schiff bases was monitored by non-isothermal analysis in atmosphere. The thermal degradation takes place in three steps for each of the complexes. The decomposition steps were analyzed and the kinetic parameters: order of the decomposition reaction ( $n$ ), activation energy ( $E_a$ ) and frequency factor ( $Z$ ) of the non-isothermal decomposition steps were computed using Broido and Horowitz-Metzger methods. Comparison of the two sets of activation energies shows that deviation between them is not so great, considering the approximations involved in the Horowitz-Metzger method. Thermodynamic parameters: entropy ( $\Delta S$ ) and Gibbs free energy ( $\Delta F$ ) of activation, were calculated using a standard relations<sup>(7)</sup> and discussed. On the basis of half decomposition temperature, the thermal stability of the compound was found to be  $Mn-L_3 > Mn-L_2 > Mn-L_4 > Mn-L_1$ . The activation energies of the thermal degradation steps lie in the range 28.24 – 47.54 kJmol<sup>-1</sup>.

### Introduction:

Schiff bases are continued to play an important role in the development of coordination chemistry. Schiff bases and their metal complexes have a variety of applications including biological<sup>1</sup> and catalytic activities<sup>2,4</sup> and as compounds of interesting photoluminescent and electroluminescent properties<sup>5</sup>. In spite of the relatively large number of reports on Schiff base metal complexes, less work has been published on calculation of the kinetic and thermodynamic parameters of their decomposition. In this paper we report on the kinetics of the thermal decomposition for four different Schiff base complexes of Mn(III). The half decomposition temperature and the basic parameters were calculated using Broido<sup>6</sup> and Horowitz-Metzger<sup>7</sup> methods. The complexes are thermally stable and their thermal decompositions are multistage processes. The complexes are subjected to a TG analysis from 50-800°C.

### Experimental:

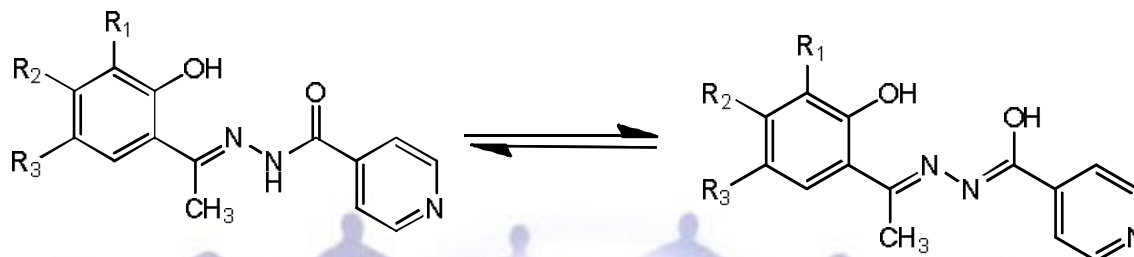
**Material:** All the chemicals used as a starting material for the synthesis of the ligand and their metal complexes were of AR grade or chemically pure, solvents were purified and dried before use. The ligand used in the work were not commercially available, hence were synthesized in our laboratory. Mn(OAc)<sub>3</sub>.2H<sub>2</sub>O was prepared by the oxidation of Mn(OAc)<sub>2</sub>.4H<sub>2</sub>O using Christensens method<sup>8</sup>. The <sup>1</sup>H NMR spectra of the ligand was taken using TMS as the internal standard on a 90 MHz on a Perkin Elmer R-32 spectrometer IR spectra (KBr) were recorded on a Perkin Elmer-842 spectrophotometer in the region 400-4000cm<sup>-1</sup> at RSIC, Punjab University, Chandigarh. Thermogravimetric analysis of the complexes was carried out on a simple manually operated thermo-balance fabricated in our laboratory.



### Synthesis of Ligand:

All the ligands: **HCRAIH** (2-Hydroxy-5-carboxyacetophenoneisonicotinoyl hydrazone), **DHAIH** (2, 5-Dihydroxyacetophenone isonicotinoylhydrazone), **HCMAIH** (2-hydroxy-5-chloro-4-methylacetophenone isonicotinoylhydrazone) and **HCNAIH** (2-hydroxy-5-chloro-3-nitroacetophenone isonicotinoylhydrazone) were prepared by the addition of hot ethanolic solution of isonicotinoylhydrazide (0.05 mol) into hot ethanolic solution of respective acetophenone (0.05 mol).

The reaction mixture was refluxed in a water bath for 4-6 hrs. The coloured product was filtered off and recrystallized from dimethyl formamide.



Ligand	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
<b>HCRAIH = L<sub>1</sub></b>	H	H	COOH
<b>DHAIH = L<sub>2</sub></b>	H	H	OH
<b>HCMAIH = L<sub>3</sub></b>	H	CH <sub>3</sub>	Cl
<b>HCNAIH = L<sub>4</sub></b>	NO <sub>2</sub>	H	Cl

### Synthesis of Mn (III) Complexes:

Equimolar quantities of (0.02 molMn(OAc)<sub>3</sub>.2H<sub>2</sub>O ) salt and the ligand were dissolved separately in absolute ethanol (25 ml) and in DMF-Ethanol respectively. Both the solution were filtered and mixed in hot condition. The reaction mixture was refluxed for 4-6 hrs in a water bath. The coloured products obtained were filtered, washed several times with hot water followed by ethanol and diethyl ether and finally dried over fused calcium chloride.

### Result and Discussion:

#### Characterization of Ligand:

##### a) Infrared Spectra of the ligand:

The IR Spectra of the ligands were recorded for the identification of their donor sites and to compare the shifts in frequencies after their complexation with Mn. All the ligand exhibit following due assignments<sup>9-11</sup>. A broad and strong band in the spectra of complexes in the region 3000-2900 cm<sup>-1</sup> is assigned to intramolecularly hydrogen bonded phenolic OH, a sharp band between 3290 and 3180 cm<sup>-1</sup> is due to N-H Stretching. The other bands in the region 1685-1665, 1617-1603, 1535-1480 and 1000-990cm<sup>-1</sup> are assigned to  $\nu(\text{C=O})$ ,  $\nu(\text{C=N})$   $\nu(\text{C-O})$  and  $\nu(\text{N-N})$  respectively.



**b) <sup>1</sup>H NMR Spectral data of ligand:**

**L1-HCRAIH-** δ 14.90 (1 H,S, Ar-COOH); 12.75 (1H,S,phenolic OH); 11.30 (1H,S,imino); 8.93 and 7.90 (4H,d, isonicotine); 7.78, 7.5 and 7.18(3H,m,phenyl) and 3.15 ppm (3H,s,methyl)<sup>12-14</sup>.

**L2-DHAIH-** δ 12.85 (1H,s,C<sub>2</sub>-OH); 11.35 (1H,s,imino); 10.44 (1H,s,phenolic C<sub>5</sub>-OH);8.84 and 7.88 (4H,d,isonicotine); 7.38,7.26 and 7.17 (3H,m,phenyl) and 3.25ppm (3H,s,methyl)

**L3-HCMAIH-** δ 12.95 (1H,s,phenolic OH); 11.4 (1H,s,imino); 8.75 and 7.98 (4H,d,isonicotine); 7.8 and 6.82(2H,m,phenyl); 3.1(3H,s,methyl); and 2.25ppm (3H,s,Ar-methyl)

**L4-HCNAIH-** δ 12.95 (1H,s,phenolic OH); 11.34 (1H,s,imino); 9.05 and 9.08 (4H,d,isonicotine); 8.15 and 7.35(2H,m,phenyl); and 3.25ppm (3H,m,methyl).

**Characterization of Complexes:**

**a) Elemental Analysis of Complexes**

Sr. No.	Compounds	Formula Weight	Colour	M % Found (Calcd.)	C% Found (Calcd.)	H % Found (Calcd.)	N % Found (Calcd.)	Cl % Found (Calcd.)
1.	Mn-L1	447.3	Mid Buff-T	12.12 (12.28)	45.16 (45.65)	4.03 (4.06)	9.27 (9.39)	----
2.	Mn-L2	419.3	Coffee	13.23 (13.10)	45.29 (45.83)	4.14 (4.33)	9.88 (10.02)	----
3.	Mn-L3	451.7	Brown	12.07 (12.16)	44.98 (45.20)	4.17 (4.24)	9.07 (9.30)	7.64 (7.84)
4.	Mn-L4	482.7	Vulcano	11.33 (11.38)	39.29 (39.81)	3.15 (3.34)	11.73 (11.60)	7.07 (7.34)

**b) Thermogravimetric Analysis of the complexes:**

All the complexes are stable upto 70°C and are decomposed mainly in three stages. Elimination of lattice or coordinate water molecule takes place in the first step, a part of ligand decomposed in second step and the complete decomposition of ligand followed by oxid-red reaction leading to the formation of metal oxide in the last one<sup>15-18</sup>.

**For Mn-L<sub>1</sub> complex:** Lattice Water upto 130 °C, Coordinate Water: 150-220 °C, Free Ligand: 230-450°C, Coordinate Ligand: above 450°C.

**For Mn-L<sub>2</sub> complex:** Lattice Water upto 120°C, Coordinate Water: 150-220°C, Pyrolysis product Mn<sub>3</sub>O<sub>4</sub>: 250-600°C.

**For Mn-L<sub>3</sub> complex:** Lattice Water upto 130°C, Coordinate Water: 220°C, Coordinate ligand: Above 350°C, Pyrolysis product: 600-700°C.

**For Mn-L<sub>3</sub> complex:** Lattice Water upto 125°C, Coordinate Water: 160-220°C, degradation of coordinate ligand: 300-450°C.

The kinetic parameter data for the complexes are given in the Table 3. On the basis of half decomposition temperature, the thermal stability of the compound is found





to be  $Mn-L_3 > Mn-L_2 > Mn-L_4 > Mn-L_1$ . The activation energies of the thermal degradation steps lie in the range 28.24 – 47.54  $\text{kJmol}^{-1}$ .

Sr. No.	Compounds	Half Decomposition Temp. ( $^{\circ}\text{C}$ )	Activation Energy ( $\text{kJmol}^{-1}$ )		Frequency Factor ( $\text{Sec}^{-1}$ )	Entropy Change ( $\text{Jmol}^{-1}\text{K}^{-1}$ )	Free Energy Change ( $\text{kJmol}^{-1}$ )
			B*	HM**			
1	Mn-L <sub>1</sub>	370	30.73	28.24	26.49	224.00	45.71
2	Mn-L <sub>2</sub>	461.0	47.54	43.46	60.04	218.32	62.97
3	Mn-L <sub>3</sub>	475.0	36.25	34.41	39.32	222.07	54.73
4	Mn-L <sub>4</sub>	455.0	36.64	41.39	45.39	220.65	61.11

### Conclusion:

The activation energy calculated by the Broido and Horowitz- Metzger methods are in good agreement with each other. Thermodynamic parameters have been calculated on the basis of thermal activation energy and values are given in Table 3. Due to abnormally low value of frequency factor [Z] it may be classified as a slow reaction and no other obvious reason can be given. The thermal stability of the compounds can be correlated with the substituent group attached to the ligands. It is found that more bulky ligand may have more thermal stability.

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