Thermal Studies and Kinetic Parameters of Copper (II) Complexes of Some Novel N-Hydroxyamidines

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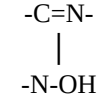
Abstract **- Thermogravimetric analysis of the copper complexes with newly synthesized Hydroxyamidine Hydrochlorides have been carried out in present investigation in order to evaluate their thermal stabilities. It was found that the nature of decomposition of all the complexes under study is nearly same. All the copper complexes start decomposing only after 200˚C indicating that water molecule is absent. The thermal data obtained from thermogravimetric curves have been used to calculate kinetic parameters viz energy of activation, frequency factor, entropy of activation by Sharp – Wentworth, Coats-Redfern and Piloyan-Novikova methods. Calculation of energy of activation (E_a), frequency factor (A), entropy of activation ($\Delta S^{\#}$) reveal that copper complex of N-Hydroxy N- (4-Methyl) Phenyl N'- (3-Methyl) Phenyl – 2-Chloro Benzamidine Hydrochloride is the most stable of all the complexes synthesized.**

Index Terms **- Activation Energy, Kinetic Parameters, N-Hydroxyamidine, Thermogravimetric Analysis.**

INTRODUCTION

Complexes having organic moiety as chelating agent are becoming increasingly important in today's world and they have wide variety of applications including anticorrosive agents, soil treatment agents to agents having medicinal importance[1-3]. N-Hydroxyamidines are monobasic and bidentate chelating reagent having the functional grouping.



They form five-memebered ring on chelation with metal ion. These compounds are stable towards light and heat and can be easily synthesized. These are appreciably soluble in various organic solvents. The solution of these compounds can be stored for a long time without deterioration. Also, their analytical properties of these can be modified by changing the substituents of phenyl ring attached to coordinating nitrogen.

These have been found to be excellent reagents for gravimetric and spectrophotometric determination of some metal ions.[4-8] These reagents react with metal ions in presence of various complexing agents like carboxylic acids, phenols, aldehydes, thiourea, azide, etc. giving coloured mixed complexes, which can be extracted into organic solvents hence useful for extraction spectrophotometric determination of metal ions.

According to the findings, there is a scarcity of information on the solid-state kinetics of copper complexes of Hydroxyamidine reagents.

Thermogravimetric analysis is a non-isothermal approach that is advantageous since it only requires one experimental curve to estimate activation energy, frequency factor, and entropy. and that the kinetic can be measured continuously across a wide temperature range with no gaps. The Coats-Redfern, Sharp-Wentworth, and Piloyan-Novikova methods were used to calculate the kinetic parameters of the copper complexes of five novel Hydroxyamidines in this communication.

EXPERIMENTAL

Preparation of Ligand and Their Copper complex

All the chemicals used were of AR grade. In the present investigation five new hydroxyamidine hydrochlorides have been synthesized by method suggested by Wallach et al[9-11]. 2-chloro benzoyl chloride is used for benzoylation of different aromatic amino compounds. The anilides obtained after recrystallization were converted into imidoyl chloride by the reaction of thionyl chloride. The imidoyl chloride solution in ether was reacted with N-

Hydroxyl amine obtained by reduction of Nitrobenzene and 4-methyl nitrobenzene

Five New Hydroxyamidine hydrochlorides prepared are

1. N – hydroxy – N - (4-methyl) – phenyl - N' – phenyl – 2 - chloro benzamidine hydrochloride (HMPCBH)
2. N – hydroxy – N - (4-methyl) – phenyl – N' - (2-chloro) phenyl – 2 - chloro benzamidine hydrochloride (HMPCCBH)
3. N – hydroxy – N - (4-methyl) – phenyl – N' - (3-methyl) phenyl - 2- chloro benzamidine hydrochloride (HMPMCBH)
4. N – hydroxy – N – phenyl - N' – phenyl – 2 - chloro benzamidine hydrochloride (HMPBH)
5. N – hydroxy – N – phenyl - N' - (3-methyl) – phenyl – 2 - chloro benzamidine hydrochloride (HPMCBH)

Copper complexes containing these reagents were made by dropping 1 percent ligand solution in alcohol into copper sulphate solution and stirring until a buff precipitate was produced. The reagent was added in excess to ensure full precipitation, and the solution was digested for 20-30 minutes over a hot water bath. The buff precipitate was filtered, then washed with 40% alcohol, then water, before being dried.

CHARACTERISATION

On the basis of m.p., elemental analysis (Table 1), UV, and IR, the novel Hydroxyamidine ligand and their copper complexes were characterised (Table 2). The Perkin –Elmer –Lambada 15 Uv/Vis Spectrophotometer with 1 cm quartz cells was used to record ultraviolet absorption spectra, which were calibrated using standard methods. Three unique absorption bands may be seen in the UV absorption spectra of Hydroxyamidine Hydrochlorides in ethanol which are attributed to π- π^* transitions. The band observed around 207 nm has been assigned as local excitation band of phenyl chromophore and the other two bands around 250-270 nm and 310-330 nm have been assigned as electron transfer bands. The IR spectra were recorded in KBr on Perkin –Elmer-1800 (FTIR) in the region 4000-450 cm^{-1}. The infrared spectra of hydroxyamidine hydrochlorides have been examined and the principal bands associated with O-H----N, C=NH^+, NH^+, and N-O stretching vibrations have been located.

Table 1 : Elemental Analysis of New N-Hydroxyamidine Reagents

Compounds	Calculated (%)			Found (%)		
	C	H	N	C	H	N
HMPCBH ($C_{20}H_{18}N_2OCl_2$)	64.34	4.83	7.51	64.32	4.70	7.48
HMPCCBH($C_{20}H_{17}N_2OCl_3$)	58.90	4.17	6.87	58.80	4.10	6.62
HMPMCBH($C_{21}H_{20}N_2OCl_2$)	65.12	5.17	7.24	65.10	4.92	7.19
HMPBH($C_{19}H_{16}N_2OCl_2$)	63.51	4.46	7.80	63.48	4.32	7.70
HPMCBH($C_{20}H_{18}N_2OCl_2$)	64.34	4.83	7.51	64.30	4.78	7.40

Table 2 : UV and IR of New N- Hydroxyamidine Reagents

Compounds	IR (cm^{-1})				UV (nm)		
	υ(Ar-H)	υ(=NH^+)	υ(C=NH^+)	υ(N-O)	λ_{max1}	λ_{max2}	λ_{max3}
HMPCBH	3040	2560	1660	940	207	256	314
HMPCCBH	3060	2565	1654	920	206	252	314
HMPMCBH	3040	2550	1645	940	208	256	314
HMPBH	3040	2550	1640	940	208	256	314
HPMCBH	3046	2563	1613	957	212	262	322

The compounds were thermogravimetrically analyzed by Mettler Toledo Instrument for obtaining TG – curves. Heating rate was kept constant at 10˚min^{-1} in air atmosphere. Coats- Redfern, Piloyan- Novikova and Sharp- Wentworth methods were employed for deducing kinetic and thermogravimetric data.

RESULT AND DISCUSSION

TGA Studies of the copper complexes with newly synthesized Hydroxyamidine Hydrochlorides have been carried out in order to evaluate their thermal stabilities (Fig 1 to 5). These starts decomposing only after 200˚C indicating that water molecule is absent in the complex[12]. The thermograms indicate that the nature of decomposition of complexes is nearly comparable. Thermal analysis also confirms the absence of coordinated water molecules in all complexes as suggested from Infrared Spectra of the complexes. The weight of ultimate pyrolysis product corresponds to metal oxide. The thermoanalytical data of decomposition of the copper complexes with some

new Hydroxyamidine Hydrochlorides are given in Table 3.

The kinetic parameters of the complex are evaluated employing Coats-Redfern, Sharp-Wentworth and Piloyan-Novikova methods.

Coats-Redfern method[13]**:** The equation for first order (n = 1) reaction is given by

$\log[-\log(1-\alpha)/T^2] = \log AR/\beta E[1-2RT/E] - E/2.303RT$

The graph between log $[-\log (1-\alpha)/T^2]$ and 1000/T gave a straight line over a long range of a values.

Piloyan-Novikova method[14]**:** The equation for first order reaction is given by

$\log [\alpha/T^2] = \log AR/\beta E - E/2.303RT$

The graph between log $[\alpha/T^2]$ and 1000/T gave a straight line over a long range of values.

Sharp-Wentworth method[15]**:** The equation for first order reaction is given by

$\log [(dc/dt)/(1-c)] = \log A/\beta - E/2.303RT$

A linear plot was obtained when a graph between log [(dc/dt)/(1-c)] and 1000/T was plotted.

The activation energy and frequency factor was calculated from slope and intercept respectively in each case.

Apparent entropy**:** The entropy has been calculated by Zsako[16] method.

The value of ΔS is given by expression

$\Delta S = 2.303 \log [Ah/kT_{½}]$

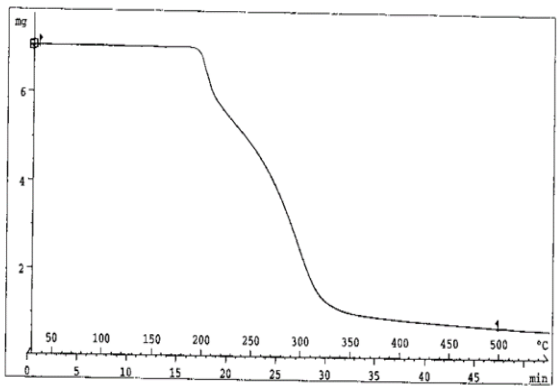


Fig 1. TG Curve for Copper Complex of HMPCBH

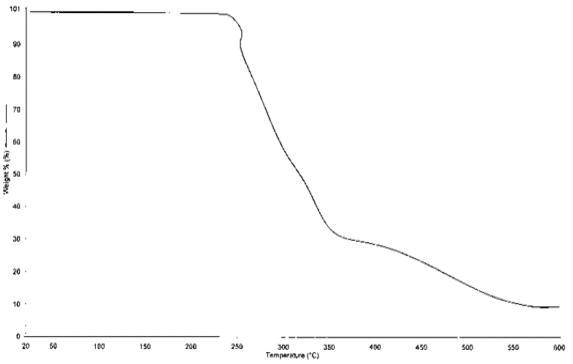


Fig 2. TG Curve for Copper Complex of HMPCCBH

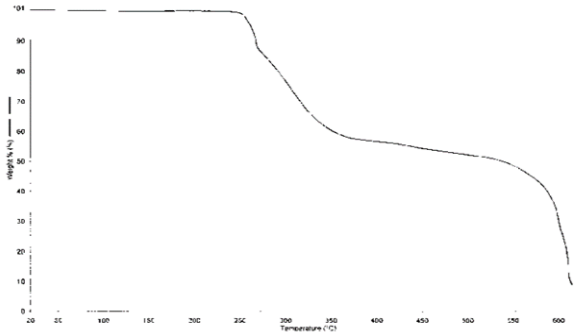


Fig 3. TG Curve for Copper Complex of HMPMCBH

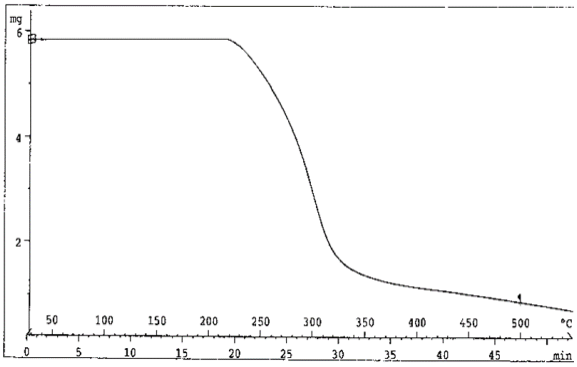


Fig 4. TG Curve for Copper Complex of HMPMCBH

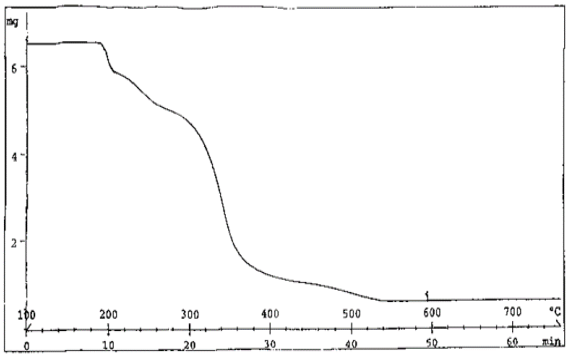


Fig 5. TG Curve for Copper Complex of HPMCBH

Table 3: Thermal Decomposition Data of Copper Complexes of New N- Hydroxyamidine

S. No.	Complex	Temperature (in ˚C)	Loss of Mass (%)		Probable Assignments
			TG	Theoretical	
1.	$(HMPCBH)_2Cu$	210 275 500	14.80 43.24 89.18	16.46 45.57 88.97	Loss of one part of ligand Loss of rest of ligand moiety Loss of another ligand
2.	$(HMPCCBH)_2Cu$	270 400 630	11.00 42.09 89.00	15.13 45.40 88.54	Loss of one part of ligand Loss of rest of ligand moiety Loss of another ligand
3.	$(HMPMCBH)_2Cu$	255 300 570	12.00 42.00 91.00	14.55 45.57 88.97	Loss of one part of ligand Loss of rest of ligand moiety Loss of another ligand
4.	$(HMPBH)_2Cu$	260 300 500	14.80 43.24 89.18	16.46 45.57 88.97	Loss of one part of ligand Loss of rest of ligand moiety Loss of another ligand
5.	$(HPMCBH)_2Cu$	210 330 530	11.36 46.87 89.30	15.88 45.80 89.50	Loss of one part of ligand Loss of rest of ligand moiety Loss of another ligand

All the five complexes under present investigation follow first order decomposition. The kinetic and thermodynamic parameters viz. energy of activation (E_a), pre-exponential factor (A or Z) and entropy of activation ($\Delta S^{\#}$) are obtained following the methods described by Sharp-Wentworth, Coats- Redfern and Piloyan-Novikova. The parameters so obtained are given in table 4.

The activation energy (E_a) values of the synthesized complexes follow the sequence as under,

$(HPMCBH)_2Cu > (HMPBH)_2Cu > (HMPMCBH)_2Cu > (HMPCCBH)_2Cu > (HMPCBH)_2Cu$

Table 4: Kinetic Parameters of Copper Complexes of Some New N-Hydroxyamidines

S. No.	Complex	Methods Used	Activation Energy (E) ($Kjmol^{-1}$)	Frequency Factor (A) (s^{-1})	Entropy of Activation (ΔS^*) ($Jkmol^{-1}$)
1.	$(HMPCBH)_2Cu$	C-R P-N S-W	38.2943 38.2943 38.2943	1.0644×10^{-2} 1.4921×10^{-2} 2.3464×10^{-2}	-34.6332 -34.2954 -33.8426
2.	$(HMPCCBH)_2Cu$	C-R P-N S-W	42.1237 47.8679 44.6703	1.1036×10^{-3} 1.5733×10^{-3} 2.9593×10^{-3}	-37.2704 -36.9157 -36.2856
3.	$(HMPMCBH)_2Cu$	C-R P-N S-W	62.2283 61.2709 57.4414	1.2176×10^{-2} 1.4720×10^{-2} 1.0481×10^{-2}	-34.5680 -34.3783 -36.6094
4.	$(HMPBH)_2Cu$	C-R P-N S-W	71.8018 71.8018 73.3967	1.7175×10^{-2} 2.7340×10^{-2} 1.6998×10^{-2}	-34.1813 -33.7164 -34.1917
5.	$(HPMCBH)_2Cu$	C-R P-N S-W	86.1621 76.5886 90.9489	2.0375×10^{-2} 2.2636×10^{-2} 2.1399×10^{-2}	-34.0614 -33.9561 -34.0123

CONCLUSION

Thermogravimetric analysis data reveal that complexes are stable up to 200˚C. Decomposition starts only after 200˚C indicating the absence of water molecule in the coordination sphere. The decomposition patterns of all the complexes under investigation are nearly same. Cupric Oxide is formed in the range 500-630˚C. Calculation of energy of activation (E_a), frequency factor (A), entropy of activation ($\Delta S^{\#}$) reveal that copper complex of N-Hydroxy N- (4-Methyl) Phenyl N'- (3-Methyl) Phenyl – 2-Chloro Benzamidine Hydrochloride is the most stable of all the complexes synthesized. The negative values for entropy of activation ($\Delta S^{\#}$) indicate that the activated complex has a more ordered structure than the reactants, and the reactions are slower than normal. This is further supported by relatively low A values.

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