SYNTHESIS AND KINETICS OF THERMAL DECOMPOSITION OF METAL COMPLEXES OF 2,5-DIHYDROXY-1,4-BENZOQUINONE

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ABSTRACT
Solid metal complexes of Cu(II), Ag(I), Y(III) and UO_2(II) with 2,5-Dihydroxy-1,4-benzoquinone are reported on the basis of elemental analysis, IR spectroscopy and electronic absorption spectroscopic studies. The mechanism of dehydration and decomposition of the complexes are reported, together with the determination of the kinetic parameters: Z, E and ΔS^* by non-isothermal methods. The first-step involves dehydration and second step the loss of ligand moiety. The dehydration and decomposition of the complexes involve random nucleation mechanism.

KEYWORDS: Thermal decomposition, metal complex, 2,5-Dihydroxy-1,4-Benzoquinone, kinetic parameters.

INTRODUCTION
The complexes are prepared and characterized by physio-chemical methods. The mechanism of decomposition and the evaluation of the kinetic parameters is reported.

Experimental
2,5-Dihydroxy-1,4-benzoquinone was prepared by reported method [1]. Purity was checked by single spot test (M.P 212.5 °C) (Lit. 213 °C). The solid complexes of Cu(II), Ag(I), Y(III) and UO_2(II) were prepared with 2,5-Dihydroxy-1,4-benzoquinone by mixing the aqueous solutions of respective metal ion (taken in large excess) and ligand (taken as sodium salt). The precipitated complexes were separated by filtration and the excess metal ions were removed by washings with water. The complexes were finally dried under vacuum over anhydrous calcium chloride.

Materials used
AnalR metal ion salts used are:- $CuCl_2.2H_2O$, $AgNO_3$, YCl_3, $UO_2(NO_3)_2$ and pure sample of ligand
IR spectra of ligand and complexes were recorded in 4000-200 cm^{-1} region using KBr pellets.
The electronic absorption spectra of the complexes were recorded as diffuse reflectance spectra on VSU2P (Carl Zies) spectrophotometer from 50,000 to 12 500 cm^{-1}. Estimation of C and H of all the complexes was carried out by combustion method using microanalytical technique. The metal (m) content was estimated by ignition of the complexes to their respective oxides.
The simultaneous DTG and DTA curves of the complexes were obtained on Paulik-Paulik-Erdey MOM derivatograph (Hungary). The apparatus was heated at the rate of 10°/min. in static air atmosphere. Alumina was used as the reference material.

RESULTS AND DISCUSSION
The elemental analysis results given in Table-I suggests the composition of complexes as: $[Cu(C_6H_2O_4).(H_2O)]_n$, $[Ag_2(C_6H_2O_4)]$, $[Y(C_6H_2O_4)_{1.5}.(H_2O)_2]_n$, and $[UO_2(C_6H_2O_4).(H_2O)_2]_n$. The complexes are stable at the

room temperature and decompose above 300 °C without melting. The bonding of the metal to the ligand is studied by compairing the IR spectrum of the ligand with those of the complexes [2,3] (Table-1). In the ligand spectrum bands at 3300 cm^{-1}, 1610 cm^{-1} and 1210 cm^{-1} are assigned to the intramolecular hydrogen bonded hydroxyl groups at positions 2 and 5, the ν(C=O) and ν(O-C) respectively. The spectra of the complexes in comparison show significant shifts in the above mentioned bands due to coordination to metal ions. The band due to intra-molecularity hydrogen bonded hydroxyl groups at position 2 and 5 disappears in the spectra of the complexes as a result of the coordination to the metal ion through the oxygen of the hydroxyl and abstraction of protons. In the complexes of Cu(II), Y(III) and UO_2(II) bands at 3500, 3400 and 3250 cm^{-1} respectively are assigned to the stretching modes of coordinated water molecules. The electronic spectral data is recorded in Table-1. The Cu(II) complexes has a magnetic moment of 1.80 B.M which support that complexes is an octahedral spin free complex having sp^3d^2 hybridization spectra. Reflectance spectra supports this conclusion. The band at 13920 cm^{-1} suggests a large tetragonally distortion. The bands at 29411 and 40120 cm^{-1} are charge transfer bands. The complex, $[Y(C_6H_2O_4)_{1.5}(H_2O)_2]_n$ is eight coordinated having distorted square antiprismatic structure [4]. The bands at 41525 and 25512 are assigned to charge transfer and intra-ligand transfers respectively. $[UO_2(C_6H_2O_4)_2(H_2O)_2]$ complex is diamagnetic having square anti prismatic structure. The reflectance spectrum bands at 22312 and 15112 are charge transfer bands [5]. The reflectance spectrum of $[Ag_2(C_6H_2O_4)]$ are assigned as ligand to metal charge transfer bands [6].

Thermal Analysis
Figures (1-2) show the simultaneous DTG and DTA curves of Cu(II), Ag(I), Y(III) and UO_2(II) with 20 mgs of each sample. The DTA curve of Ag(II) complex shows no endothermic peaks corresponding to the loss of water molecules but it shows one exothermic peaks at 427 °C.

Cu(II) complex shows one endothermic peak at 243 °C and one strong exothermic peak at 427 °C. Y(III) complex shows are strong endothermic peak at 314 °C and one strong exothermic peak at 647 °C. UO$_2$(II) complex shows one endothermic peaks at 355 °C and one exothermic peak at 673 °C. The first arrest in TGA curves corresponding to DTA peaks of the complex shows a weight loss of 5.29% for Cu(II) complex (Cal. Loss 5.00%), 4.9% for Y(III) (Cal. Loss 4.54%), 3.01% for UO$_2$(II) complex (Cal. 3.51%).

In the light of spectral, magnetic studies and thermal studies, it can be inferred that water molecules are coordinated to metal ions except in Ag(I) complex. There is rapid decomposition of the complexes after the loss of coordinated water. The loss on pyrolysis corresponds to the formation of their respective oxides CuO, Ag$_2$O, Y$_2$O$_3$ and U$_3$O$_8$ respectively.

Kinetic of Decomposition/Dehydration

The fractional weight loss (α) and corresponding $(1-\alpha)^n$ values were calculated from TG curves (Figs. 1-2). The plots of log $\frac{\text{om}}{\text{π}}$ against T^{-1} (Fig. 3),

$\frac{d}{dt}$ l← $\log$;st T^{-1} (Fig. 4) and log[-ln $(1-\alpha)$ against θ (Fig. 5) for piloyan-Novikova [7], Coats-Redfern [8-9] and Horomitz-Metzger [10-12] methods respectively are found best linear fits, where $\theta = T-T_m$, T_m = peak temperature. These models suggest random nucleation mechanism of first step decomposition of the complex. The values of energy of activation (E), pre-exponential factor (z) and entropy of activation (ΔS^*)

recorded in Table-II are obtained using graphs (Figs. 3,4 and 5). E can be found out from the slope of linear plot. The value of Z can be calculated by using Equation-I.

$$Z = \frac{E}{RTm} \beta \exp\left(\frac{E}{RT}\right) \qquad .I$$

Entropy of activation (ΔS^*) is generally obtained form the equation-II

$$Z = \frac{KT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \qquad .II$$

Where β = heating rate, K = Boltzman constant and h = Planck's constant

The α Vs T(K) (Fig. 6) plots also suggest random nucleation mechanism [13]. It is obvious from the plots that in all the cases there is no physical desorption in the initial stages and also that the decomposition is not proceeded by any induction period. This suggests no surface nucleation or branching in the first step of decomposition. The curves begin with acceleratory period followed by regions of maximum rate.

Conclusion: It is concluded that 2,5-Diydroxy-1,4-benzoquinone has two chelated hydroxyl and carbonyl functions in two vicinal positions 2,5 and 1,4. The hydroxyl groups suffer abstraction of protons thereby giving rise to a divalent [anion]. The ligand form polymeric complexes [14] due to two chelating sites at opposite positions. The solid complexes undergo random nucleation mechanism dehydration on thermal decomposition.
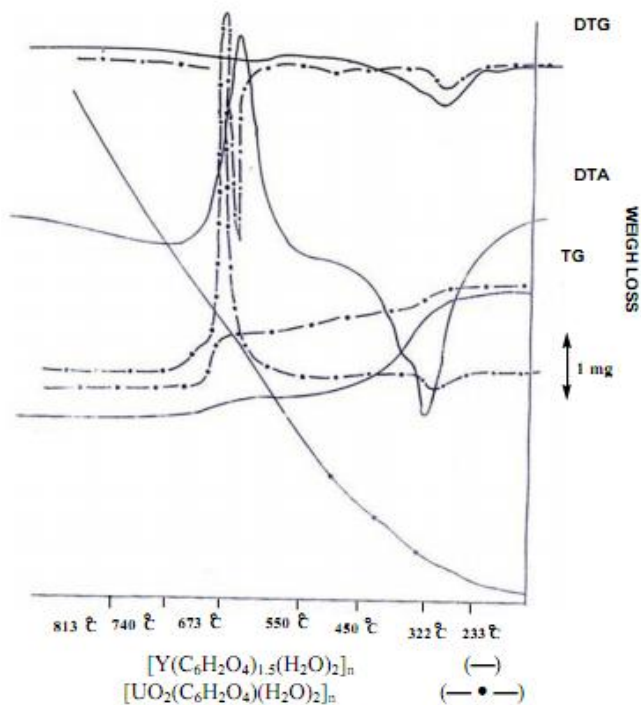

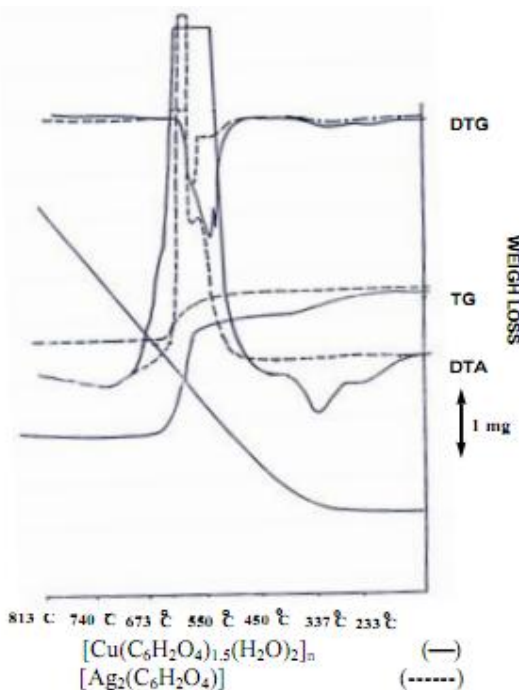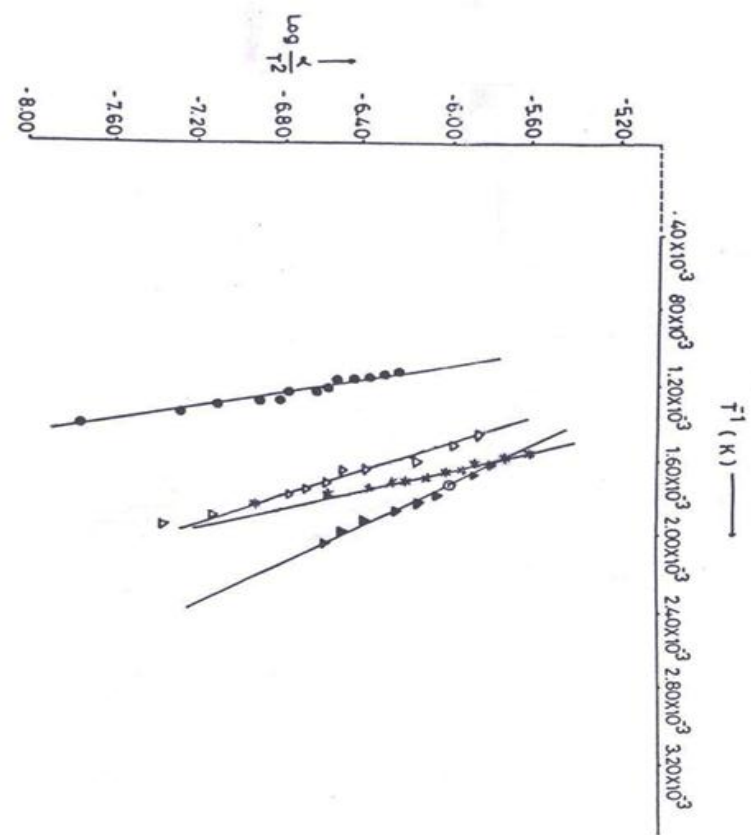[Y(C$_6$H$_2$O$_4$)$_{1.5}$(H$_2$O)$_2$]$_n$ (—)
[UO$_2$(C$_6$H$_2$O$_4$)(H$_2$O)$_2$]$_n$ (— • —)

FIGURE 1

[Cu(C$_6$H$_2$O$_4$)$_{1.5}$(H$_2$O)$_2$]$_n$ (—)
[Ag$_2$(C$_6$H$_2$O$_4$)] (------)

FIGURE 2

TABLE –I: Elemental Analysis, IR principal bands, Electronic Spectral band and μ_{eff} of the complexes.

S. No.	Metal complex	Colour	μ_{eff} (B.M)	C(calc./Found)	H(calc/Found)	M(calc/Found)	ν(C=O)	ν(O=C)	ν(M=O)	Electronic absorption bands (cm⁻¹)
							IR spectral Bands (Cm⁻¹)			
1	$[Cu(C_6H_2O_4).(H_2O)_2]_n$	Brownish green	1.80	30.31/30.26	2.52/2.95	26.72/27.51	1470	1280	740	40120(m), 29411(m), 27700(s) 20408(s), 13920(w)
2	$[Ag_2(C_6H_2O_4)]$	Black	---	20.36/20.99	0.56/0.60	60.97/59.21	1540	1270	760	23529(b), 14285(b)
3	$[Y(C_6H_2O_4)_{1.5}.(H_2O)]_n$	Pink	---	32.55/31.59	2.10/2.25	26.78/25.51	1570	1280	570	41525(w), 25512(b), 18825(b)
4	$[UO_2(C_6H_2O_4).(H_2O)_2]_n$	Orange	0.0	16.21/16.53	1.35/1.55	58.55/58.23	1550	1240	710	22312(b), 15112(b)
5	$C_6H_4O_4$ (ligand)	Yellow	---	51.58/51.52	2.87/2.84	45.56/45.51	1610	1210	---	---- ---- ---- ----

TABLE- II: Decomposition Kinetic Parameters of some complexes of 2,5-Dihydroxy-1,4-benzoquinone

Complex	Equation	E KJ mol⁻¹	ZS⁻¹	S*JK⁻¹ mol⁻¹	Model	Decomposition starts at temp. (K)	Endothermic peak temp. (K)	Exothermic peak temperature (K)
$[Cu(C_6H_2O_4)(H_2O)_2]_n$	Piloyan-Novikova	76.59	56.61	-75.20	- - -	474	609	866
	Coats-Redfern	71.03	1.12	-107.93	R.N.	-	-	-
	Horowitz-Metzger	52.88	8.08×10^{-2}	-129.80	R.N.	-	-	-
$[Ag_2(C_6H_2O_4)]$	Piloyan-Novikova	105.31	30.10	-81.95	- - -	722	-	873
	Coats-Redfern	114.88	46.53	-78.31	R.N.	-	-	-
	Horowitz -Metzger	134.18	8.49×10^{-2}	-130.52	R.N.	-	-	-
$[Y(C_6H_2O_4)_{1.5}(H_2O)_2]_n$	Piloyan-Novikova	105.31	30.10	-81.95	- - -	474	595	931
	Coats-Redfern	54.44	9.59	-89.74	R.N.	-	-	-
$[UO_2(C_6H_2O_4)(H_2O)_2]_n$	Piloyan-Novikova	76.59	56.61	-75.20	- - -	510	587	843
	Coats-Redfern	70.20	33.39	-79.58	R.N.	-	-	-
	Horowitz -Metzger	84.46	10.36×10^{-2}	-127.60	R.N.	-	-	-

R. N. = Random Nucleation Mechanism

FIGURE 3

FIGURE 4

[Ag$_2$(C$_6$H$_2$O$_4$)]   —●
[Cu(C$_6$H$_2$O$_4$)(H$_2$O)$_2$]$_n$ —▲
[UO$_2$(C$_6$H$_2$O$_4$)$_2$H$_2$O]$_n$ —*

FIGURE 5

[Cu(C$_6$H$_2$O$_4$)(H$_2$O)$_2$]$_n$ —▲
[Y(C$_6$H$_2$O$_4$)$_{1.5}$(H$_2$O)$_2$]$_n$ —*
[UO$_2$(C$_6$H$_2$O$_4$)2H$_2$O]$_n$ —Δ
[Ag$_2$(C$_6$H$_2$O$_4$)]   —●

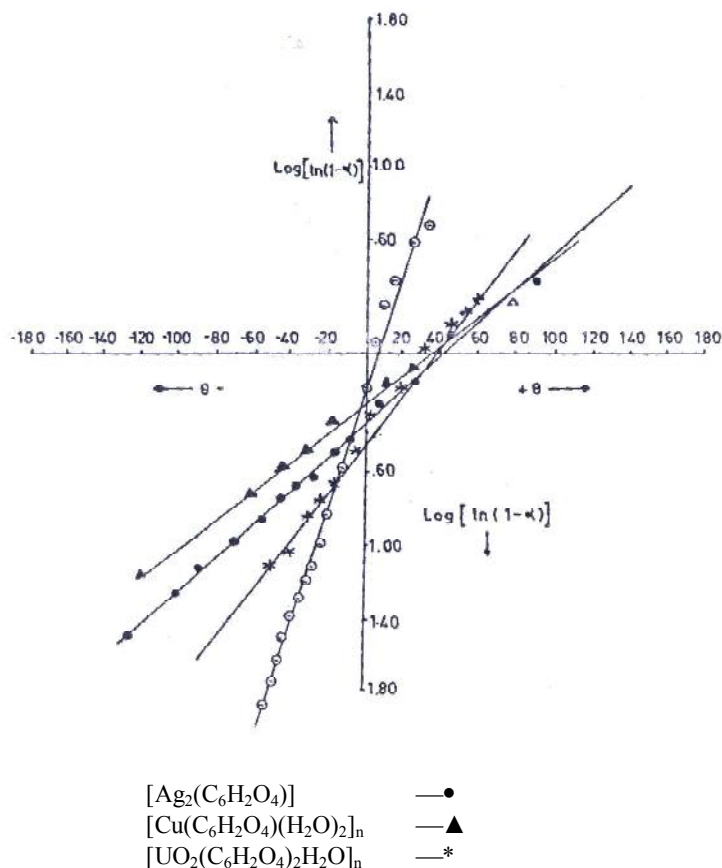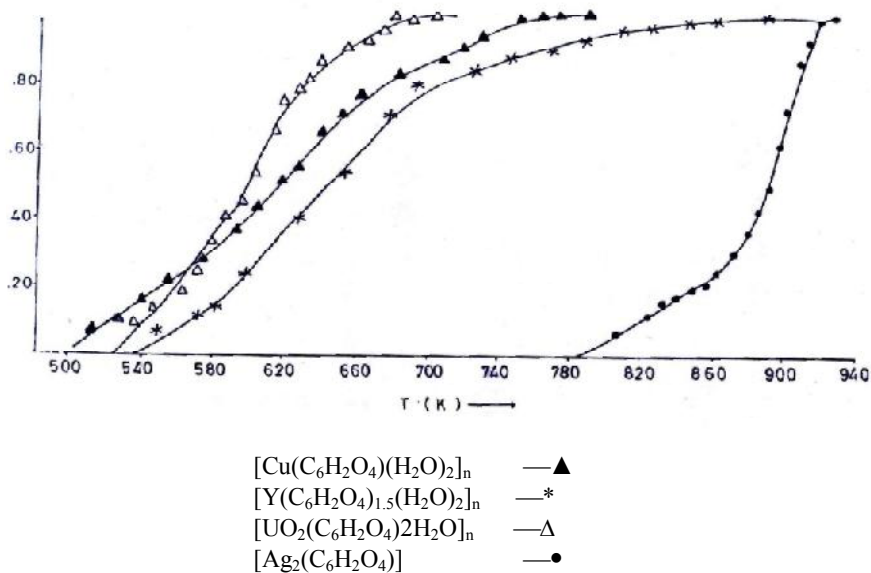**FIGURE 6**

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