Thermal Studies of Copper(II) Dihydroxy Chalcones

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Cu(II)-5'-methyl-2,2'-dihydroxy chalcones, Cu(II)4',5'-dimethyl -2,2'-dihydroxy chalcone and Cu(II)5'-chloro-2,2'-dihydroxy chalcone were prepared and their thermograms and DTG recorded on the MOM-Q-Derivatograph. A detailed mathematical and graphical treatment yielded the thermodynamic and kinetic parameters. Chloro group being a virtual sink of electrons will increase the charge on copper ion and hence the ligand will be let off only at higher temperature. Chloro group introduces the lowest steric hindrance.

INTRODUCTION

Chalcones have been used in various fields. The antifungal and antibacterial activities of this class of compounds have been reported by Kushawa et al.[1] Chalcones having hetero moieties like quinolyl, furyl and pyridyl at 3-position also showed microbial activities[2]. Antitumour activity has been reported by Devitt et al.[3] for chalcones with hetero substituents like pyridyl and thionyl groups. The coronary dilating property for chalcones was also investigated[4]. The anticancer activity against leukaemia was studied by Donelly et al.[5] in a series of acrylophenones. Some chalcones were found to possess germicidal[6-8], fungicidal[9], carcinogenic[10] and antimicrobial[11] activities. Chalcones have been used as insecticides and oxidase systems[12]. They also find uses as analytical reagents[13]. Some work in the potentiometric studies has been reported on the complexes of Cr(III), Al(III), Zn(II) and Co(II) with 2'-dihydroxy chalcones.[14]

Literature survey clearly indicated that the work on the thermal studies of the complexes of the dihydroxy chalcones with copper(II) have not been done earlier. However, the kinetics of thermal decomposition of some metal complexes have been studied by some workers[15]. Taking into consideration the importance of chalcones, the three dihydroxy chalcone complexes of copper(II) and their complete thermal study was done to investigate their thermodynamic and kinetic parameters.

EXPERIMENTAL

Preparation of dihydroxy chalcones: A mixture of p-chlorophenol (30 mL), acetic anhydride (30 mL) and H_2SO_4 (1 mL) was refluxed and the only mass was extracted with ether. p-Chlorophenyl acetate (20 g) thus obtained was mixed with

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anhydrous AlCl$_3$ and pyridine (20 mL) and the mixture was heated to 120–160°C and then decomposed with HCl to yield 2-hydroxy-5-chloro acetophenone.

To a solution of salicylaldehyde (0.02 M) and 2-hydroxy-5-chloro-acetophenone (0.02 M) in alcohol (30 mL) was added in aqueous solution of KOH (10 mL, 50%). The reaction mixture was kept for 4–5 h with occasional shaking. The precipitate thus obtained after puring the reaction mixture on ice and after carefully acidification was 5′-chloro-2,2′-dihydroxy chalcone (5′-Cl, 2,2′-DHC).

5′-Methyl-2,2′-dihydroxy chalcone (5-Me, 2,2′-DHC) was prepared as above; in stead of *p*-chlorophenol, *p*-cresol was used.

4′,5′-Dimethyl-2,2′-dihydroxy chalcone (4,5′-dione, 2,2′-DHC) was prepared as above in stead of *p*-chlorophenol, we use 3,4-dimethyl phenol.

Preparation of Copper(II) complexes

Reaction of aqueous copper(II) acetate (AR grade) with a slight excess of the respective chalcones in alcohol resulted in the precipitation of complexes after prolonged shaking.

Copper was estimated by thiocyanate method, weighing the analytical complexes as Cu(C$_5$H$_5$N)$_2$](SCN)$_2$.

Thermograms and DTG of the three Cu(II) complexes (Fig. 1) were recorded on automatic four function MOM-Q-derivatograph maintaining identical environment and were reduced to 1/6th of the original size. The heating rate was 5°/min.
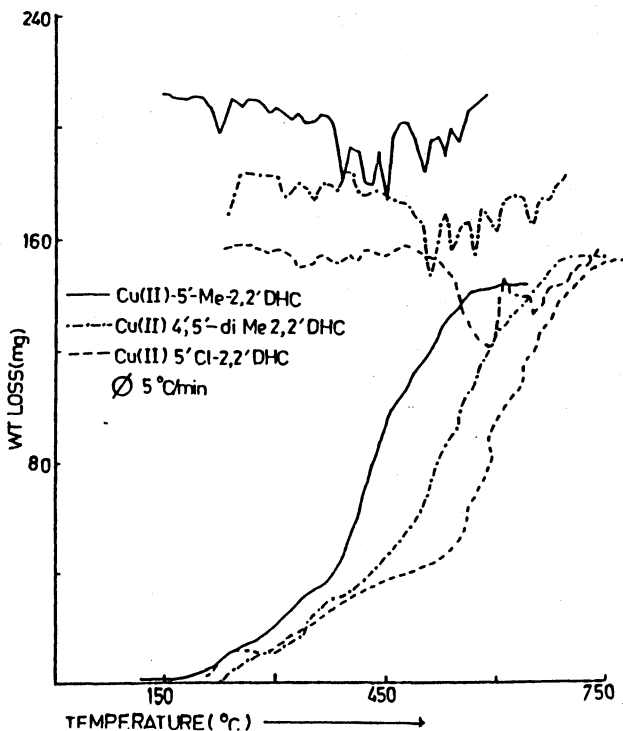

Fig. 1.

The elemental analysis of the ligands and copper(II) complexes are presented in Table-1.

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TABLE-1

ELEMENTAL ANALYSIS OF LIGANDS AND Cu(II) COMPLEXES
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Complex/Ligand	Found/(Calcd.) %		
	C	H	Cu
2,2′-OH-5′-Me-DHC	75.40 (75.59)	5.47 (5.51)	–
2,2′-OH-4′,5′-diMe-DHC	76.25 (76.12)	6.01 (5.97)	–
2,2′-OH-5′-Cl-DHC	65.35 (65.59)	4.10 (4.01)	–
Cu(II) (5′-Me-DHC) (H$_2$O)	57.50 (57.56)	4.18 (4.19)	18.90 (19.05)
Cu(II) (4′,5′-diMe-DHC) (H$_2$O)	58.40 (58.70)	4.59 (4.60)	18.15 (18.28)
Cu(II) (5′-Cl-DHC) (H$_2$O)	50.30 (50.84)	3.15 (3.11)	18.10 (17.95)

RESULTS AND DISCUSSION

The fraction of total mass decomposed (α) is given as

$$\alpha = \frac{W_0 - W_t}{W_0 - W_r} \tag{1}$$

where W_0 = initial weight of the compound,

W_t = weight of compound at t°

W_r = weight of residue at the completion of heating.

$g(\alpha)$ values were calculated[16] as

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)} \tag{2}$$

where n is the order of reaction.

The order of reaction n and the E_a values were found out by Freeman and Carroll method[17].

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} \quad vs. \quad \frac{\Delta(1/T)}{\Delta \log W_r}$$

E_a values calculated from slops of the line and order of reaction, *i.e.*, n calculated from intercept of the line and are given in Table-2.

TABLE-2

$\dfrac{\Delta \log (dw/dt)}{\Delta \log W_r}$	$\dfrac{\Delta (1/T)}{\Delta \log W_r}$	
Cu(II) (5′-Me-2,2′-DHC)		
2.6217	1.32	
2.7969	1.32	
2.9128	1.33	$E_a = 61.98$ kJ mol^{-1}
3.0547	1.41	$n = 1.35$
3.4327	1.48	
4.9217	1.69	
4.4709	1.83	
Cu(II) (4′,5′-diMe-2,2′-DHC)		
2.6019	1.08	
2.8623	1.10	$E_a = 69.21$ kJ mol^{-1}
2.2009	1.18	$n = 1.10$
3.7161	1.31	
4.2503	1.49	
Cu(II) (5′-Cl-2,2′-DHC)		
2.3617	0.95	
2.5520	0.96	
2.6812	0.98	
2.7525	1.00	$E_a = 73.82$ kJ mol^{-1}
3.2007	1.10	$n = 1.15$
3.3029	1.16	
4.6027	1.46	
7.8029	2.32	

The basic equation[18]

$$\frac{d\alpha}{dt} = (A/\phi)(1 - \alpha)^n \quad \exp(-E/RT) \qquad (3)$$

was modifed to get

$$\log\left[\frac{g(\alpha)}{T^3}\right] = \log\left[\frac{kR}{h\phi E}\right] + \frac{\Delta S}{2.303R} - \frac{E}{2.303RT} \qquad (4)$$

the explanation of the terms being elaborately given by Mundhe *et al.*[19].

The plots of $\log [g(\alpha)/T^3]$ *vs* $1/T$ are simply given in the form of equations of the type $y = mx + c$ (least square method followed) and are given in Table-3. Since equation (4) yielded ΔS values, all the thermodynamic parameters for Cu(II) complexes of DHC could be accurately estimated and are listed in Table-4.

TABLE-3

EQUATION OF STRAIGHT LINES FOR E_a VALUES (LEAST SQUARE METHOD)

Complex	Expression A*T = Expression B*T	
Cu(II) (5′-Me-2,2′-DHC)	−1146.50 − 7.08 T	−10,000 + 19.60 T
Cu(II) (4′,5′-diMe-2,2′-DHC)	−1666.60 − 6.71 T	−6,000 + 12.90 T
Cu(II) (5′-Cl-2,2′-DHC)	−2641.50 − 5.85 T	−2,833.30 + 11.28 T

$A* = \log [g(\alpha)/T^3]$ and $B* = -\ln [d\alpha/dt]$

TABLE-4

THERMODYNAMIC PARAMETERS FOR Cu(II) COMPLEXES OF DHC

Complex	E_a (ΔH) kJ mol^{-1}	$-\Delta S^*$ J K^{-1} mol^{-1}	ΔF^* kJ mol^{-1}
Cu(II) (5′-Me-2,2′-DHC)	61.98	245.7	135.7
Cu(II) (4′,5′-diMe-2,2′-DHC)	69.21	237.7	140.5
Cu(II) (5′-Cl-2,2′-DHC)	73.82	220.7	140.0

* At 300 K

It will be noticed that the ΔH values increase in the order Cu(II) 5′-Me-2,2′-DHC < Cu(II) 4′,5′-diMe-2,2′-DHC < Cu(II) 5′-Cl-2,2′-DHC, the chloro group influencing the E_a values most. It is expected that chloro group being a virtual sink of electrons will increase the charge on copper ion most and hence the ligand will be let off only at higher temperatures.

The expressions[19] give Z, the frequency factor, B values being manipulated from Doyle's tables[20] using Zsako's procedure[21].

$S^\#$, the apparent activation energy, and A, the pre-exponential terms, were calculated in an identical procedure laid out in the paper[19]. Table-5 sums up the values of α_{av}, $-\log P(x)$, B, Z, $S^\#$ and A.

TABLE-5

PARAMETERS FOR KINETICS OF DECOMPOSITION

Complex	α(av)	$-\log P(x)$	B	Z (Number)	$-S^\#$ (J mol^{-1})	A (Number)
Cu(II) (5′-Me-2,2′-DHC)	0.4909	6.5040	6.3334	24.0870	113.5	6.71×10^7
Cu(II) (4′,5′-diMe-2,2′-DHC)	0.4361	6.3000	6.0581	11.4460	117.1	1.77×10^4
Cu(II) (5′-Cl-2,2′-DHC)	0.4316	6.2250	5.9769	7.9596	119.0	3.45×10^3

The probability or steric factors were found out from the expression P = A/Z and are

Cu(II) 5′-Me-2,2′-DHC	2.78×10^6
Cu(II) 4′,5′-diMe-2,2′-DHC	1.54×10^3
Cu(II) 5′-Cl-2,2′-DHC	4.33×10^2

which indicates that chloro group introduces the lowest steric hindrance.

The DTG peaks given in Table-6 show that in the case of chloro DHC ligand complex there are only two peaks at 863 K and 923 K indicating that the ligand is ultimately given off only at 923 K.

TABLE-6
DTG PEAK TEMPERATURES (K) FOR COMPLEXES

Complex	Peak No.	Peak temp. (K)
Cu(II) (5'-Me-2,2'-DHC)	1	493
	2	663
	3	699
	4	723
	5	773
	6	803
	7	823
Cu(II) (4',5'-diMe-2,2'-DHC)	1	583
	2	623
	3	673
	4	803
	5	843
	6	873
	7	823
Cu(II) (5'-Cl-2,2'-DHC)	1	863
	2	923

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