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Thermal decomposition kinetics of Cu(II) chelates of substituted chalcones

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Abstract

The thermal decomposition of Cu(II) complexes of 3-(phenyl)-1-(2′-hydroxynaphthyl)-2-propen-1-one (PHPO), 3-(4-chlorophenyl)-1-(2′-hydroxynaphthyl)-2-propen-1-one (CPHPO), 3-(4-methoxyphenyl)-1-(2′-hydroxynaphthyl)-2-propen-1-one (MPHPO), 3-(3,4-dimethoxyphenyl)-1-(2′-hydroxynaphthyl)-2-propen-1-one (DMPHPO) was studied by thermogravimetry. Mathematical analysis of the data has allowed us to determine various parameters using the Freeman–Carroll equation, the integral method using the Coats–Redfern equation and the approximation method using the Horowitz–Metzger equation. The trend of the kinetic parameters was found to be different from that of the thermal stability order. The low values of Z suggest the slow nature of the reactions.

INTRODUCTION

Very few systems have been reported [1] showing the relationship between thermal stability of metal chelates and structure of the chelating agents. Wendlandt and co-workers [2–5] and Hill and co-workers [6,7] studied the thermal properties of metal chelates with different types of complexing ligands. Structural studies on several metal chelates of β-diketones and 2-hydroxycarbonyl compounds have been reviewed by Holm and O'Connor [8]. The metal chelates of divalent transition metals with some *o*-hydroxychalcones stand out as a distinct class of *o*-hydroxycarbonyl compounds with low spin square-planar configuration, which do not easily form adducts. Extensive conjugation was found to be responsible for the strong-field nature of the ligand [9]. Chalcones usually exhibit germicidal [10], bactericidal [11], fungicidal [12] and carcinogenic activities [13].

In continuation of our earlier work [14–18] on thermal decomposition kinetics of metal chelates, we now report the thermal stability of the copper chelates of 3-(phenyl)-1-(2′-hydroxynaphthyl)-2-propen-1-one (PHPO), 3-

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(4-chlorophenyl)-1-(2′-hydroxynaphthyl)-2-propen-1-one (CPHPO), 3-(4-methoxyphenyl)-1-(2′-hydroxynaphthyl)-2-propen-1-one (MPHPO), and 3-(3,4-dimethoxyphenyl)-1-(2′-hydroxynaphthyl)-2-propen-1-one (DMPHPO) and evaluation of kinetic parameters employing the differential Freeman–Carroll equation [19], the integral method using the Coats–Redfern equation [20] and the approximation method using the Horowitz–Metzger equation [21].

EXPERIMENTAL

The chalcones were prepared by the condensation of 2-hydroxy-1-acetonaphthone with benzaldehyde, chlorobenzaldehyde, methoxybenzaldehyde and dimethoxybenzaldehyde employing the Claisen–Schmidt con-

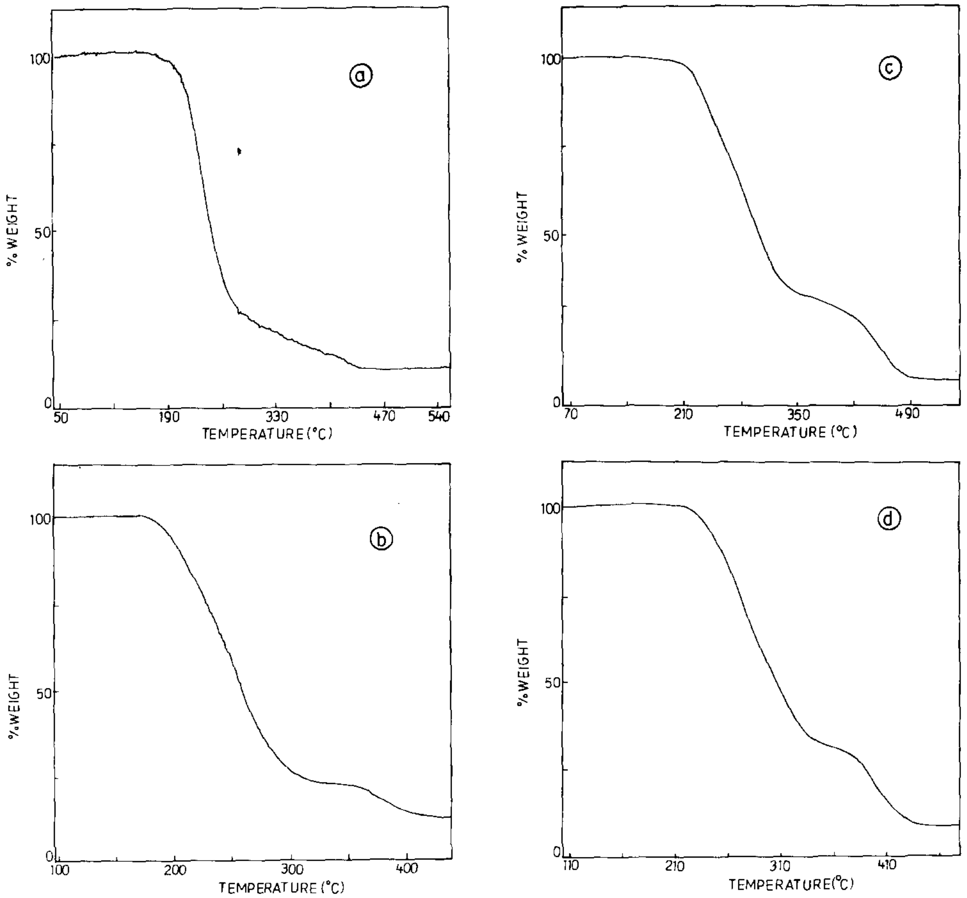

Fig. 1. Thermograms of (a) $Cu(PHPO)_2$, (b) $Cu(CPHPO)_2$, (c) $Cu(MPHPO)_2$, (d) $Cu(DMPHPO)_2$.

densation reported earlier [22]. The copper complexes of chalcones were prepared by refluxing a toluene solution of copper acetate and the ligand, in 1:2 molar ratio, in the presence of sodium acetate (pH 6–7.5) for 1 h. The precipitates were filtered, washed with toluene and dried in a vacuum desiccator over fused calcium chloride. The purity of the sample was checked by elemental analysis. The thermograms were recorded using a Perkin-Elmer T GS-2 thermobalance in ambient air and at a heating rate of 6 K min^{-1}.

Typical TG curves are presented in Fig. 1. Kinetic data are evaluated from these TG traces using the equations noted above (see Fig. 2–4).

RESULTS AND DISCUSSION

All the complexes are coloured powders which are insoluble in water. The elemental analyses of the chelates showed copper to ligand ratios of 1:2. The complexes were found to be stable in air and non-hygroscopic. The final pyrolysis product of all the complexes corresponds to CuO. The relative thermal stability of the chelates is (Table 1) $\text{Cu(CPHPO)}_2 < \text{Cu(PHPO)}_2 < \text{Cu(MPHPO)}_2 < \text{Cu(DMPHPO)}_2$.

Decomposition kinetics

The analysis of data using the Freeman–Carroll equation gives the order of the decomposition reaction near unity for all these complexes. The

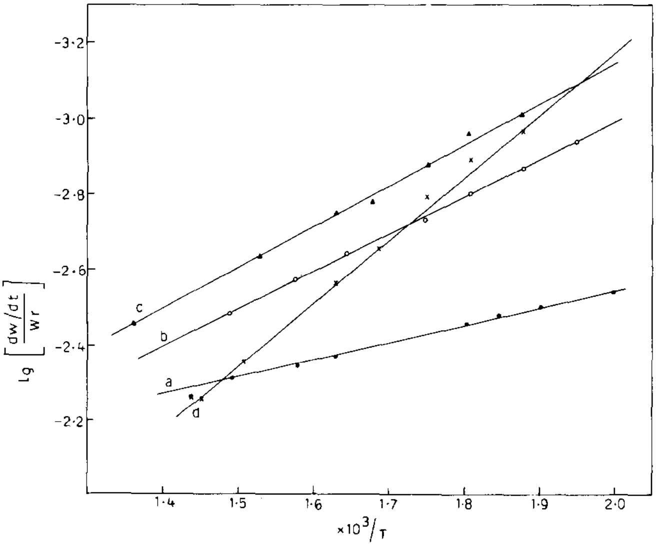

Fig. 2. Freeman–Carroll plots of a, Cu(PHPO)_2; b, Cu(CPHPO)_2; c, Cu(MPHPO)_2; and d, Cu(DMPHPO)_2.

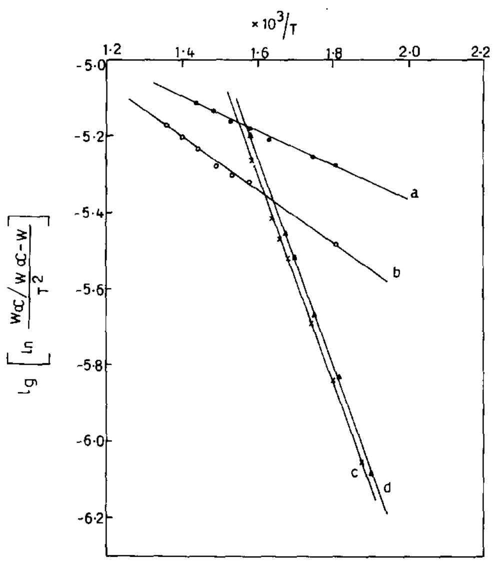

Fig. 3. Coats–Redfern plots of a, Cu(PHPO)$_2$; b, Cu(CPHPO)$_2$; c, Cu(MPHPO)$_2$; and d, Cu(DMPHPO)$_2$.

values of activation energy E^* obtained by all three methods for the copper chelates are given in Table 2. The negative values of ΔS^* indicate that the activated complex has a more ordered structure than the reactants

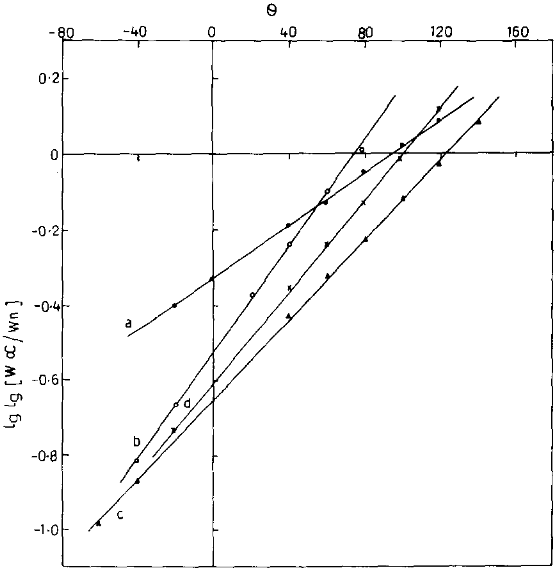

Fig. 4. Horowitz–Metzger plots of a, Cu(PHPO)$_2$; b, Cu(CPHPO)$_2$; c, Cu(MPHPO)$_2$; and d, Cu(DMPHPO)$_2$.

TABLE 1

Thermal decomposition data

Chelate	Decomposition temp. (°C)	Residue (percentage)			Order of reaction Freeman–Carroll method
		Theoretical		Experiment	
		Metal	Oxide		
$Cu(PHPO)_2$	210	10.42	13.04	12.48	1.07
$Cu(CPHPO)_2$	200	9.36	11.72	12.43	1.15
$Cu(MPHPO)_2$	228	9.49	11.88	11.22	1.17
$Cu(DMPHPO)_2$	241	8.71	10.92	11.24	1.08

[23] and further the low values of Z indicate the slow nature of the reactions [24].

The values of E^* and Z increase in the order $Cu(PHPO)_2 < Cu(CPHPO)_2 < Cu(MPHPO)_2 < Cu(DMPHPO)_2$.

TABLE 2

Kinetic data

Chelate	Parameters [a]	From Freeman–Carroll equation	From Coats–Redfern equation	From Horowitz–Metzger equation
$Cu(PHPO)_2$	E^* (kcal mol^{-1})	2.75	2.01	8.74
	Z (s^{-1})	5.73×10^{-2}	2.59×10^{-3}	5.95
	ΔS^* (e.u.)	−28.38	−31.06	−24.38
	G^* (kcal mol^{-1})	17.88	18.57	21.74
	Kr (Su^{-1})	5.70×10^{-2}	2.57×10^{-3}	5.90
$Cu(CPHPO)_2$	E^* (kcal mol^{-1})	4.58	2.96	11.86
	Z (s^{-1})	2.68×10^{-1}	8.21×10^{-3}	95.14
	ΔS^* (e.u.)	−27.09	−31.27	−22.02
	G^* (kcal mol^{-1})	19.56	20.25	24.04
	Kr (Su^{-1})	2.67×10^{-1}	8.19×10^{-3}	94.12
$Cu(MPHPO)_2$	E^* (kcal mol^{-1})	7.32	11.62	14.34
	Z (s^{-1})	1.09	3.29×10	3.97×10^{2}
	ΔS^* (e.u.)	−25.94	−22.99	−20.85
	G^* (kcal mol^{-1})	22.71	25.25	26.71
	Kr (Su^{-1})	1.08	32.66	3.92×10^{2}
$Cu(DMPHPO)_2$	E^* (kcal mol^{-1})	8.72	14.30	16.39
	Z (s^{-1})	3.33	4.28×10^{2}	44.79×10^{2}
	ΔS^* (e.u.)	−24.99	−20.76	−18.73
	G^* (kcal mol^{-1})	23.04	26.19	27.12
	Kr (Su^{-1})	3.31	4.18×10^{2}	44.15×10^{2}

[a] *Kr*, specific reaction rate.

The kinetic parameters show a somewhat different trend from that of thermal stability. This may be due to the fact that the decisive criteria in kinetics are often quite different from those which decide thermal stability.

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