Thermal Decomposition Kinetics of Ni(II) Chelates of Substituted Chalcones

K.G.MALLIKARJUN

Department of chemistry, Jawahar Navodaya Vidyalaya
Peddapuram – 533 437, East Godavari, (A.P.) India.

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Abstract The thermal decomposition of Ni(II) complexes of 3-(phenyl)-1-(2'-hydroxy-naphthyl)-2-propen-1-one (PHPO), 3-(4-chlorophenyl)-1-(2'-hydroxy-naphthyl)-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 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 reaction.

Keywords: Thermogravimetry, Chalcones, Nickel Compounds, Frequency factor,

Introduction

Very few systems have been reported¹ showing the relationship between thermal stability of metal chelates and structure of the chelating agents. Wendlandt and co-workers²⁻⁵ 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 adduct. Extensive conjugation was found to be responsible for the strong field nature of the ligand.⁹ Chalcones usually exhibit germicidal¹⁰ bactericidal,¹¹ fungicidal¹² and carcinogenic activities.¹³

In continuation of our earlier work¹⁴⁻¹⁹ on thermal decomposition kinetics of metal chelates, the present investigation deals the thermal stability of the Nickel chelates 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) and evaluation of kinetic parameters employing the differential Freeman-Carroll equation²⁰ the integral method using the Coats-Redfern equation²¹ and the approximation method using the Horowitz-Metzger equation.²²

Experimental

The chalcones were prepared by the condensation of 2-hydroxy-1-acetonaphthone with benzaldehyde, chlorobenzaldehyde, methoxybenzaldehyde and dimethoxybenzaldehyde employing the Claisen-Schmidt condensation reported earlier.²³ The copper complexes of chalcones were prepared by refluxing a toluene solution of nickel acetate and the ligand in 1:2 molar ratios, in the presence of dilute ammonia (pH 8.5-9.0) for 1h. 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 TGS-2 thermo balance in ambient air and at a heating rate of 6K min⁻¹. Kinetic data were evaluated from TG traces using the equations noted in **Table-1**.

Table 1. Kinetic data

Chelate	Parameters	From Freeman-Carroll equation	From Coats-Redfern equation	From Horowitz-Metzger equation
Ni(PHPO) ₂	E* (kcal mol ⁻¹)	2.84	2.27	8.95
	Z(s ⁻¹)	5.63 X 10 ⁻²	2.49 X 10 ⁻³	6.04
	ΔS* (e.u.)	- 29.49	- 33.08	- 25.19
	G* (kcal mol ⁻¹)	16.69	18.41	21.24
	K _r (Su ⁻¹)	5.61 X 10 ⁻²	2.43 X 10 ⁻³	6.01
Ni(CPHPO) ₂	E* (kcal mol ⁻¹)	4.79	3.19	12.24
	Z (s ⁻¹)	2.54 X 10 ⁻¹	8.07 X 10 ⁻³	96.18
	ΔS* (e.u.)	- 28.25	- 32.16	- 23.06
	G* (kcal mol ⁻¹)	18.33	18.66	17.10
	K _r (Su ⁻¹)	2.51 X 10 ⁻¹	7.93 X 10 ⁻³	95.49
Ni(MPHPO) ₂	E* (kcal mol ⁻¹)	7.14	11.18	13.95
	Z (s ⁻¹)	1.01	2.98 X 10 ⁻¹	3.76 X 10 ²
	ΔS* (e.u.)	- 26.14	- 23.75	- 21.92
	G* (kcal mol ⁻¹)	20.29	23.13	24.98
	K _r (Su ⁻¹)	0.99	28.70	3.69 X 10 ²
Ni(DMPHPO) ₂	E* (kcal mol ⁻¹)	8.69	14.06	16.04
	Z (s ⁻¹)	3.16	4.12 X 10 ⁻²	44.57 X 10 ²
	ΔS* (e.u.)	- 25.37	- 21.22	- 18.92
	G* (kcal mol ⁻¹)	21.89	25.06	25.82
	K _r (su ⁻¹)	3.13	4.09 X 10 ²	44.35 X 10 ²

Results and Discussion

All the complexes are coloured powders which are insoluble in water. The elemental analysis of the chelates showed nickel 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 NiO. The relative thermal stability of the chelates is (**Table 2**) Ni(CPHPO)₂ < Ni(PHPO)₂ < Ni(MPHPO)₂ < Cu(DMPHPO)₂. Mathematical analysis of the TG curves was carried out using the differential Freeman-Carroll equation, the integrate method using the Coats-Redfern equation and the approximation method using the Horowitz-Metzger equation.

Table 2. Thermal decomposition data

Chelate	Decomposition Temp. (°C)	Residue (Percentage)		Order of reaction Freeman-Carroll Method
		Theoretical Metal	Experiment Oxide	
Ni(PHPO) ₂	215	10.04	12.78	13.21
Ni(CPHPO) ₂	208	9.50	12.08	12.56
Ni(MPHPO) ₂	230	9.11	11.59	11.35
Ni(DMPHPO) ₂	244	8.31	10.57	12.04

FREEMANN-CARROLL EQUATION

Freeman-Carroll equation which may be written in the form.

$$\frac{\Delta \log (dW / dt)}{\Delta \log W_r} = \frac{-(E^* / 2.303R) \Delta (T^{-1})}{\Delta \log W_r} + n$$

Where $W_r = W_\alpha - W$, W_α is the mass loss at the completion of reaction, W is the mass loss up to time t , T is the absolute temperature at time t , n is the order of reaction. R is the gas constant in calories and E^* is the energy of activation in K cal mol⁻¹. W_r and T can be directly obtained from the TG traces. The temperature slopes dW / dT were converted into time slopes dW / dt , using the relation²³

$$\frac{dW}{dt} = \frac{dW}{dT} \cdot \frac{dT}{dt} = \left(\frac{dW}{dT} \right) \phi$$

where ϕ is the heating rate. The usual first-order rate law expression

$$\frac{dW}{dt} = k(a - x)$$

can be written in the following form using the terms W and W_r

$$\frac{dW}{dt} = kW_r$$

Combining this with the Arrhenius equation

$$K = Z \exp (-E^* / RT)$$

We obtain

$$\log \left(\frac{dW / dt}{W_r} \right) = -\frac{E^*}{2.303RT} + \log Z$$

Plot of $\log [(dw / dt) / W_r]$ against T^{-1} were drawn. They gave straight lines in all cases with slopes $-E^* / 2.303R$ from which E^* values were obtained. Z was calculated from the above equation and the entropy of activation ΔS^* was obtained from the relation²⁴

$$\Delta S^* = 2.3.3R \log (Zh / kT_s)$$

Where k is the Boltzmann constant, h is the Planck constant and T_s is the peak temperature from DTG. The free energy of activation G^* was calculated using the following equation²⁵

$$G^* = E^* - T_s \Delta S^*$$

$$K_r = Z \exp (-E^* / RT_s)$$

COATS-REDFERN EQUATION

$$\log \left[\ln \frac{W_{\infty}}{W_{\infty} - W} \right] = \log \left[\frac{ZR}{\phi E^*} \left(1 - \frac{2RT}{E^*} \right) \right] - \frac{E^*}{2.303RT}$$

Where W_{∞} = mass loss at the completion of the reaction,

W = mass loss at time,

Z = frequency factor,

Φ^* = linear rate of heating

E^* = activation energy of the reaction.

Assuming the decomposition of Ni(II)-chalcone chelates to follow first order kinetics ($n=1$) a plot of $\log \{ \ln [W_{\infty} / (W_{\infty} - W)] / T^2 \}$ against $1/T$ was drawn which gave straight lines in all cases with a slope of $-E^* / 2.303R$ from which the activation energy was calculated.

HOROWITZ-METZGER EQUATION

$$\log \log \frac{W_{\infty}}{W_r} = \frac{E^* \phi}{2.303RT_s^2} - \log 2.303$$

Where, W_{∞} = mass loss at the completion of the reaction,

$W_r = W_{\infty} - W$,

W = mass loss at time t ,

T_s = peak temperature,

R = gas constant.

A plot of $\log \log W_{\infty} / W_r$ against θ was drawn which gave straight lines in all the cases with the slope $E^* / 2.303RT_s^2$ from which E^* values were obtained.

Decomposition kinetics

The analysis of data using the Freeman-Carroll equation gives the order of the decomposition reaction near unity for these complexes. The values of activation energy E^* obtained by all three methods for the nickel chelates are given (**Table 1**). The negative values of ΔS^* indicates that the activated complex has a more ordered structure than the reactants²⁴ and further the low values of Z indicate the slow nature of the reaction²⁷.

The values of E^* and Z increase in the order $\text{Ni}(\text{PHPO})_2 < \text{Ni}(\text{CPHPO})_2 < \text{Ni}(\text{MPHPO})_2 < \text{Ni}(\text{DMPHPO})_2$. The kinetic parameters show a somewhat different trend from that of thermal stability. This may be due to the fact the decisive criteria in kinetics are often quite different from those which decide thermal stability.

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