

## Thermal decomposition kinetics of $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ complexes with 3-hydroxypyridine in a dynamic nitrogen atmosphere

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### Abstract

The thermal decomposition of  $[\text{Co}(\text{3-OHpy})_4\text{Cl}_2]$  and  $[\text{Ni}(\text{3-OHpy})_4\text{Cl}_2]$  was carried out using TG, DTG and DSC methods. The intermediate and residue for each decomposition stage were identified from TG curves. The kinetics and mechanism of the ligand degradation for each complex were established. The kinetic parameters  $E$ ,  $A$  and  $\Delta S$  were calculated from the TG curves using mechanistic and non-mechanistic integral equations. For both complexes the three-dimensional diffusion  $D_3$  mechanism (Jander equation) controls the process of degradation, followed by the random nucleation mechanism for the second stage. The heat of reaction  $\Delta H_{\text{Total}}$  was determined using the DSC curves.

### INTRODUCTION

In recent years there has been considerable interest in complexes formed by hydroxypyridine and related ligands because such donors are common components of some biological molecules [1, 2]. The thermolysis of some transition metals complexes with 1-hydroxypyridine-2-thione has been studied by Rolando and co-workers [3]. They found that the thermal stabilities of the complexes are in the sequence  $\text{Co}^{2+} < \text{Ni}^{2+}$ . They attributed their stabilities to their molecular structures. The cobalt complex forms an octahedral structure, whereas the nickel complex has a square planar structure. Although a number of transition metal complexes containing hydroxypyridine as a ligand have been studied, the kinetic aspects of the thermal decomposition have very rarely been studied. Hence, we report our investigations on the thermal decomposition kinetics of

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cobalt(II) and nickel(II) complexes with 3-hydroxypyridine, which both have octahedral structures. [4].

## EXPERIMENTAL

The complexes of  $[\text{Co}(\text{3-OHpy})_4\text{Cl}_2]$  and  $[\text{Ni}(\text{3-OHpy})_4\text{Cl}_2]$  have been prepared previously [4]. An ethanolic solution of  $\text{CoCl}_2$  or  $\text{NiCl}_2$  was added to 3-hydroxypyridine dissolved in ethanol. The mixture was stirred at room temperature for 2 h. The solid produced was isolated by filtration, washed with cold ethanol and then with dry diethyl ether, and finally dried in vacuo at room temperature. Microanalyses for C, H and N were performed on a Carlo Erba elemental analyzer model 1106. The Cl content was determined by a conventional method [5]. The metal contents were assayed using a Varian AA-1475 series atomic absorption spectrophotometer.

TG, DTG and DSC analyses for the complexes were performed using a TA 3000 Mettler thermobalance with a heating rate of  $10^\circ\text{C min}^{-1}$  and 10 mg sample weight. The cell was fed with  $\text{N}_2$  gas with a flow rate of  $50 \text{ ml}(\text{NTP}) \text{ min}^{-1}$  in the range of temperatures 50–990°C. The DSC analyser used was a DSC-30 Mettler system using the same conditions as in the TG analysis, except that sample weight was 5 mg and the final temperature was 590°C. Non-isothermal TG data were processed using a BASIC program developed by Beg et al. [6] with an IBM PS/2 30 micro-computer.

## RESULTS AND DISCUSSION

Analytical results for the complexes and proposed formulae are given in Table 1. The IR, UV–vis., NMR and mass spectra, together with magnetic

TABLE 1  
Elemental analyses of the complexes

Theoretical (found) (wt%)					
M	C	H	N	Cl	
$\text{Co}(\text{3-OHpy})_4\text{Cl}_2$					
11.56 (11.74)	47.98 (47.10)	3.95 (3.98)	10.98 (10.96)	13.90 (13.78)	
$\text{Ni}(\text{3-OHpy})_4\text{Cl}_2$					
11.51 (11.86)	47.10 (47.41)	3.95 (4.08)	10.99 (11.15)	13.90 (13.87)	

TABLE 2

Thermal decomposition data for cobalt(II) and nickel(II) complexes in dynamic nitrogen atmosphere from TG and DTG analyses

Peak temp. from DTG (°C)			Loss of mass (wt%)		Probable composition of expelled group
$T_i$	$T_f$	$T_m$	TG	Theory	
3-Hydroxypyridine					
116	210	189	69.47	68.42	-C <sub>5</sub> H <sub>5</sub>
210	258	253	30.53	31.58	-NO
			100.00 <sup>a</sup>	100.00 <sup>a</sup>	
[Co(3-OHpy) <sub>4</sub> Cl <sub>2</sub> ]					
156	308	247	30.79	30.98	-2C <sub>5</sub> H <sub>5</sub> N
308	434	328	14.35	13.91	-2Cl
434	833	480	40.27	40.39	-2C <sub>5</sub> H <sub>5</sub> NO, - $\frac{1}{2}$ O <sub>2</sub>
892	949	902	2.45	3.13	- $\frac{1}{2}$ O <sub>2</sub>
			87.86 <sup>a</sup>	88.41 <sup>a</sup>	
[Ni(3-OHpy) <sub>4</sub> Cl <sub>2</sub> ]					
119	206	194	6.17		
206	288	274	34.74	37.26	-2C <sub>5</sub> H <sub>5</sub> NO
288	376	296	14.81	13.91	-2Cl
376	504	703	35.46	37.26	-2C <sub>5</sub> H <sub>5</sub> NO
849	906	889	3.44	3.14	+ $\frac{1}{2}$ O <sub>2</sub>
			91.18 <sup>a</sup>	88.43 <sup>a</sup>	

<sup>a</sup> Total loss of mass (wt%).

data [4] reveal a six-coordinated environment for the cobalt or nickel ion [7–12].

The thermoanalytical data for the complexes given in Table 2. The complexes of cobalt and nickel decompose via intermediates to give the metal oxide as an end product. The percentage of mass loss and probable composition of the expelled groups are also indicated in Table 2.

TG and DTG results for the pure ligand (Fig. 1) are given for comparison. The TG curve shows degradation in one stage starting at 116°C and complete at 258°C. The DTG curve shows that the decomposition occurred in two consecutive stages at  $T_m$  values of 189°C and 233°C. The first stage corresponds to the removal of the C<sub>5</sub>H<sub>5</sub> with a loss of 69.47 wt% (theoretical loss = 68.42 wt%). This is followed by removal of NO gas with loss of 30.93 wt% (theoretical loss = 31.57 wt%). It is evident that the DSC curve has two endothermic peaks with total enthalpy of 3052 J g<sup>-1</sup> as shown in Table 3.

The TG degradation of [Co(3-OHpy)<sub>4</sub>Cl<sub>2</sub>] reveals three decomposition stages, as predicted by the DTG curve (Fig. 2). The first stage is due to the

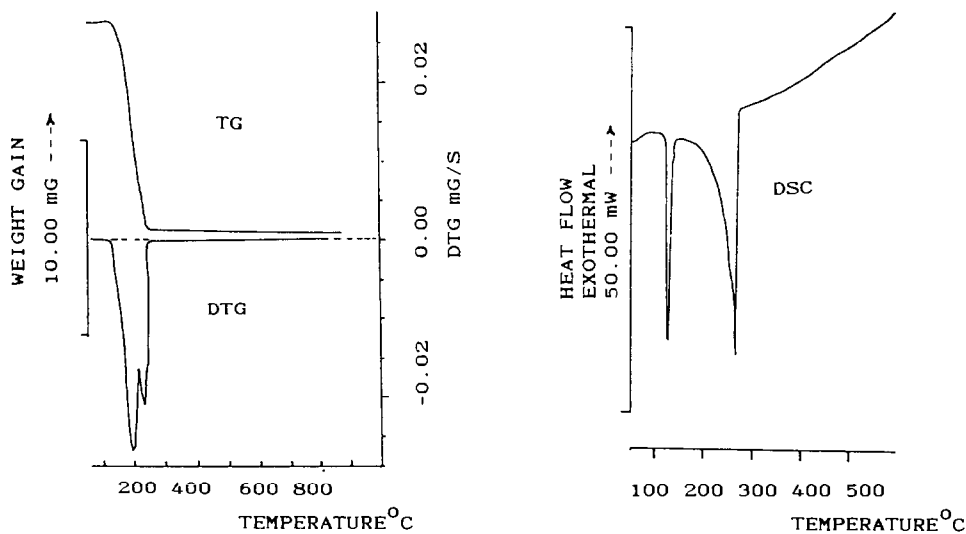


Fig. 1. TG, DTG and DSC curves for hydroxypyridine.

removal of  $2C_3H_5N$ , which is followed by removal of  $2Cl$  in the second stage at  $328^\circ C$ . At  $430^\circ C$  the rest of hydroxypyridine molecules are degraded, leaving  $Co_2O_3$  as a final residue. The DSC curve clearly illustrates that there are one endothermic and two exothermic stages in that range of temperatures, with a total enthalpy of  $2313 J g^{-1}$  (Table 3).

The TG and DTG decomposition curves for  $[Ni(3-OHpy)_4Cl_2]$  started

TABLE 3

DSC temperature and  $\Delta H$  for the thermal decomposition of the complexes in dynamic  $N_2$  atmosphere

Stage	DSC Temp. ( $^\circ C$ )	$\Delta H_{Total}$ ( $J g^{-1}$ )
3-Hydroxypyridine		
I	128(endo)	} 3052
II	266(endo)	
$[Co(3-OHpy)_4Cl_2]$		
I	175(endo)	} 2313
II	261(exo)	
III	429(exo)	
$[Ni(3-OHpy)_4Cl_2]$		
I	122(endo)	} 1615
II	184(endo)	
III	271(endo)	
IV	284(exo)	
V	384(endo)	
VI	536(endo)	

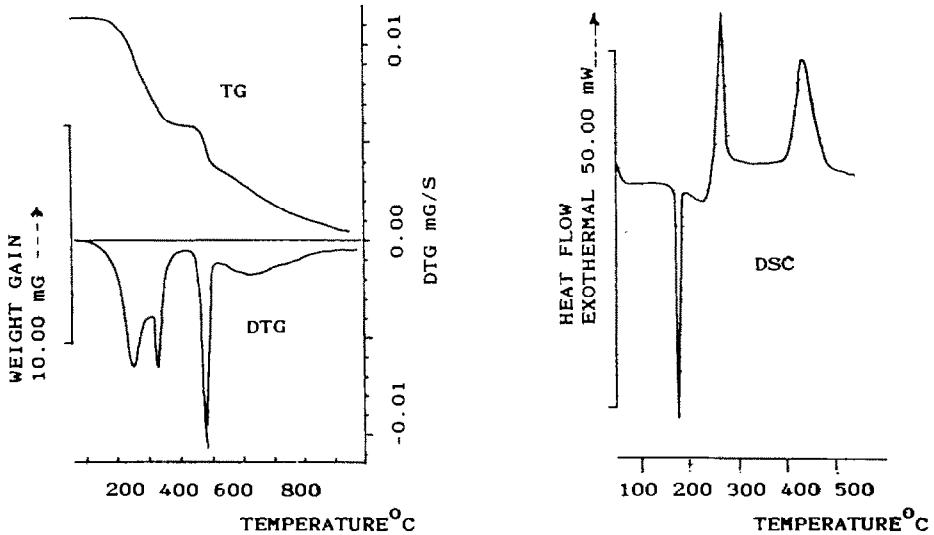


Fig. 2. TG, DTG and DSC curves for the trans  $[\text{Co}(\text{3-OHpy})_4\text{Cl}_2]$  complex.

at  $119^\circ\text{C}$ , which clearly differs from the start temperature of  $[\text{Co}(\text{3-OHpy})_4\text{Cl}_2]$  ( $156^\circ\text{C}$ ). Further, the TG curve shows three stages of decomposition, with a total mass loss of 88.80 wt% (theoretical loss = 88.43 wt%). The DSC curve (Fig. 3) shows several endothermic peaks, with only one exothermic peak located at  $284^\circ\text{C}$ . This differs from the decomposition mechanism of the cobalt complex.

The non-isothermal TG curves for  $[\text{Co}(\text{3-OHpy})_4\text{Cl}_2]$  and  $[\text{Ni}(\text{3-OHpy})_4\text{Cl}_2]$  exhibit various stages of decomposition. Evaluation of the

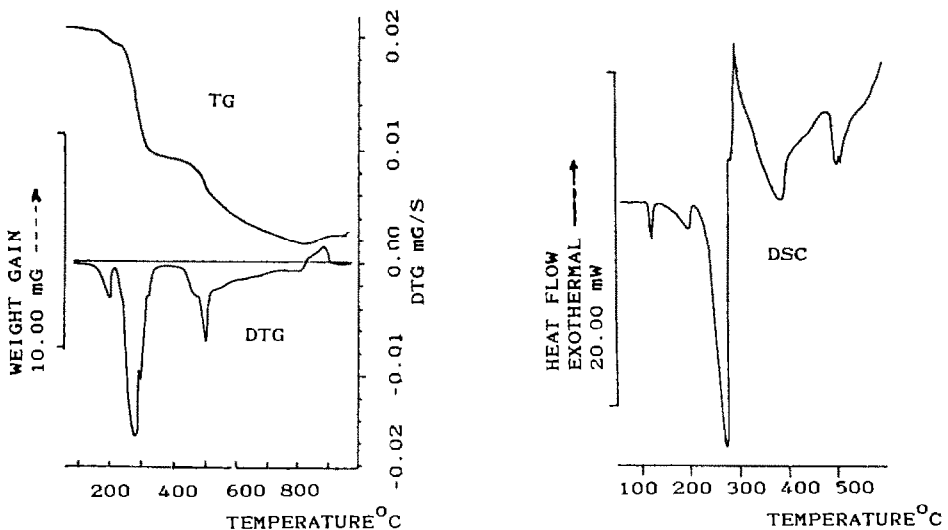


Fig. 3. TG, DTG and DSC curves for the trans  $[\text{Ni}(\text{3-OHpy})_4\text{Cl}_2]$  complex.

reaction mechanism from non-isothermal methods has been discussed by Sestake and Berggren [13] and Satava [14]. Their procedure is based on the assumption that non-isothermal reaction proceeds isothermally in an infinitesimal time interval, so the rate can be expressed by an Arrhenius-type equation

$$\frac{\partial \alpha}{\partial t} = A e^{-E/RT} f(\alpha) \quad (1)$$

where  $A$  is the pre-exponential factor,  $t$  is the time and  $f(\alpha)$  depends on the mechanism of the process. For a linear heating rate ( $Q = dT/dt$ ), substitution into eqn. (1) gives

$$\frac{\partial \alpha}{f(\alpha)} = \int_0^T \frac{A}{Q} e^{-E/RT} \partial T \quad (2)$$

Integration of the left-hand side of eqn. (2) gives

$$\int_0^\alpha \frac{\partial \alpha}{f(\alpha)} = g(\alpha) = \int_0^T \frac{A}{Q} e^{-E/RT} \partial T \quad (3)$$

where  $g(\alpha)$  is the integrated form of  $f(\alpha)$ . A series of  $f(\alpha)$  forms is proposed by Satava [14] and the mechanism is obtained from that plot which gives the best representation of the experimental data. For evaluating the kinetic parameters from the mechanistic equations, the right-hand side of eqn. (3) was used in the Coats–Redfern [15] equation recommended in several papers [16, 17]. The general form of the equation used is

$$\ln g(\alpha)/T^2 = \ln \frac{AR}{QE} - \frac{E}{RT} \quad (4)$$

Along with the mechanistic equation, two non-mechanistic methods and suggested by Coats–Redfern [15] and Horowitz and Metzger [18] were also used for comparison. The reaction order can easily be estimated by comparing the  $r$ -values using  $n = 0.33, 0.5, 0.66, 1$  and  $2$  in the plots

$$1 - (1 - \alpha)^{1-n}/(1 - n)T^2 \text{ vs. } \frac{1}{T} \quad (\text{for } n \neq 1) \quad (5)$$

$$\log[-\log(1 - \alpha)]/T^2 \text{ vs. } \frac{1}{T} \quad (\text{for } n = 1) \quad (6)$$

Using the above treatment, the kinetic parameters  $n$ ,  $E$  and  $\log A$  were estimated for  $\alpha \approx 0.5$  using non-mechanistic Coats–Redfern and Horowitz–Metzger equations, and presented in Table 4. The order for the reaction in these stages provide  $n = 2$  for both complexes with high correlation coefficient  $r$ -values. The values of  $E$  for both methods are lower

TABLE 4

Kinetic parameters for the decomposition of the complexes using non-mechanistic equations

Coats–Redfern			Horowitz–Metzger			Reaction order ( <i>n</i> )
<i>E</i> (kJ mol <sup>-1</sup> )	log <i>A</i> (s <sup>-1</sup> )	<i>r</i>	<i>E</i> (kJ mol <sup>-1</sup> )	log <i>A</i> (s <sup>-1</sup> )	<i>r</i>	
[Co(3-OHpy) <sub>4</sub> Cl <sub>2</sub> ]						
33.98	1.47	0.97217	39.92	1.48	0.97358	1
29.24	1.34	0.96211	35.47	0.98	0.96766	0
30.77	1.43	0.96574	36.91	1.14	0.96974	1/3
31.55	1.48	0.96748	37.64	1.23	0.97073	1/2
32.35	1.53	0.96915	38.39	1.31	0.97171	2/3
39.16	1.94	0.97971	44.80	2.02	0.97859	2
[Ni(3-OHpy) <sub>4</sub> Cl <sub>2</sub> ]						
61.75	2.98	0.97804	75.82	4.96	0.98242	1
51.80	2.60	0.97556	65.01	3.86	0.97965	0
54.96	2.77	0.97657	88.43	4.21	0.98073	1/3
56.60	2.86	0.97706	70.21	4.39	0.98121	1/2
58.27	2.95	0.97745	72.04	4.58	0.98165	2/3
73.16	3.74	0.97862	88.25	6.22	0.98381	2

for the cobalt complex than for the nickel complex, which might be due to the higher catalytic action of cobalt in an autocatalytic ligand oxidation.

The values of *E*, log *A* and  $\Delta S$  obtained from the mechanistic equations, along with the correlation coefficient for the kinetic plots from the TG curves have been evaluated for the three decomposition stages. The values of the kinetic parameters corresponding to the highest *r*-values are given in Table 5. The negative  $\Delta S$  values indicate a more ordered intermediate active state [19].

Table 5 shows that decomposition in the first stage for both complexes was governed by the three-dimensional diffusion ( $D_3$ ) spherical symmetry

TABLE 5

Kinetic parameters for the decomposition of the complexes using mechanistic equations together with the Coats–Redfern method

Stage	<i>E</i> (kJ mol <sup>-1</sup> )	log <i>A</i> (s <sup>-1</sup> )	$\Delta S$ (J K <sup>-1</sup> mol <sup>-1</sup> )	<i>r</i>	Kinetic model
[Co(3-OHpy) <sub>4</sub> Cl <sub>2</sub> ]					
I	73.61	2.94	-92.26	0.97648	$D_3$
II	17.75	1.46	-121.05	0.94021	$F_{n=2}$
III	53.61	1.00	-101.41	0.97926	$F_{n=2}$
[Ni(3-OHpy) <sub>4</sub> Cl <sub>2</sub> ]					
I	125.28	5.49	-62.88	0.98040	$D_3$
II	11.99	2.03	-125.55	0.88808	$F_{n=1}$
III	23.89	5.71	-122.11	0.99204	$R_2$

(Jander equation) followed in the second stage by the random nucleation mechanism ( $F_3$ ). Differences occurred in the last decomposition stage, where the phase boundary mechanism ( $R_3$ ) controlled the decomposition of the cobalt complex, in contrast to the random nucleation mechanism ( $F_{n=2}$ ) for nickel complex.

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