Journal of Thermal Analysis, Vol. 41 (1994) 859-870

THERMAL DECOMPOSITION OF NICOTINATE COMPLEXES OF COBALT AND NICKEL IN DYNAMIC NITROGEN ATMOSPHERE

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(Received June 2, 1992; in revised form June 7, 1993)

Abstract

Thermal decomposition of cobalt and nickel nicotinate was studied by TG, DTG and DSC. The mechanism of decomposition has been established from TG and DSC data. The kinetic parameters namely E, A together with ΔH were calculated from DSC curves using mechanistic and non-mechanistic integral equations.

Keywords: complexes, DSC, kinetics, nicotinate complexes of cobalt and nickel, TG

Introduction

Recently, increasing interest has been bestowed on the thermal decomposition of transition metal carboxylate complexes in the solid state [1, 2]. Both isothermal and non-isothermal methods have been used to evaluate the kinetics and mechanism of the thermal decomposition reaction [3]. A search through the literature revealed that no attempts have been made to undertake a quantitative study on the kinetics and mechanism of the thermal dehydration and decomposition of transition metal nicotinate complexes reactions. Thus, the present study investigates the kinetic, mechanistic and thermodynamic aspects of the thermal decomposition of nicotinate complexes of Co^{II} and Ni^{II} in the solid phase using non-isothermal TG, DTG and DSC techniques.

Experimental

Nicotinate complexes of Co^{II} and Ni^{II} were prepared by dissolving the metal carbonate in a hot solution of nicotinic acid. Excess metal carbonate unreacted was filtered from the hot solution. The filterate was concentrated over a steam bath till the complexes were crystallized and separated and washed with hot water. The resulting complexes were characterized by spectral and chemical methods. The metal content was analyzed using a varian AA-1475 series atomic absorption spectroscopy. H and C contents were obtained using a Carlo Erba microelemental analyzer model 1106. Data were cited in Table 1. IR spectra of the complexes were obtained using KBr disc technique in the range of 4000–200 cm^{-1} on a Pye Unicam SP 3300 IR spectrophotometer.

Thermoanalytical curves were recorded using a TA-3000 Mettler thermobalance for TG and DTG analysis and DSC-30 Mettler system for DSC measurements. Both cells were fed with a dynamic flow of nitrogen of 50 ml NTP min^{-1} in the temperature range of 50–1000°C for thermogravimetric measurements with a heating rate of 10 $deg \cdot min^{-1}$ and 10 mg sample weight. The DSC curve was obtained in the range of 50–600°C with 5 mg sample weight. Non-isothermal TG data were processed using a computer program designed by Beg *et al.* [4] with a PS/2 30 IBM microcomputer.

Results and discussion

Analytical measurements of Co^{II} and Ni^{II} concentrations together with the % of C, H and N as in Table 1 can predict the stoichiometric structure of the complexes as $M(Nic)_2 \cdot 4H_2O$ where $M = Co^{II}$ or Ni^{II} ions. The most important vibrational IR spectra bands of the complexes were cited in Table 2. The vibrational bands assigned in the range 3500–2700 cm^{-1} indicate the presence of crystallization water which is not co-ordinated. The $\nu_{C=O}$ vibrational bands in the complexes show a marked shift to higher frequencies while the bands due to the ring vibrations show a shift to lower frequency. The poor solubility of the compounds suggests a polymeric structure. The complexes are thus considered to have a planar arrangement with a nitrogen atom and oxygen atoms of the carboxylate group of each nicotinic acid bound to two different cobalt or nickel atoms to give chain-like structure. It is further suggested that each cobalt or nickel atom is bound to oxygen in the adjacent layers to give six coordinated environment for the metal atoms. The water molecules are attached by hydrogen bonding.

TG, DTG and DSC curves of nicotinic acid and nicotinate complexes of Co^{II} and Ni^{II} are given in Figs 1–3. TG and DTG of pure nicotinic acid involves one stage of decomposition started at 140°C and was completed at 304°C with a % mass loss of 100. TG and DTG curves of nicotinate complexes of Co^{2+} or Ni^{2+} show several stages of decomposition, four stages for cobalt nicotinate and two

Table 1 Elemental analysis of nicotinate complexes

Complexes	% Metal		% C		% H		% N	
	theo.	found	theo.	found	theo.	found	theo.	found
Cobalt nicotinate	16.05	16.18	39.24	39.41	3.27	3.44	7.63	7.69
Nickel nicotinate	16.00	16.31	39.27	39.50	3.27	3.37	7.63	7.71

Table 2 Infrared spectra of nicotinate complexes

Complex	$\nu_{OH(H_2O)}$	ν_{COOH}	ν_{COO^-}	ν_{CO}	$\nu_{ring\text{-}vib.}$	$\nu_{M\text{-}N}$
Nicotinic acid	–	1680	–	1310	1570	–
$Co(Nico.)_2 \cdot 4H_2O$	3500–2700	–	1600	1360	1550	350
$Ni(Nico.)_2 \cdot 4H_2O$	3500–2800	–	1600	1370	1540	400

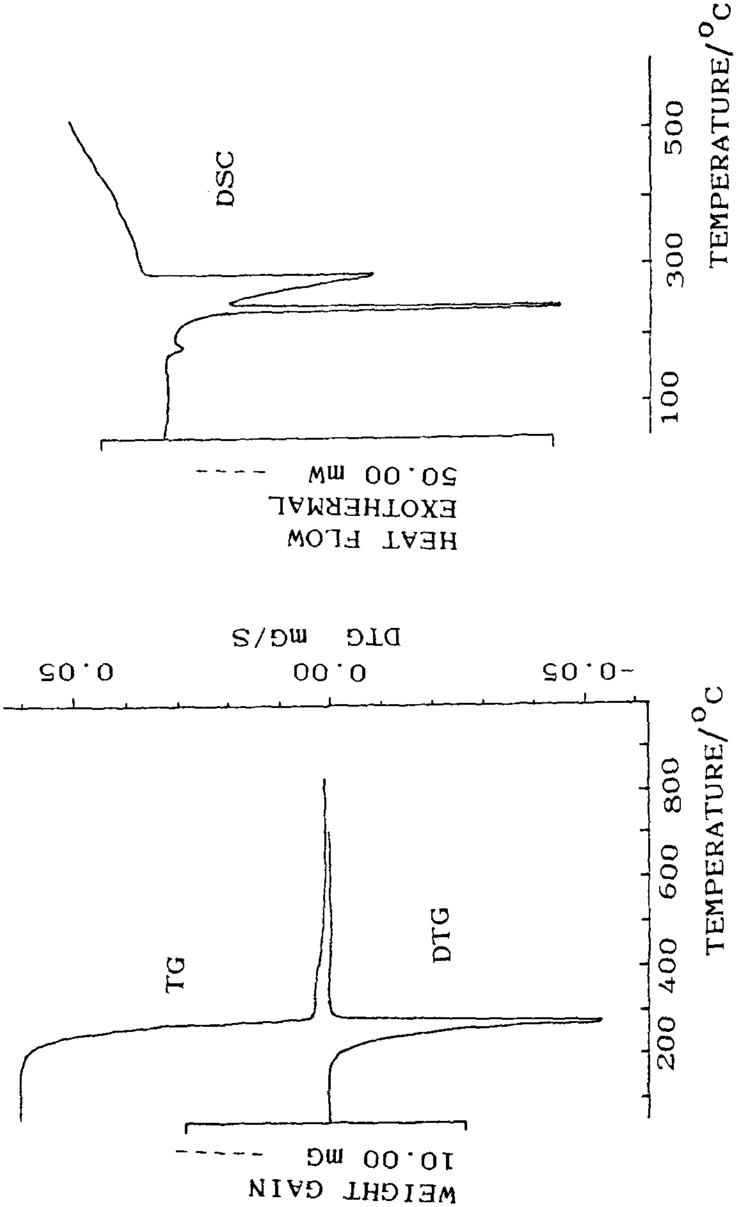

Fig. 1 TG, DTG and DSC for nicotinic acid

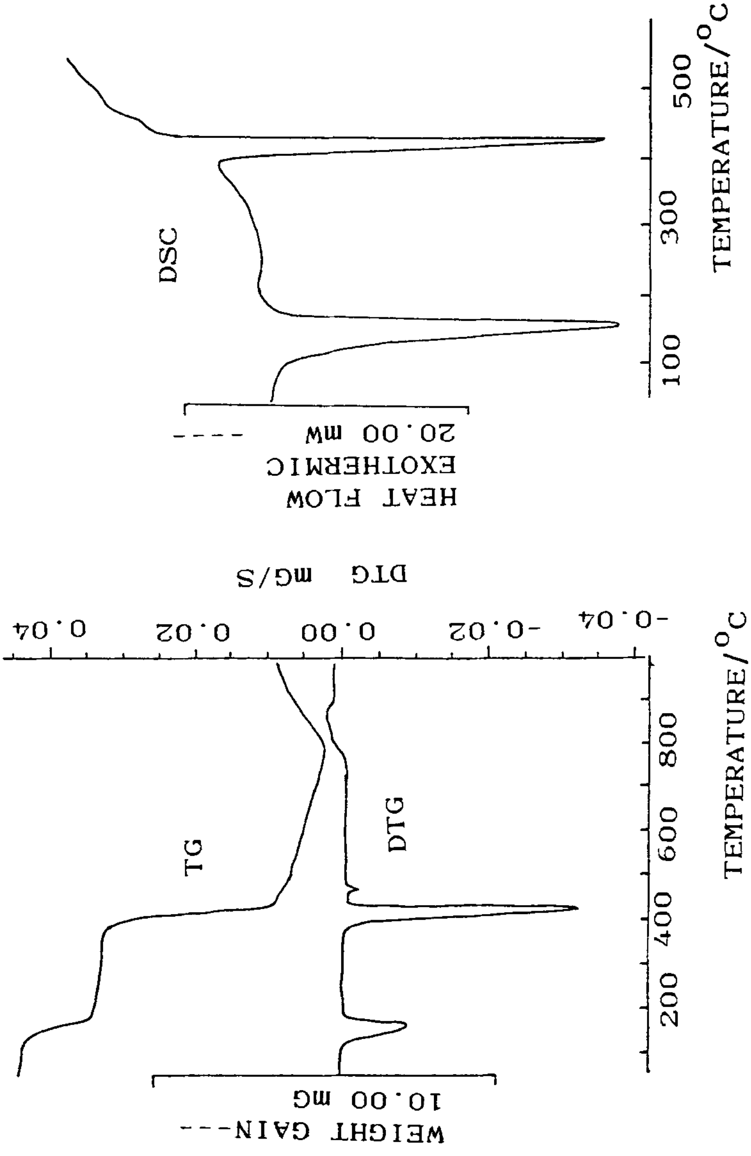

Fig. 2 TG, DTG and DSC for cobalt nicotinate complex

Table 5 Kinetic parameters for the decomposition of Co^{2+} and Ni^{2+} nicotinate complexes using non-mechanistic equations

Complex	Coats-Redfern			Horowitz-Metzger			Reaction
	E	lg*A*	*r*	*E*	lg*A*	*r*	order
Cobalt Nicotinate	92.55	3.67	0.96882	110.71	5.96	0.96488	1
	57.84	2.39	0.95755	73.54	2.99	0.97390	0
	68.01	2.82	0.95557	84.42	3.87	0.97141	1/3
	73.60	3.06	0.95391	90.41	4.35	0.96995	1/2
	79.55	3.30	0.95235	96.79	4.85	0.96836	2/3
	140.22	5.69	0.937361	161.83	9.95	0.95337	2
Nickel Nicotinate	42.91	1.56	0.90485	60.78	1.99	0.91639	1
	34.59	1.31	0.84352	51.34	1.21	0.91295	0
	37.25	1.44	0.84423	54.34	1.46	0.91073	1/3
	38.61	1.51	0.84437	55.90	1.59	0.90963	1/2
	40.01	1.58	0.84456	57.49	1.72	0.90854	2/3
	52.33	2.16	0.84455	71.47	2.87	0.90963	2

$E \neq \mathrm{kJ \cdot mol^{-1}}$ $A \neq \mathrm{s^{-1}}$

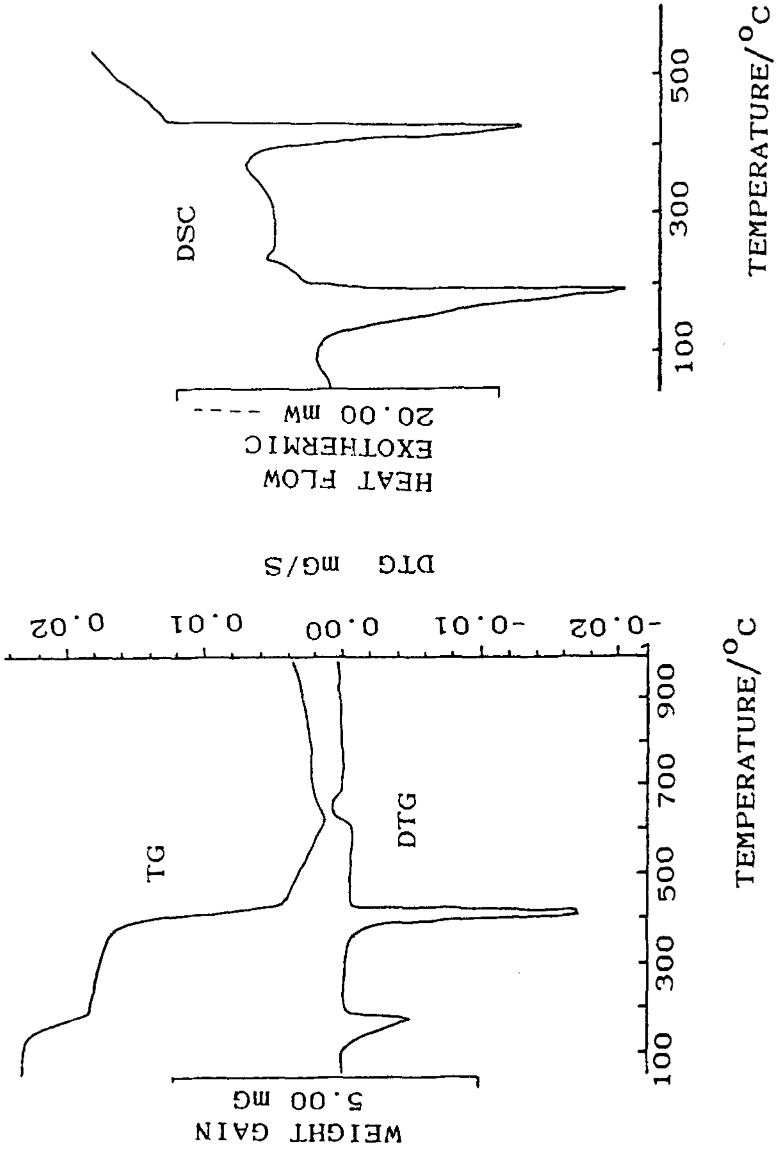

Fig. 3 TG, DTG and DSC for nickel nicotinate complex

of nickel nicotinate complexes. The temperature of inception T_i, temperature of completion T_f and maximum temperature of decomposition T_m together with mass loss percentages for each stage are given in Table 3.

From data in Table 3, cobalt nicotinate appears to decompose in the following steps:

$$Co(C_6O_2N)_2{\cdot}4H_2O \xrightarrow{162^\circ C} Co(C_6O_2N)_2 + 4H_2O$$

$$Co(C_6O_2N)_2 \xrightarrow{424^\circ C} CoCO_3 + CO + 2C_5H_5N$$

$$CoCO_3 \xrightarrow{472^\circ C} CoO + CO_2$$

$$CoO + 1/2O_2 \xrightarrow{870^\circ C} Co_2CO_3$$

Nickel nicotinate shows different decomposition pattern compared to cobalt complexes as shown in the following steps:

$$Ni(C_6O_2N)_2{\cdot}4H_2O \xrightarrow{179^\circ C} Ni(C_6O_2N)_2 + 4H_2O$$

$$Ni(C_6O_2N)_2 \xrightarrow{419^\circ C} NiO + 2C_5H_5N + 2CO$$

It is known that either NiO or Co_2O_3 oxides are of *p*-type solids which can chemisorb excess O_2 on its surface. This is the reason of TG inflection at higher temperatures.

DSC curves of the complexes Figs 2, 3 show endothermic peaks. Their temperatures and ΔH_{total} are cited in Table 4.

Table 4 Endothermic reaction temperatures and ΔH values for the thermal decomposition of nicotinate complexes

Complex	Stage	Temp/°C (DSC)	ΔH / Jg^{-1}	ΔH_{total} / Jg^{-1}
Cobalt Nicotinate	I	162	641.0	
	II	427	461.7	3906.8
Nickel Nicotinate	I	189	563.6	
	II	423	427.3	2992.5

The DSC profile of the complexes of Co^{2+} and Ni^{2+} showed two endothermic peaks. The first peak is located at 162 and 189°C for Co^{2+} and Ni^{2+} complexes, respectively, which is due to the dehydration process. It is interesting to note that dehydration of Ni^{2+} complex took place at higher temperature due to its thermodynamic stability. The second peak was located at 427 and 423°C which is due to the ligand decomposition. The last stages were out of the scale of our DSC instrument, while TG and DTG curves detected the formation of either Co_2O_3 or NiO as final thermal decomposition products.

TG curves for the complexes exhibited various decomposition stages. Evaluation of the reaction mechanism from non-isothermal methods has been discussed by Sestak and Berggren [5] and Satava [6]. The procedure is based on the assumption that non-isothermal reaction proceeds isothermally with a rate can be expressed by an Arrhenius-type equation:

$$\frac{d\alpha}{dt} = Ae^{-E/RT}f(\alpha) \tag{1}$$

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

$$\frac{d\alpha}{f(\alpha)} = \int_{o}^{T} \frac{A}{\varphi} e^{-E/RT} dT \tag{2}$$

on integration

$$\int_{o}^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_{o}^{T} \frac{A}{\varphi} e^{-E/RT} dT \tag{3}$$

where $g(\alpha)$ is the integrated form of $f(\alpha)$. A series of $f(\alpha)$ is proposed and the mechanism [7] is obtained from the one which gives the best representation of the experimental data. Using the proposed reaction mechanisms given by Satava [6] and using Coats and Redfern [8] equation, the general form of the equation used is :

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

Along with the mechanistic equation two non-mechanistic methods suggested by Coats and Redfern [8] and Horowitz and Metzger [9] were also used for comparison. The reaction order can be easily estimated by comparing the correlation coefficient values using $n = 0.33$, 0.5, 0.66, 1 and 2 in the equations.

$$1-(1-\alpha)^{1-n}/(1-n)\ T^2\ vs.\ 1/T \text{ for } n = 1 \tag{5}$$

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

Table 3 Phenomenological data for the thermal decomposition of nicotinate complexes of Co^{2+} and Ni^{2+} from TG curves in dynamic nitrogen atmosphere

Stage	Decomposition mode	T_i	T_f	T_m	Mass loss /%	
					obser.	theo.
I-Nicotinic acid						
	Total Decomposition	140	304	284	100	100
II-Cobalt Nicotinate						
1	4 mol H_2O	72	281	162	16.62	21.79
2	1 mol CO + 2 mol C_5H_5N	281	459	424	50.63	55.58
3	1 mol CO_2	459	781	472	12.86	12.00
4	3/2 mol O_2	786	947	870	+11.30	+13.80
	Total % mass loss				80.11	89.37
III-Nickel Nicotinate						
1	4 mol H_2O	113	199	179	19.20	21.79
2	2 mol C_5H_5N + 2 mol CO	308	475	419	55.25	55.58
	Total % mass loss				74.45	77.37

Using the above treatment, the kinetic parameters n, E, r and lg A were estimated using the non-mechanistic equations. Data obtained are cited in Table 5.

Table 6 Kinetic parameters for the decomposition of nicotinate complex of Co^{2+} and Ni^{2+} using mechanistic equations for TG curve

Mechanistic equation and model		Form of g(α)	Parameters	Nicotinate complex of	
				Co^{II}	Ni^{II}
1	(D_2)	$\alpha + (1-\alpha)\ln(1-\alpha)$	E	146.15	85.28
			lg A	5.51	3.06
			r	0.96167	0.87400
2	(D_3)	$[1-(1-\alpha)^{1/3}]^2$	E	170.37	90.93
			lg A	6.15	3.02
			r	0.95791	0.87249
3	(D_4)	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	E	154.14	87.16
			lg A	5.53	2.85
			r	0.96048	0.87354
4	(F_1)	$-\ln(1-\alpha)$	E	57.84	34.59
			lg A	2.39	1.31
			r	0.95755	0.84352
5	(A_2)	$[-\ln(1-\alpha)]^{1/2}$	E	40.64	16.01
			lg A	1.77	0.49
			r	0.93572	0.76447
6	(A_3)	$[-\ln(1-\alpha)]^{1/3}$	E	23.35	7.03
			lg A	0.97	0.14
			r	0.91706	0.61888
7	(R_2)	$1-(1-\alpha)^{1/2}$	E	73.61	38.61
			lg A	2.93	1.38
			r	0.95400	0.84438
8	(R_3)	$1-(1-\alpha)^{1/3}$	E	79.55	40.02
			lg A	3.09	1.37
			r	0.95239	0.844719

$A = s^{-1}$ $E = kJ \cdot mol^{-1}$

It appears that the correlation coefficients (r) are in the range 0.9688–0.9048 indicating nearly perfect fits. The order of these fits shows a first order reaction. The kinetic parameters computed with Horowitz-Metzger equation are higher than Coats-Redfern data. The higher values of E for cobalt nicotinate may be ascribed to reaction of Co^{II} with oxygen produced via decomposition and may involve oxidative addition to give a transient Co^{IV} species where it reacts with another Co^{II} to produce a binuclear peroxo-bridged species this can strengthen the complex.

The values of E and A obtained for the mechanistic equations along with the correlation coefficients for the kinetic plots from TG are presented in Table 6. It can be seen that the highest correlation coefficient values obtained are for D_2 mechanism. (Two dimensional diffusion, cylindrical symmetry.)

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Zusammenfassung — Mittels TG, DTG und DSC wurde die thermische Zersetzung von Cobalt- und Nickelnikotinat untersucht. Der Zersetzungsmechanismus wurde anhand der TG- und DSC-Daten entwickelt. Die kinetischen Parameter E, A wurden zusammen mit ΔH anhand der DSC-Kurven mit Hilfe von mechanistischen und nichtmechanistischen Integrationsgleichungen berechnet.