

## **KINETICS AND MECHANISM OF THE NON-ISOTHERMAL DECOMPOSITION Some Ni(II)-carboxylate-imidazole ternary complexes**

*E. M. Abd Alla<sup>1</sup> and M. I. Abdel-Hamid<sup>2</sup>*

<sup>1</sup>Chemistry Department, Faculty of Science, Minia University, Minia

<sup>2</sup>Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

(Received December 20, 1999; in revised form March 20, 2000)

### **Abstract**

The thermal decomposition of some Ni(II)-carboxylate-imidazole complexes in a nitrogen atmosphere was studied non-isothermally. From the non-isothermal thermoanalytical data, it was found that these complexes decompose through a stepwise release of imidazole molecules and/or CO ones forming unstable intermediates which produce metal oxide or the metal as a final decomposition product. TG in conjunction with DTG were used to evaluate the kinetic and thermodynamic parameters of the decomposition reaction. The kinetic studies were performed employing a computer-oriented kinetic analysis of each set of  $W-T$  data obtained under constant heating rate. The diffusion processes are the decisive mechanisms for the decomposition. The values of  $\Delta E$ ,  $A$ ,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for activation were calculated for the complexes and correlated to variation in their structure.

**Keywords:** DTG, Ni(II)-carboxylate-imidazole complexes, TG

### **Introduction**

The study of metal complexes containing the imidazole moiety is considered to be important in the context of understanding the nature of metal ion complexation in biological systems [1]. Although metallic-complexes containing ligands have been synthesized and studied intensively regarding both their structure and spectroscopic behaviour [2–5], only few studies concerning the thermal behaviour of such complexes have been reported [6–12]. Thermal analysis has been widely and successfully applied in determination [13, 14] of the stoichiometry and thermochemistry of the rate processes which contribute to the decomposition of these compounds. These stages may overlap and may be reversible, making non-isothermal kinetic data of dubious value.

The present article reports the synthesis, characterization and thermal behaviour of some Ni(II)-aromatic or aliphatic acids-imidazoles mixed ligand complexes. A computer-oriented program was used to evaluate both the thermodynamic and kinetic parameters as well as the appropriate model characterizing the non-isothermal degradation of such systems in the solid phase.

## Experimental

### *Preparation*

All chemicals used in the present study were of analytical grade (BDH Chemicals). The heterocyclic imidazole was of Aldrich products. The aromatic acids (phthalic, salicylic) and the aliphatic acids (succinic, malic) were of Prolabo products.

The different Ni(II) ternary complexes of aliphatic acids (succinic, malic) as primary ligand and imidazole as secondary ligand were prepared from the basic metal salt  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2$ , using the following method [10].

A mixture of the corresponding aliphatic acid (2 mmol),  $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  (1 mmol) and imidazole (5 mmol) was heated using water bath in 100 ml of absolute ethanol with magnetic stirring, and allowed to reflux for 2 h. The hot alcoholic mixture was then filtered. The obtained microcrystalline solid was filtered, washed with absolute ethanol and dried in vacuum.

On the other hand the Ni(II) ternary complexes containing the aromatic phthalic and salicylic acids were prepared by mixing 1 mmol of an ethanolic solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with an ethanolic solution of the aromatic acid (1 mmol) in the presence of potassium hydroxide (3 mmol). The precipitated potassium chloride was filtered off and the solution was concentrated and then filtered directly into an ethanolic solution of the imidazole (2–5 mmol). The resulting mixture was kept overnight in an ice bath. The precipitated crystalline complexes were filtered, washed several times with ethanol and then dried in air.

### *Chemical analysis*

The C, H and N contents of the mixed ligand chelates were determined on a Perkin Elmer 240 C apparatus. IR spectra were recorded using a 4000–400  $\text{cm}^{-1}$  range on a Shimadzu IR-470 spectrophotometer using KBr pellets.

### *Thermal studies*

TG and DTG were performed according to the technique described by Wendland and Collins [15], using DuPont-thermal Analyst 2000 equipped with 951 TG unit at a heating rate  $10^\circ\text{C min}^{-1}$  and dynamic nitrogen ( $30 \text{ cm}^3 \text{ min}^{-1}$ ).

## Results and discussion

### *Characterization of the isolated solid ternary complexes*

The ternary complexes, namely Ni(II)-malic-imidazole, Ni(II)-succinic-imidazole, Ni(II)-phthalic-imidazole and Ni(II)-salicylic-imidazole were isolated. Microanalytical data for the mixed ligand complexes (Table 1) prove to be commensurate with the general molecular formula  $\text{MLL}'_2$  for Ni(II)-salicylate and malate where the molecular for-

**Table 1** Microchemical analysis and physical properties of the synthesized mixed ligands chelates

Complex	Molecular formula	Mol mass	<i>m.p.</i> /°C	Colour	Found (calculated) composition/%		
					C	H	N
(A) [Ni(phthalate)(imid) <sub>4</sub> ]	[Ni(C <sub>8</sub> H <sub>4</sub> O <sub>4</sub> )(C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>4</sub> ]	494.63	235	pale violet	48.20 (48.52)	4.33 (4.04)	22.85 (22.64)
(B) [Ni(salicylate)(imid) <sub>2</sub> ·H <sub>2</sub> O]	[Ni(C <sub>7</sub> H <sub>5</sub> O <sub>3</sub> )(C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O]	349.66	115	pale blue	44.90 (44.62)	3.95 (4.29)	15.90 (16.02)
(C) [Ni(succinate)(imid) <sub>4</sub> ]	[Ni(C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> )(C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>4</sub> ]	446.91	185	pale violet	43.28 (42.96)	4.77 (4.47)	24.85 (25.06)
(D) [Ni(malate)(imid) <sub>2</sub> ]	[Ni(C <sub>4</sub> H <sub>4</sub> O <sub>5</sub> )(C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>2</sub> ]	326.75	290	pale blue	37.10 (36.72)	3.77 (3.67)	17.34 (17.14)

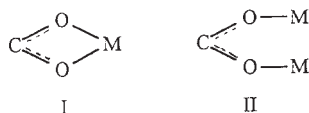
mula  $NiLL'_4$  is suggested for Ni(II)-phthalate and succinate-imidazole mixed ligand complexes, where  $L$  is aliphatic or aromatic dicarboxylic acid and  $L'$  is imidazole.

**Table 2** Tentative assignment of the important infrared frequencies ( $cm^{-1}$ ) of the Ni(II)-aromatic, aliphatic acid-imidazole ternary complexes

Assignment	Phthalic	Salicylic	Succinic	Malic
$\nu_{OH}$	–	3380	–	3380
$\nu_{NH}$	3200 b	3100 b	3120, 3050	3100, 3050
$\nu_{C-H}$	2920, 2820, 2600	2910, 2805, 2600	2920, 2850, 2700, 2600	2910, 2850, 2700, 2600
$\nu_{COO^-}$ asym.	1610	1615	1615	1595
$\nu_{C=N}$	1590	1588	1580	1580
$\nu_{COO^-}$ sym.	1420	1380	1410	1415

The IR spectra (Table 2) of the complexes containing malate and salicylate moieties as the primary ligands show a distinctive band in the  $3400\text{--}3280\text{ cm}^{-1}$  range which can be assigned to the free OH-group stretching vibration in these complexes. However, the weak character of the band (appearing as shoulder) in the complexes containing salicylic acid as a primary acid ligand can likely be ascribed to the contribution of the OH group of salicylic acid in complex formation with the central metal ion. The observed bands in the  $3150\text{--}2950\text{ cm}^{-1}$  region in all the synthesized complexes can be attributed to the secondary ligand N–H stretching vibration of imidazole. These observations substantiate the suggestion that the imidazole molecules coordinate to the central metal ion in their neutral form. The bands in the  $2960\text{--}2600\text{ cm}^{-1}$  region (medium to weak), in both aromatic and aliphatic acid complexes can be assigned to the C–H stretching vibrations in both the primary and secondary ligands. The distinct band appeared in the  $1615\text{--}1595\text{ cm}^{-1}$  region in all complexes, and is typical of coordinated carboxylate stretching vibration band [16]. This assignment is based on the fact that the nonionised and uncoordinated  $CO_2$  stretching band occurs at  $1750\text{--}1700\text{ cm}^{-1}$ , whereas the ionized and coordinated  $CO_2^-$  stretching vibration band appears in the  $1650\text{--}1590\text{ cm}^{-1}$  [16] region in all complexes which is consistent with the conclusion that the divalent anions of the primary ligand, aliphatic and aromatic acids are coordinated to the central metal ion as bidentate  $O^-$ ,  $O^-$  ligands. The band appearing in the  $1435\text{--}1380\text{ cm}^{-1}$  region is likely ascribed to the symmetric stretching vibration of the coordinated carboxylates [16]. In some complexes the band in the  $1630\text{--}1580\text{ cm}^{-1}$  region can be attributed to the imidazole C=N stretching vibration.

The spectra of all complexes confirm the absence of free carboxylic acid groups. The usual reduction in  $\nu(COO)$  compared with free  $-CO_2H$  is observed, characteristic of bonding types I and II in the complexes [17].



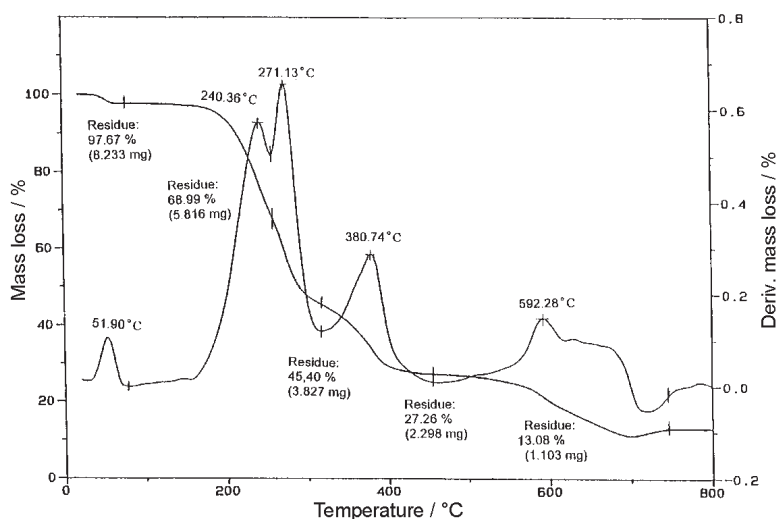
### Thermal analyses

TG and DTG were conducted in a nitrogen atmosphere. The obtained TG and DTG curves for the different synthesized Ni(II)-aromatic acids (A, B), aliphatic acids (C, D)-imidazole ternary complexes are shown in Figs (1–4).

#### Aromatic acid complexes

##### Complex (A)

Figure 1 for [Ni(phthalate)(imid)<sub>4</sub>], complex (A), shows that the complex decomposes via five thermal events. The first one is a small mass loss at 51°C, followed by pronounced four mass loss events maximized at 240, 271, 380 and 592°C.



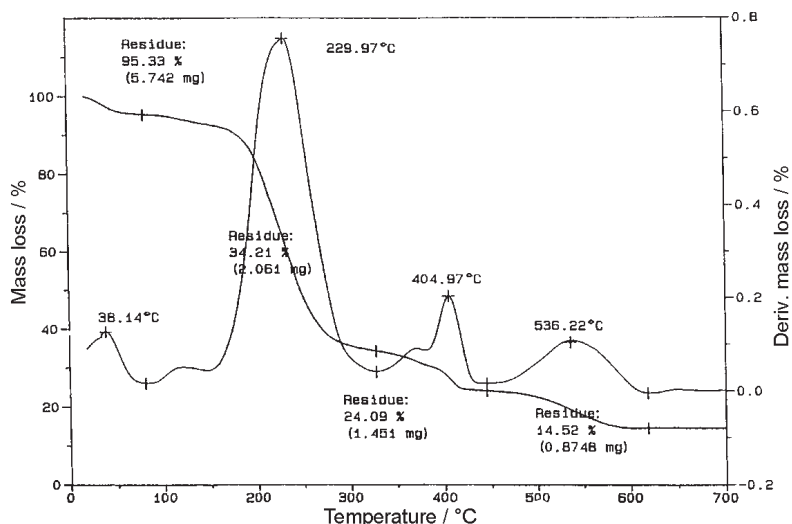
**Fig. 1** TG and DTG curves of complex (A) – [Ni(phthalate)(imid)<sub>4</sub>]; heating rate 10°C min<sup>-1</sup> and sample mass 8.43 mg

The first event that takes place at such low-temperatures can be attributed to the removal of the physically adsorbed water. The second pronounced peak, maximized at 240°C, is accompanied by a mass loss amounting to 31.01%, a value which is close to that calculated for the release of one molecule of and one molecule of phenyl radical which are formed as a result of the rupture of the weakest bond between the carboxyl group and the aromatic ring [18]. The respective mass loss (54.6%), corresponding to the third overlapped stage, matched with the calculated value anticipated to the elimination of two molecules of CO and another molecule of imidazole. This behaviour confirms that the first two imidazole molecules in the complex (A) are not isoenergetically bound and thus their elimination takes place via two different overlapping steps. The thermal event, maximized at 380°C, is accompanied by a 72.74% mass loss. This value goes parallel to the theoretical one (72.6%) which is attributed

to the removal of the third molecule of imidazole and the formation of an intermediate that has the composition Ni(imid)+C. Finally, the last stage, which extends over a wide range of temperature viz. 580–750°C, brings the total mass loss up to 86.92% of the parent complex. Such mass loss is close to the calculated (86.01%) value expected for the formation of Ni+C as a final product.

### Complex (B)

Examining the TG and DTG curves constructed for [Ni(salicylate)(imid)<sub>2</sub>·H<sub>2</sub>O], complex (B) Fig. 2, one can observe four mass loss stages. The first stage, maximized at 38°C, is responsible for the desorption of physically adsorbed water. The second pronounced event at 230°C is accompanied by a mass loss which amounts to 65.8%. This value finds a parallelism with the calculated value (65.5%) responsible for the elimination of different gaseous products leaving Ni(imid) as a solid residue. Inspection of the thermal event which is maximized at 405°C, one can conclude that NiO represents the solid product formed at the end of this stage. The final decomposition stage brings the total mass loss to a value of 85.5% which is higher than that calculated for the deposition of metallic Ni (84.0%).



**Fig. 2** TG and DTG curves of complex (B) – [Ni(salicylate)(imid)<sub>2</sub>·H<sub>2</sub>O]; heating rate 10°C min<sup>-1</sup> and sample mass 6.023 mg

### Aliphatic acid complexes

The constructed thermoanalytical curves corresponding to the synthesized Ni-aliphatic acid C,D-imidazole ternary complexes are given in Figs (3 and 4), respectively. A fast look on the curves, one can raise the following points: i) These com-

plexes are anhydrous, and ii) Their decomposition processes are simple in comparison with those for the aromatic ones.

Complex (C)

The TG and DTG curves obtained for the complex (C), [Ni(succinate)(imid)<sub>4</sub>] (Fig. 3), reveals that the decomposition process proceeds via two main stages. The first event is a

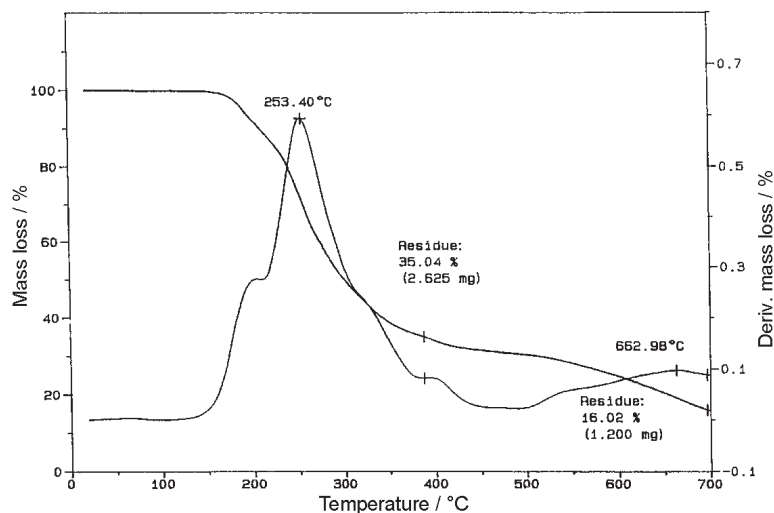


Fig. 3 TG and DTG curves of complex (C) – [Ni(succinate)(imid)<sub>4</sub>]; heating rate 10°C min<sup>-1</sup> and sample mass 7.49 mg

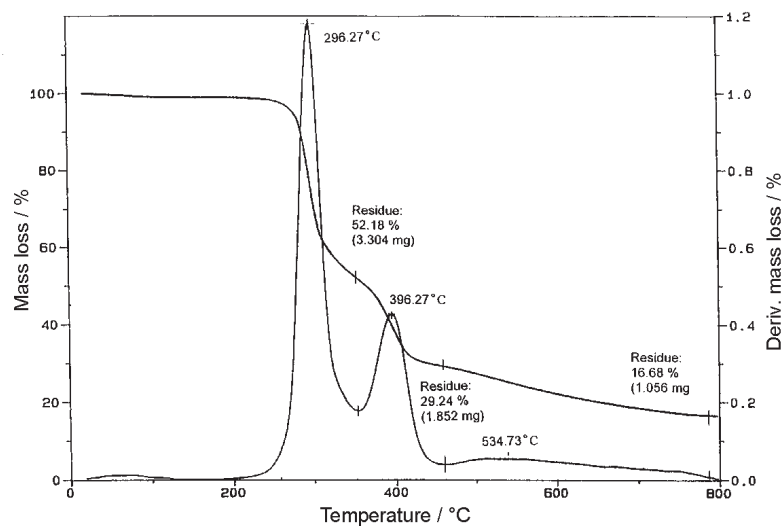


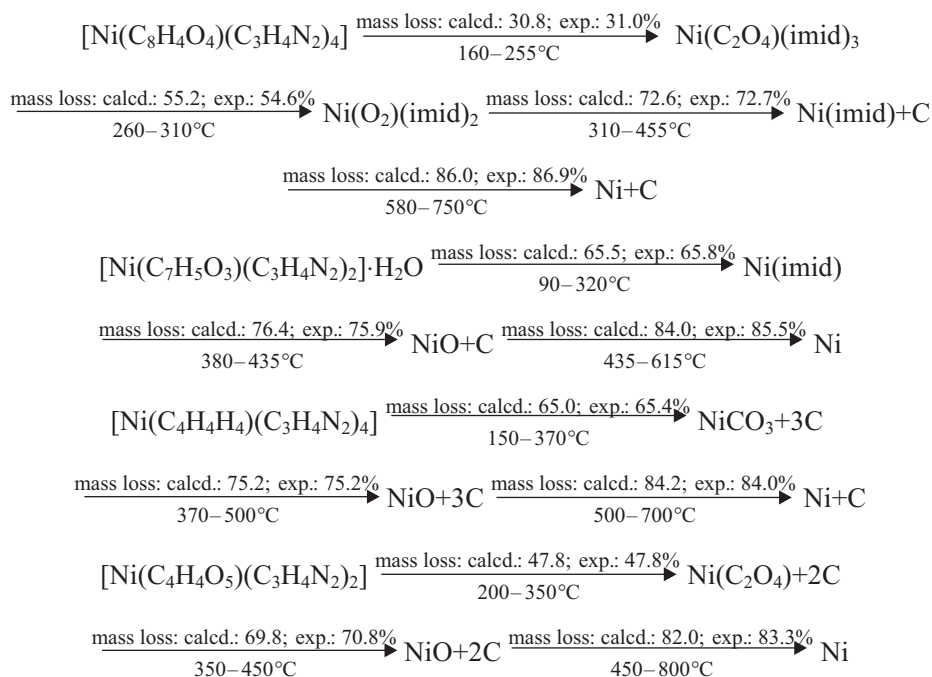
Fig. 4 TG and DTG curves of complex (D) – [Ni(malate)(imid)<sub>2</sub>]; heating rate 10°C min<sup>-1</sup> and sample mass 6.332 mg

composite one which has a three mutually overlapping peaks maximized at 253°C. The overall mass loss for the first stage amounts to 65.4%. This result indicates that the thermal decomposition process proceeds with the formation of NiCO<sub>3</sub> as an intermediate (65.0%). Raising the temperature beyond the above range would lead to the decomposition of the carbonate finally to (Ni+C) with a loss of 84.0% via the formation of NiO as an intermediate described by a weak step (mass loss 75.2%).

#### Complex (D)

The TG curve for the Ni(malate)(imid)<sub>2</sub>, complex (D), exhibits two distinct stages maximized at 296 and 396°C and are followed by a broad decomposition stage covering the temperature range (450–800°C). The mass loss, belonging to the first event, has a value of 47.8% which is very close to the calculated value representing the formation of Ni(C<sub>2</sub>O<sub>4</sub>) as intermediate. The second event involves a mass loss of 70.8% which can be ascribed to the decomposition of NiC<sub>2</sub>O<sub>4</sub> to form NiO (69.8%). Calculation based on the total mass loss 83.3% covering the final decomposition stage suggests the formation of Ni as a final product.

The general decomposition scheme of the different complexes can be summarized in the following mechanisms:



It is known that the reaction rate of a solid thermal decomposition leading to the evolution of a gaseous product, can be expressed by the general equation



$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where  $\alpha = (w_0 - w) / (w_0 - w_f)$ ,  $w_0$ ,  $w$  and  $w_f$  are the initial, actual and final sample masses, respectively.

The rate constant  $k$  is frequently assumed to obey the Arrhenius law

$$k = Ae^{-E/RT} \tag{2}$$

where  $A$  is the pre-exponential factor,  $E$  is the apparent activation energy,  $R$  is the gas constant and  $T$  the absolute temperature.

Integral methods use the equation of thermogravimetry in its integral form [19]

$$g(\alpha) = \frac{AE}{R\phi} P(x) \tag{3}$$

where  $g(\alpha)$  is the conversion integral,  $\phi$  is the heating rate  $dT/dt$  and  $P(x)$  is the exponential integral  $\int_x^\alpha \frac{e^{-u}}{u^2} du$  where  $u = E/RT$ .

The conversion integral  $g(\alpha)$  can be calculated easily if the conversion function  $f(\alpha)$  is assumed to be of the form

$$f(\alpha) = (1 - \alpha)^n \tag{4}$$

where  $n$  is the apparent reaction order.

**Table 3** Mechanism based equations

Rate controlling process	Mechanism	$g(\alpha)$
One dimensional diffusion	$D_1$	$\alpha^2$
Two dimensional diffusion	$D_2$	$\alpha + (1 - \alpha) \ln(1 - \alpha)$
Three dimensional diffusion (Jander function)	$D_3$	$[1 - (1 - \alpha)^{1/3}]^2$
Three dimensional diffusion (Ginstling–Brounshtein function)	$D_4$	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$
Phase boundary reaction $n=1, 2$ and $3$	$R_n$	$[1 - (1 - \alpha)^{1/n}]$
Random nucleation and its subsequent growth; $m=2$ and $3$ (Avrami–Erofeev function)	$A_m$	$[-\ln(1 - \alpha)]^{1/m}$
First order kinetics	$F_1$	$\ln(1 - \alpha)$

Kinetic analysis was performed using a computer program written in advanced Basic [19] for computing kinetic parameters as well as the decomposition mechanisms using four different mathematical kinetic methods [20–24]. The program is capable of performing kinetic analysis of values for the extent of reaction and the rate of reaction obtained from the experimental non-isothermal TG data and of subjecting the data to re-

**Table 4** Kinetic data for the non-isothermal decomposition of (Ni-aromatic, aliphatic acid-imidazol) ternary complexes

Complex	Stage	$E/$ kJ mol <sup>-1</sup>	$\text{Log}A/$ s <sup>-1</sup>	Kinetic model	Method	$\Delta S/$ J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta G/$ J mol <sup>-1</sup>	$\Delta H/$ J mol <sup>-1</sup>
(A)	I	174.740	8.45	D <sub>4</sub>	Coats-Redfern	-38.04	194.26	170.48
	II	284.458	13.10	F <sub>n2</sub>	Coats-Redfern	00.38	284.25	279.94
	III	223.303	9.10	F <sub>n2</sub>	Coats-Redfern	-33.49	245.17	217.87
	IV	131.271	5.49	F <sub>n0</sub>	Horowitz-Metzger	-64.52	186.95	124.10
(B)	I	115.776	9.98	F <sub>n2</sub>	Dharwadkar	-25.23	128.46	111.59
	II	289.387	28.23	F <sub>n2</sub>	Horowitz-Metzger	125.36	304.39	383.75
	III	177.994	5.78	F <sub>n1</sub>	Coats-Redfern	-61.86	227.98	171.28
(C)	I	70.137	3.76	F <sub>n2</sub>	Coats-Redfern	-77.13	110.86	65.75
	II	127.325	4.55	D <sub>2</sub>	Horowitz-Metzger	-72.64	195.46	119.53
(D)	I	222.966	18.64	F <sub>n2</sub>	Dharwadkar	46.33	196.65	218.24
	II	295.913	11.39	F <sub>n2</sub>	Coats-Redfern	-14.55	305.63	290.36
	III	116.551	3.93	F <sub>n2</sub>	Coats-Redfern	-77.30	179.01	109.83

gression analysis (least-squares method). The entropy of activation ( $\Delta S$ ) was calculated from the equation [25]

$$A = \frac{KT_m}{h} e^{-\Delta S/R} \quad (5)$$

where  $K$  is the Boltzmann constant,  $h$  the Planck constant and  $T_m$  the peak maximum temperature.

Then the calculation extend to compute the other thermodynamic parameters. The probable reaction mechanisms are listed in Table 3 and the corresponding correlation coefficients were calculated. The kinetic data obtained from the non-isothermal decomposition of the different complexes together with the appropriate kinetic model are cited in Table 4. The values of the different correlation coefficients were used to select the  $g(\alpha)$  values that best fit the actual mechanism of the studied decomposition reaction.

Inspection of Table 4 shows that the predominating mechanism for the decomposition processes have best fit with  $D_4$ ,  $Fn_1$  and  $Fn_0$  for the aromatic type complexes while  $D_2$  and  $Fn_2$  for the aliphatic ones. From the above findings, one can conclude that the diffusion processes are decisive mechanisms for the decomposition and that the rate of the decomposition is controlled by the rate at which the gaseous products can diffuse away from the reaction centers [26]. Regarding the values of the enthalpy corresponding to the total decomposition stages, they possess higher values for the aromatic complexes in comparison with those of the aliphatic one. This can be interpreted as due to the difference in their lattice stability.

Moreover, from the study of the decomposition of several carboxylate like complexes [18], one can conclude that the  $\alpha$ -carbon-H bond is the weakest and that, on reaction, this proton is transferred to an oxygen atom of another carboxylate group. Reduction of the metal ion is followed by the formation of CO which, in turn, can further reduce metal ions and the reaction yields finally the metal. In aromatic carboxylates, specially for salicylate complex, the bond between the carboxyl group and the aromatic ring is the weakest one. The phenyl radical formed on rupture of this linkage is capable of proton abstraction from the corresponding water of crystallization, so that the solid product is expected to the metal through the formation of metal oxide as an unstable intermediate. The above consideration finds a parallelism with the trend of variation of both kinetic and thermodynamic parameters for aliphatic complexes and aromatic ones.

From the correlations found between magnitudes of  $E$  for all the complexes under investigations and the enthalpy of formation of the appropriate metal oxides, one can conclude that the activation steps in the carboxylate breakdown was rupture of the  $-M-O$  linkage. This approach was applied [27] to the range of nickel salts for which  $E$  values were available, assuming that this parameter contained contributions from the following terms (i) an energy requirement for the dissociation of each  $-CO_2-Ni$  bond, (ii) a reduction of the energy barrier resulting from autocatalysis where the anion was chemisorbed on a metal particle and (iii) a reduction in the energy barrier where resonance stabilization of the activated anion complex was possible. This model was consistent with the observations available [27–29].

Finally, the values of  $\Delta S$  which are listed in Table 4 show negative values of entropy. This indicates the more ordered structures of the activated state compared to that of the corresponding reactant. Moreover, the decomposition processes of the different complexes under consideration may be compared on the basis that the easily decompose complex possessed a less negative entropy. This postulation is find a parallelism in less negative  $\Delta S$  values recorded for complex (B).

## References

- 1 H. Sigel, B. E. Fischer and B. Prijs, *J. Am. Chem. Soc.*, 99 (1977) 4489.
- 2 J. Reedijk, *Recl. Trav. Chim.*, 88 (1969) 145.
- 3 A. Santoro, A. D. Mighel, M. Zocchi and C. W. Reimann, *Acta Crystallogr. Sect. B*, 25 (1969) 84.
- 4 H. M. J. Hendriks and J. Reedijk, *Recl. Trav. Chim.*, 98 (1979) 95.
- 5 J. Reedijk and G. C. Verschoor, *Acta Crystallogr. Sect. B*, 29 (1973) 721.
- 6 P. S. Gomm, A. E. Underhill and R. W. A. Oliver, *J. Inorg. Nucl. Chem.*, 34 (1972) 1879.
- 7 J. C. Van Dam, G. Hakvoort, J. C. Jansen and J. Reedijk, *J. Inorg. Nucl. Chem.*, 37 (1975) 713.
- 8 M. C. Navarro Ranninger and M. Gayoso Andrade, *J. Thermal Anal.*, 14 (1978) 281.
- 9 J. G. Van Berkum, G. Hakvoort and J. Reedijk, *Thermochim. Acta*, 43 (1981) 49.
- 10 J. Masson, A. Busnot, F. Busnot, J. F. Hemidy and J. F. Le Querler, *Thermochim. Acta*, 122 (1987) 221.
- 11 R. Curini and S. Materazzi, *Thermochim. Acta*, 164 (1990) 237.
- 12 A. Busnot, J. Masson, J. F. Hemidy and J. F. Querler, *Thermochim. Acta*, 194 (1992) 265.
- 13 W. W. Wendlandt and J. P. Smith, *Thermal Properties of Transition Metal Ammine Complexes*, Elsevier, Amsterdam 1967.
- 14 D. Dollimore, in R. C. MacKenzie (ed.), *Differential Thermal Analysis*, Academic Press, New York 1970, Chp. 14.
- 15 W. W. Wendlandt and L. W. Collins, *Thermal Analysis*, Dowden-Nutchingol and Ross, 1976, p. 256.
- 16 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3<sup>rd</sup> ed., Wiley, New York 1978, p. 331.
- 17 J. R. Allan, B. R. Carson, D. L. Gerrard and S. Hoey, *Thermochim. Acta*, 158 (1990) 91.
- 18 J. Kitchen and J. L. Bear, *Thermochim. Acta*, 1 (1970) 537; *J. Inorg. Nucl. Chem.*, 31 (1969) 2415; 32 (1970) 49.
- 19 M. A. Beg and M. A. Qaiser, *Thermochim. Acta*, 173 (1990) 281.
- 20 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
- 21 A. W. Coats and J. P. Redfern, *Nature*, 201 (1964) 68.
- 22 H. H. Horowitz and G. Metzger, *Anal. Chem.*, 35 (1963) 1464.
- 23 J. Zsakó, *J. Phys. Chem.*, 72 (1968) 2406.
- 24 J. Zsakó and J. Zsakó, Jr., *J. Thermal Anal.*, 19 (1980) 333.
- 25 R. M. Gabr, M. M. Girgis and A. M. El Awad, *Thermochim. Acta*, 196 (1992) 279.
- 26 P. D. Garn, in H. Kambe and P. D. Garn (eds.), *Thermal Analysis, Comparative Studies on Materials*, Wiley, New York 1974, p. 100.
- 27 R. J. Acheson and A. K. Galwey, *J. Chem. Soc. A*, (1967) 1174.
- 28 M. J. McGinn, B. R. Wheeler and A. K. Galwey, *Trans. Faraday Soc.*, 67 (1971) 1480.
- 29 M. J. McGinn, B. R. Wheeler and A. K. Galwey, *Trans. Faraday Soc.*, 66 (1970) 1809.