

## **THERMAL DECOMPOSITION REACTIONS OF NICKEL(II) COMPLEXES UNDER QUASI-EQUILIBRIUM CONDITIONS.**

**Part I. Study of the relationship between thermal parameters and degree of distortion of the coordination polyhedron of the complexes  $\text{NiL}_4(\text{NCS})_2$  (L = piperidine, pyridine or 3-ethylpyridine)**

E. JÓNA

*Department of Inorganic Chemistry, Slovak Technical University,  
880 37 Bratislava (Czechoslovakia)*

I. HORVÁTH and M. KUBRANOVÁ

*Institute of Inorganic Chemistry, Centre of Chemical Research, Slovak Academy of Sciences,  
CS-842 36 Bratislava (Czechoslovakia)*

M. KOMAN

*Department of Inorganic Chemistry, Slovak Technical University,  
880 37 Bratislava (Czechoslovakia)*

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### **ABSTRACT**

The relationship between the thermal parameters (quasi-equilibrium decomposition temperature, activation energy and frequency factor) and the degree of the tetragonal distortion of the  $\text{NiL}_4(\text{NCS})_2$  complexes (L = piperidine, pyridine or 3-ethylpyridine) was studied. It was found that with increasing degree of tetragonal distortion of the coordination polyhedron of these complexes, the activation energy  $E_a$  also increases while the decomposition temperature (determined by quasi-isothermal measurements) decreases. The reasons for these differences are discussed.

### **INTRODUCTION**

The coordination polyhedron of nickel(II) is known to be relatively rigid [1,2]. The greater rigidity of nickel(II) complexes compared with that of copper(II) complexes is manifested in a stereochemical change from octahedral to square planar [3] owing to tetragonal distortion of the coordination polyhedron.

A measure of the relative tetragonal distortion in an octahedron is the ratio  $R_e/R_a$  [4] where  $R_e$  and  $R_a$  are the mean values of the central atom–ligand distances in the equatorial plane and in the axial direction,

respectively. Langfelderová et al. [5] found that the activation energy of the thermal decomposition of complexes  $M_2^I Cu(SO_4)_2 \cdot 6H_2O$  is related to the degree of tetragonal distortion ( $R_e/R_a$ ) of the  $[Cu(H_2O)_6]^{2+}$  cation. In the present study, the relationship between the thermal parameters (decomposition temperature, activation energy and heat of decomposition) and the degree of distortion of the octahedron in the complexes  $NiL_4(NCS)_2$  ( $L =$  piperidine, pyridine or 3-ethylpyridine) was studied. The structural parameters [6–8] were studied in the relation to the decomposition temperature estimated under quasi-equilibrium conditions (Q-derivatograph, quasi-isobaric, quasi-isothermal operation [9,10]), which is suitable for characterising the thermodynamic stability of isostructural compounds [11]. This method enables the thermal decomposition reaction to be studied independently of the pernicious effects of heat and gas transfer.

## EXPERIMENTAL

### *Synthesis and analysis of the samples*

The polycrystalline compound  $Ni(\text{pipe})_4(NCS)_2$  was prepared using solid  $Ni(NCS)_2$  (0.02 mol), benzene and liquid piperidine (0.1 mol). The mixture was boiled with stirring using a reflux condenser. The suspension obtained was then poured into a crystallising dish and allowed to crystallize freely [6,12]. The synthesis of the complexes  $Ni(\text{py})_4(NCS)_2$  and  $Ni(3\text{-Etpy})_4(NCS)_2$  has been described previously [7,8].

The compounds obtained were analysed for their nickel, carbon, hydrogen and nitrogen content.

### *Quasi-equilibrium decomposition measurements*

The Q-derivatograph under quasi-isobaric and quasi-isothermal conditions was used to study the decomposition process. This experimental technique results in stabilisation of the decomposition temperature, i.e. the experiment proceeds under quasi-isothermal conditions [9]. Using various sample holders, it is possible to keep the pressure of the gaseous products almost constant (conical crucible, about 90 kPa; covered standard crucible, about 20 kPa; open standard crucible, about 5 kPa).

### *Heat of decomposition and the kinetic parameters*

A Du Pont 990 thermoanalyser was used for the differential scanning calorimetry (DSC) and isothermal thermogravimetric (ITG) measurements. The decomposition of the samples (5–6 mg for DSC and 15–20 mg for ITG)

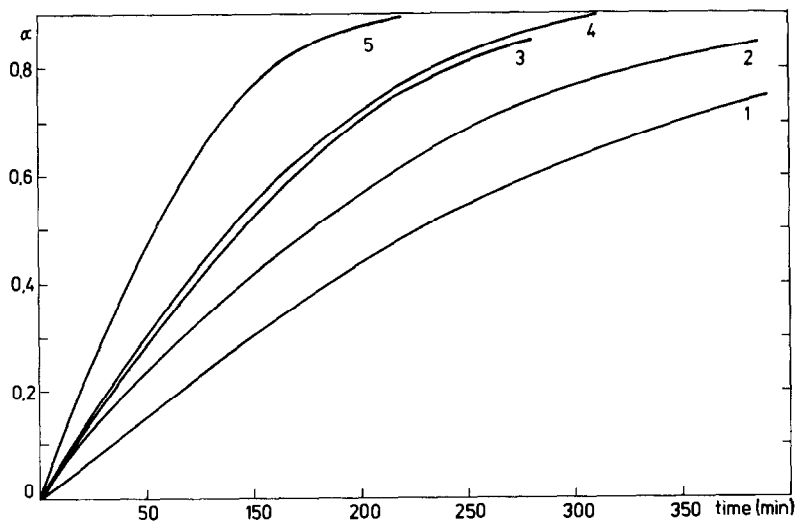


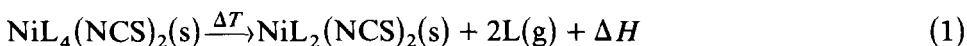
Fig. 1. Isothermal patterns of the thermal decomposition of  $\text{Ni}(\text{pipe})_4(\text{NCS})_2$ : curve 1,  $56^\circ\text{C}$ ; curve 2,  $58^\circ\text{C}$ ; curve 3,  $60^\circ\text{C}$ ; curve 4,  $60.5^\circ\text{C}$ ; curve 5,  $63.5^\circ\text{C}$ .

was carried out in a flowing nitrogen atmosphere ( $1\text{ cm}^3\text{ s}^{-1}$ ). A fraction ( $0.1\text{ mm} < d < 0.3\text{ mm}$ ) was used in the experiments. For the DSC, a constant heating rate of  $10^\circ\text{C min}^{-1}$  was used. The enthalpy changes were calculated via the relation  $\Delta H = kA/m$ , where  $k$  is the temperature-dependent constant extracted from the calibration curve,  $A$  is the DSC peak area and  $m$  is the mass of the sample. The isothermal TG patterns for the complex  $\text{Ni}(\text{pipe})_4(\text{NCS})_2$  (reaction 1) in the form of fraction reacted ( $\alpha$ ) vs. time is shown in Fig. 1. Analogous plots have been recorded previously for the decomposition of the complexes  $\text{Ni}(\text{py})_4(\text{NCS})_2$  and  $\text{Ni}(3\text{-Etpy})_4(\text{NCS})_2$  [10,11]. When looking for the appropriate kinetic model of decomposition, the experimental data were compared with the set of solid state reaction models in the relative time scale according to ref. [12]. The rate constants were extracted and Arrhenius parameters (activation energy  $E_a$  and frequency factor  $A$ ) were calculated.

## RESULTS AND DISCUSSION

The stoichiometry (stepwise character) of the thermal decomposition of solid nickel(II) complexes generally depends on various factors [13]: their crystal structure, the experimental conditions used in the measurements, and the properties of the ligands (electronic and steric). The thermal curves (at the constant heating rate) obtained for the  $\text{NiL}_4(\text{NCS})_2$  complexes studied show that the volatile ligands are released in two ( $\text{L} = \text{pyridine}$ ) or three

steps (L = piperidine and 3-ethylpyridine) [14,15]. In the first step of thermal decomposition, two volatile ligands escape according to the equation



where  $\Delta H$  represents the heat of the endothermal process. The coordination number six remains constant during decomposition, although structural rearrangement of the inner coordination sphere does occur [10]. Two releasing volatile ligands are substituted with the sulphur atoms originating from the adjacent NCS groups which in this way become multifunctional. In the study reported here a series of three  $\text{NiL}_4(\text{NCS})_2$  complexes were decomposed according to eqn. (1).

#### *Thermal decomposition under quasi-equilibrium conditions*

The Q-TG curves (Figs. 2–4), which were traced under quasi-isothermal heating conditions using different crucibles (open crucible, covered crucible, and conical crucible), provide comprehensive information about the reaction stoichiometry as well as the decomposition temperature.

The curves shown in Figs. 2–4 and the data listed in Table 1 show that under the conditions used the complexes studied decompose according to eqn. (1), with the exception of  $\text{Ni}(\text{E-Etpy})_4(\text{NCS})_2$  (conical crucible, Fig. 4).

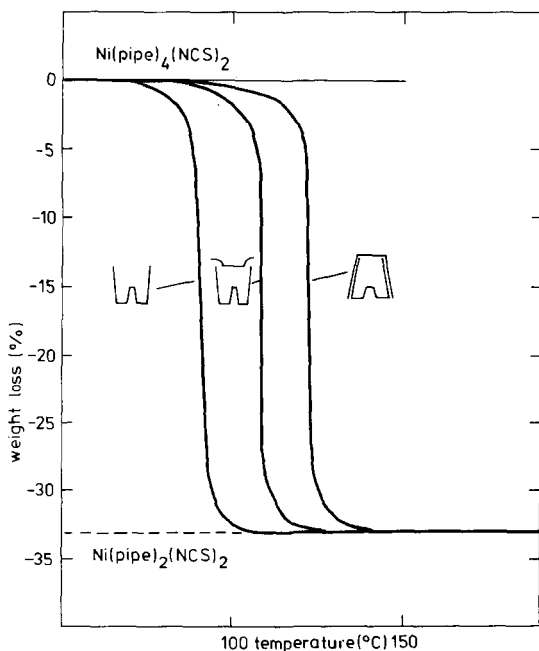


Fig. 2. Q-TG curves of  $\text{Ni}(\text{pipe})_4(\text{NCS})_2$  using various crucibles (quasi-isothermal heating programme; sample mass, 200 mg).

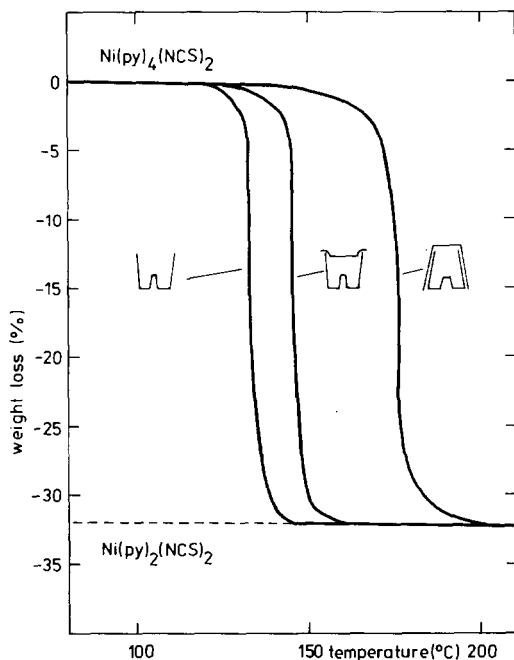
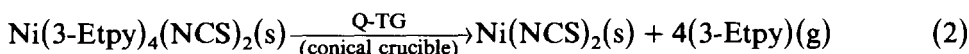


Fig. 3. Q-TG curves of  $\text{Ni}(\text{py})_4(\text{NCS})_2$  using various crucibles (quasi-isothermal heating programme; sample mass, 200 mg).




In this case no stable intermediate  $\text{Ni}(\text{3-Etpy})_2(\text{NCS})_2$  is formed and the stoichiometry of thermal decomposition may be described by the equation



The decomposition temperatures derived from the quasi-isothermal measurements can be used to set up a qualitative sequence of the thermodynamic stabilities of the compounds in identical thermal decomposition reactions [16]. According to the quasi-equilibrium data (Table 1) the thermodynamic stability of  $\text{NiL}_4(\text{NCS})_2$  compounds can be ordered in the follow-

TABLE 1

Stoichiometry of the thermal decomposition and the decomposition temperatures ( $T_D$ ) of the  $\text{NiL}_4(\text{NCS})_2$  complexes under quasi-equilibrium conditions (using various crucibles)

L						
	Stoichiometry	$T_D$ ( $^{\circ}\text{C}$ )	Stoichiometry	$T_D$ ( $^{\circ}\text{C}$ )	Stoichiometry	$T_D$ ( $^{\circ}\text{C}$ )
Pipe	-2(pipe)	90	-2(pipe)	108	-2(pipe)	122
Py	-2(py)	133	-2(py)	145	-2(py)	173
3-Etpy	-2(3-Etpy)	135	-2(3-Etpy)	153	-4(3-Etpy)	272

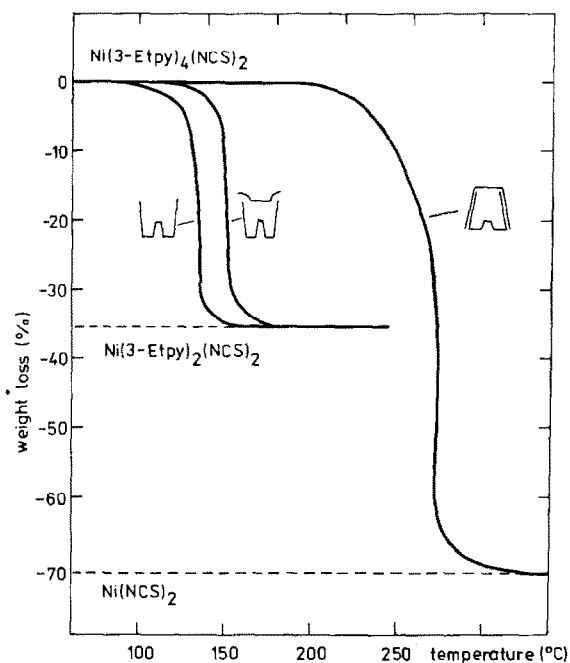


Fig. 4. Q-TG curves of  $\text{Ni}(3\text{-Etpy})_4(\text{NCS})_2$  using various crucibles (quasi-isothermal heating programme; sample mass, 200 mg).

ing sequence:

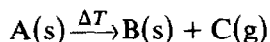


This sequence may be referred to the values of the interatomic distances  $R_e$  ( $R_e/R_a$ , Table 3).

#### *Kinetics and enthalpy change in decomposition*

There are two possible ways to study the mechanism of the thermal decomposition of solid complexes [17].

(a) Determination of the rate-controlling step (nucleation, diffusion, chemical reaction) in the solid state reaction



(b) Determination of the type of substitution mechanism (dissociative or associative) acting in the heterogeneous substitution reaction.

Using ITG measurements, the kinetics and mechanism (a) of the decomposition of  $\text{NiL}_4(\text{NCS})_2$  according to eqn. (1) were studied. Comparison of the experimental (isothermal) patterns with the model functions showed that the mechanism of decomposition (rate-controlling step) is the same for all

TABLE 2

Kinetic and thermochemical parameters of the isothermal decomposition of  $\text{NiL}_4(\text{NCS})_2$  complexes (eqn. (1))

Parameter	Coordination compound		
	$\text{Ni}(\text{pipe})_4(\text{NCS})_2$	$\text{Ni}(\text{py})_4(\text{NCS})_2$	$\text{Ni}(\text{3-Etpy})_4(\text{NCS})_2$
<i>Kinetic</i>			
$T$ ( $^{\circ}\text{C}$ )	56–63	76–82	82–91
Degree of conversion	$\alpha \in (0; 0.9)$	$\alpha \in (0.02; 1.0)$	$\alpha \in (0; 0.9)$
$E_a$ ( $\text{kJ mol}^{-1}$ )	137	111	70
$\ln A$ ( $\text{s}^{-1}$ )	40	29	19
<i>Thermochemical</i>			
$\Delta H$ ( $\text{kJ mol}^{-1}$ )	135	124	110

the complexes studied. The rate of decomposition may be described by the rate equation for the contracting area:

$$[1 - (1 - \alpha)^{0.5}] = kt \quad (4)$$

In order to calculate the rate constants and the Arrhenius parameters the isothermal runs were linearised using eqn. (3), indicating that decomposition starts on the surface of the crystals and proceeds uniformly into their centres. Thus the total decomposition rate may be considered to be controlled by the chemical process [17].

The macrokinetic parameters of the thermal decomposition processes are listed in Table 2. The values of the activation energy  $E_a$  and frequency factor  $A$  are ruled by the compensation effect  $\ln A = aE_a + b$  (Fig. 5), demonstrating the analogy with the mechanism of the decomposition processes studied [16]. Activation energy values increase in the following

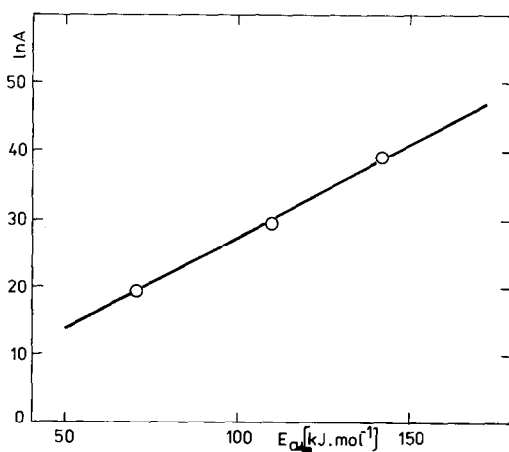


Fig. 5. Compensation plot for the thermal decomposition of the  $\text{NiL}_4(\text{NCS})_2$  complexes.

sequence:  $\text{Ni}(3\text{-Etpy})_4(\text{NCS})_2 < \text{Ni}(\text{py})_4(\text{NCS})_2 < \text{Ni}(\text{pipe})_4(\text{NCS})_2$ . This sequence contradicts the estimated thermodynamic stability of the compounds. A possible explanation would be that the rate of decomposition is determined not only by the splitting of the Ni-L bonds, but also by a polymerisation process (the formation of  $\text{NiL}_2(\text{NCS})_2$ ) in which these bonds are remodelled [18].

The  $\text{Ni}(\text{pipe})_4(\text{NCS})_2$  complex showed a higher  $E_a$  value as compared with the obtained  $\Delta H$  value (Table 2). This is in accordance with the requirement for an endothermal one-step reaction. The higher values of  $\Delta H$  for complexes with L = pyridine or 3-ethylpyridine may indicate the occurrence of a several-step reaction connected with the formation of an intermediate; this has been described previously [19].




#### *The relationship between thermal and structural parameters*

The crystals of  $\text{NiL}_4(\text{NCS})_2$  have a monomeric molecular structure. The Ni(II) atom exhibits distorted (slightly compressed) octahedral coordination geometry formed by two N atoms from the NCS groups and four N atoms from the heterocyclic ligands. The equatorial plane of these complexes is formed by four N atoms from the heterocyclic molecule (Ni-N (average) being  $R_e$ ) and the axial positions are occupied by two N atoms from NCS groups (Ni-N being  $R_a$ ). The comparison of the values of  $R_e/R_a$  (a measure of the relative tetragonal distortion [4]) shows a smaller tetragonal distortion for pyridine complexes compared with that found for the piperidine complex. It is evident from Table 3 that the  $R_e/R_a$  values for the pyridine complexes (1.038 and 1.048) are considerably different from that of the piperidine complex (1.160). Thus the properties of heterocyclic ligands play an important role in the tetragonal distortion of these complexes [1,2]. The degree of tetragonal distortion found for  $\text{NiL}_4(\text{NCS})_2$  increases in the sequence (Table 3)  $\text{Ni}(3\text{-Etpy})_4(\text{NCS})_2 < \text{Ni}(\text{py})_4(\text{NCS})_2 < \text{Ni}(\text{pipe})_4(\text{NCS})_2$ .

For the complexes studied, a decrease in the quasi-equilibrium decomposition temperatures ( $T_D$ ) with an increasing degree of tetragonal distortion ( $R_e/R_a$ ) is observed. However, it was found that the activation energy

TABLE 3

Thermal and structural parameters of  $\text{NiL}_4(\text{NCS})_2$  complexes

L	$T_D$ ( $^{\circ}\text{C}$ )			$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )	A	Structural data	
							$R_e/R_a$	Ref.
pipe	90	108	122	135	137	$2 \times 10^{17}$	1.160	6
py	133	145	173	124	111	$4 \times 10^{12}$	1.048	7
3-Etpy	135	153	272	110	70.0	$2 \times 10^8$	1.038	8



$E_a$  increases as  $R_e/R_a$  increases. We assume that with the increase of the degree of tetragonal distortion the total energy content of these systems decreases, e.g. the magnitude of the energy barrier ( $E_a$ ) increases. It seems therefore that elongation of the Ni–N(L) bonds in the equatorial plane affects the thermodynamic decomposition temperatures more than the value of  $E_a$ , which is connected with the total energy content of the systems.

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