Heterogeneous reactions of solid nickel(II) complexes XIX. Enthalpy change and mechanism in thermal decomposition of $Ni(NCS)_2py_4$

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The values of activation energy, frequency factor, and enthalpy change were used for an investigation of the kinetics of thermal decomposition reactions

I. $Ni(NCS)_2py_4\ (s) = Ni(NCS)_2py_2\ (s) + 2py\ (g) + \Delta H_1$

II. $Ni(NCS)_2py_2\ (s) = Ni(NCS)_2\ (s) + 2py\ (g) + \Delta H_2$

The first-order kinetics was found to be applicable in the initial stages of the reactions ($\alpha \in \langle 0; 0.2 \rangle$ — reaction (I) and $\alpha \in \langle 0; 0.5 \rangle$ — reaction (II)). The following stages of the decomposition obey the rate equation of the contracting area in the form

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

It was found that ΔH_2 is lower than the activation energy, which suggests an endothermal one-step reaction. The lower activation energy in the reaction (I) in comparison with ΔH_1 may evidence the formation of a metastable intermediate $[Ni(NCS)_2py_3]$ during decomposition.

Использованы величины энергий активации, частотного фактора и разницы энтальпий с целью исследования кинетики следующих реакций термического разложения

I. $Ni(NCS)_2py_4\ (s) = Ni(NCS)_2py_2\ (s) + 2py\ (g) + \Delta H_1$

II. $Ni(NCS)_2py_2\ (s) = Ni(NCS)_2\ (s) + 2py\ (g) + \Delta H_2$

Обнаружено, что на начальных стадиях реакции применима кинетика первого порядка ($\alpha \in \langle 0;0,2 \rangle$ для реакции I и $\alpha \in \langle 0;0,5 \rangle$ для реакции II). Последующие стадии разложения подчиняются скоростному уравнению стягивающейся поверхности в виде

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

Найдено, что величина ΔH_2 ниже, чем величина энергии активации, что соответствует одностадийной эндотермической реакции. Более низкое значение энергии активации реакции I по сравнению с ΔH_1 может

свидетельствовать об образовании метастабильного интермедиата $[Ni(NCS)_2py_3]$ в процессе разложения.

The complex $Ni(NCS)_2py_4$ (py — pyridine) is a model compound in the investigation of the thermal decomposition of Ni(II) solid complexes according to the scheme

$$Ni(NCS)_2L_4\ (s) = Ni(NCS)_2L_2\ (s) + 2L\ (g) + \Delta H_1 \qquad (A)$$
$$Ni(NCS)_2L_2\ (s) = Ni(NCS)_2\ (s) + 2L\ (g) + \Delta H_2 \qquad (B)$$

where L represents the organic ligand molecule and ΔH_1, ΔH_2 are the enthalpy changes in the endothermal decomposition processes [1, 2].

Previous studies [3—12] dealt mostly with the stoichiometry and kinetics of thermal decomposition of $Ni(NCS)_2py_4$ using dynamic, nonisothermal methods. In the present paper the relations between kinetic (activation energy, frequency factor) and thermochemical (enthalpy change) parameters are discussed. This work is a part of the study of mechanism in heterogeneous substitution reactions of the nickel(II) solid complexes.

Experimental

Chemicals and analytical methods

The synthesis of $Ni(NCS)_2py_4$ was carried out using $NiCl_2 \cdot 6H_2O$, KNCS, and pyridine (all anal. grade, Lachema, Brno). The nickel content was determined complexometrically using murexide indicator. The contents of carbon, hydrogen, and nitrogen were determined using the C. Erba model 11-02 automatic elemental analyzer.

The synthesis of $Ni(NCS)_2py_4$

The complex compound was prepared by the reaction of $NiCl_2 \cdot 6H_2O$ and KNCS in the ratio $n(Ni) : n(NCS) = 1 : 2$ dissolved in ethanol, followed by filtration of the KCl precipitate formed. To a solution of $Ni(NCS)_2$ pyridine was added in the ratio $n(Ni) : n(py) = 1 : 4$. The crystalline product was isolated, washed with ethanol and ether and dried in the air.

The composition of the prepared compound was found by analysis (12.01 mass % Ni, 17.04 mass % N, 53.80 mass % C, and 3.90 mass % H) to be in close agreement with theoretical expectation (11.95 mass % Ni, 17.11 mass % N, 53.97 mass % C, and 4.10 mass % H).

The morphology and size of the crystals are shown in Fig. 1. The TG, DTG, and DSC curves of the thermal decomposition of the complex are presented in Figs. 2 and 3.

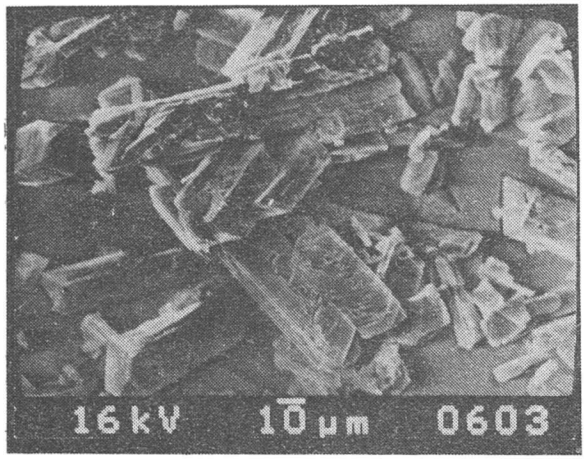


Fig. 1. The crystals of $Ni(NCS)_2py_4$ (scanning microscope Jeol SMU-3, sample covered with gold during rotation).

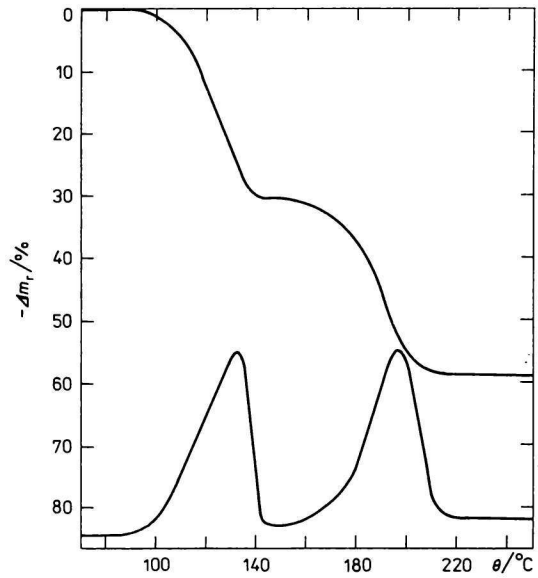


Fig. 2. The TG and DTG curves of the thermal decomposition of $Ni(NCS)_2py_4$ (nitrogen atmosphere, weight of the sample 10.20 mg, heating rate 5 °C min^{-1}).

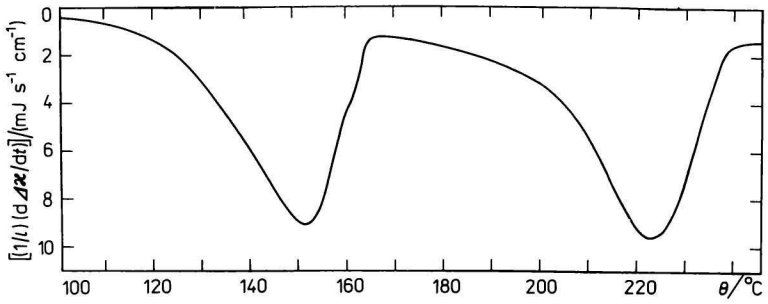


Fig. 3. DSC curve of the thermal decomposition of $Ni(NCS)_2py_4$ (nitrogen atmosphere, weight of the sample 5.61 mg, heating rate 10 °C min^{-1}).

Thermoanalytical methods

Thermoanalytical measurements were made using the DuPont 990 thermoanalyzer. The TG data were taken at a heating rate 10 °C min^{-1} or isothermally (the weight of the sample was 15—18 mg). An atmosphere of flowing nitrogen (at the rate 1 cm^3 s^{-1}) was used. Fig. 4 shows the isothermal patterns for the reaction scheme (*A*) in the form of fraction reacted (α) *vs.* time, where $\alpha = Z_t/Z_f$ (Z_t and Z_f are the actual and final weight losses, respectively). The analogous plots were found for the decomposition (*B*).

When looking for the appropriate kinetic model of decomposition the experimental data were compared with the set of the models in the relative time scale according to [13]. The

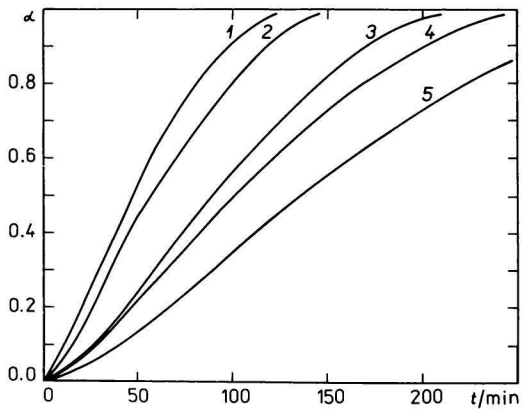


Fig. 4. Isothermal patterns of the thermal decomposition of the $Ni(NCS)_2py_4$ according to the reaction scheme (*A*) (nitrogen atmosphere, weight of the samples 10—12 mg).
1. 77 °C; *2.* 76 °C; *3.* 74 °C; *4.* 73 °C; *5.* 68 °C.

rate constants and Arrhenius parameters (activation energy E_A and frequency factor A) were then obtained by linearization of the isothermal plots.

Enthalpy measurements were made using a DSC cell (DuPont 990 DSC module working up to 725 °C) in a nitrogen atmosphere (heating rate 10 °C min^{-1}, flow of N_2 1 cm^3 s^{-1}, weight of the sample 5—6 mg). ΔH values were obtained from the DSC peak area from the relation

$$\Delta H = k \quad S \quad m^{-1} \tag{1}$$

where k is a constant depending on temperature and experimental conditions obtained by calibration of the DSC module using some standard materials (In, Sn, Zn, SiO_2, K_2SO_4), S and m are the DSC peak area and the sample mass, respectively.

Results and discussion

There are two possible ways in the study of the thermal decomposition of the solid complexes:

1. Determination of kinetics and the rate-controlling step (nucleation, growth of nuclei, diffusion) in the solid state reaction: AB(s) = A(s) + B(g).

2. Determination of the type of the substitution mechanism (dissociative D or associative A) in heterogeneous reaction

$$MX_n \xrightarrow{-X} MX_{n-1} \xrightarrow{+Y} MX_{n-1}Y \quad D \tag{C}$$

$$MX_n \xrightarrow{+Y} MX_nY \xrightarrow{-X} MX_{n-1}Y \quad A \tag{D}$$

where X and Y are the entering or leaving ligand molecules.

Using isothermal TG measurements, the kinetics and mechanism of the decomposition of $Ni(NCS)_2py_4$ according to the scheme (*A*) and (*B*) were studied separately. The comparison of isothermal patterns with the model functions showed that the mechanism does change during decomposition for both (*A*) and (*B*) processes. Data for the initial stages of decomposition ($\alpha < 0.2$ for (*A*) and $\alpha < 0.5$ for (*B*)) closely obey the first-order equation

$$\ln(1-\alpha) = -kt \tag{2}$$

The rate of decomposition in the next stages of the reactions (*A*) and (*B*) may be described by the rate equation for the contracting area

$$[1-(1-\alpha)^{0.5}] = kt \tag{3}$$

To calculate the rate constants as well as Arrhenius parameters the linearization of the isothermal runs was made using eqns (*2*) and (*3*).

The rate and activation parameters listed in Tables 1 and 2 indicate that E_A values in the initial stages for both (*A*) and (*B*) reactions are larger than those determined for following stages of the reaction, where the contracting area equation (*3*) is valid. It suggests that nucleation of the new phase controls the rate in the initial stages followed by the growth process (eqn (*3*)).

The observed obedience of the experimental data to the models (*2*) and (*3*) confirms this assumption. The first-order expression (*2*) reflects the initiation of the reaction at a number of preferred sites distributed in the whole volume of the reactant. The rate equation (*3*) describes the two-dimensional growth of these nuclei.

Table 1

The rate constants (k) of the thermal decomposition of $Ni(NCS)_2py_4$

Reaction scheme	θ/°C	k 10^3/min^{-1}	
		Interval of conversion degree α	
		$\alpha\in\langle 0;0.2\rangle$	$\alpha\in\langle 0.2;1.0\rangle$
(*A*)	76	7.7	6.7
	77	10.8	7.8
	78	12.3	8.7
	79	15.2	10.0
	82	27.6	12.5
(*B*)	126	8.8	5.2
	127	9.6	5.5
	129	11.9	7.0
	139	42.5	n.d.

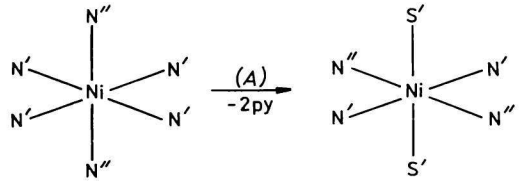
Table 2

Activation and thermochemical parameters of the thermal decomposition of $Ni(NCS)_2py_4$

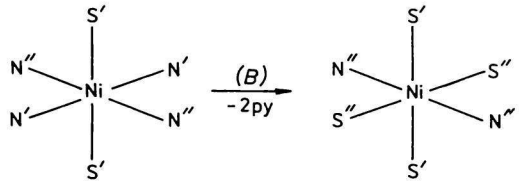
Reaction scheme	Initial compound	Interval of conversion degree α	E	A	ΔH
			kJ mol^{-1}	s^{-1}	kJ mol^{-1}
(*A*)	$Ni(NCS)_2py_4$	$\alpha\in\langle 0;0.2\rangle$	213.3	1.1×10^{29}	124.3
		$\alpha\in\langle 0.2;1.0\rangle$	110.5	3.8×10^{12}	
(*B*)	$Ni(NCS)_2py_2$	$\alpha\in\langle 0;0.5\rangle$	159.0	6.0×10^{18}	138.0
		$\alpha\in\langle 0.5;1.0\rangle$	143.0	5.3×10^{14}	

The values of frequency factor yield within 10^{12}—10^{18} s^{-1}, which assumes that both models may be applicable [14]. The optical observation would be required to supplement the thermal data.

The coordination number (C.N.) 6 is during decomposition constant, although the structural rearrangement of the inner coordination sphere does occur [8, 15].



(E)



(F)

N′ — N(py); N″ — N(NCS); S′, S″ — S(SCN).

Two releasing pyridine ligands are substituted with the sulfur atoms originating from the adjacent NCS groups which in this way are becoming multifunctional. These structural changes influence both the energy barrier in formation of the activated complex (E_A) as well as the possibility of its suitable orientation (frequency factor A), when the reaction product is formed.

The enthalpy change of the reaction (B) is smaller or approximately equal to the value of activation energy, which is in accordance with the requirement for endothermal one-step reaction (the reaction without formation of the metastable intermediate).

The reaction enthalpy ΔH_1, on the contrary, is greater than activation energy for prevailing part of conversion ($\alpha \in \langle 0.2; 1.0 \rangle$). This behaviour may evidence the formation of the unstable intermediate during reaction [14], *e.g.* $Ni(NCS)_2py_3$ the probable existence of which was reported previously [9, 16].

The reaction (A) would then proceed according to the scheme

$$Ni(NCS)_2py_4 \xrightarrow{-py} Ni(NCS)_2py_3 \xrightarrow{-py} Ni(NCS)_2py_2 \qquad (G)$$

In accordance with the dissociative mechanism described by (C), suggested for the pseudooctahedral complexes along with papers [11, 17], the intermediate with

a lower coordination number (C.N. = 5) may be formed. This intermediate in the next stage of decomposition yields the stable product of the reaction (*A*) $Ni(NCS)_2py_2$, with C.N. = 6.

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