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KINETICS AND ENTHALPY CHANGE IN DECOMPOSITION OF $Ni(NCS)_2(3\text{-}R\text{-}PYRIDINE)_4$ COMPLEXES (R = ETHYL, Cl, Br, CN, NH_2)*

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Isothermal TG and DSC measurements were used to study the effect of the pyridine substituent (3-R) on the kinetics and enthalpy change in the thermal decomposition of $Ni(NCS)_2(3\text{-R-py})_4$ complexes.

The found activation energies (E) of the interface advance decreased with the increase in volume of the substituent, allowing the assumption of a dissociative activation mechanism in the thermal decomposition reaction.

The relations between (E) and ΔH and the occurrence of the kinetic compensation effect $\ln A = f(E)$ are discussed.

With thiocyanate ion and 3-R-pyridine, Ni(II) ions form mixed ligand complexes of pseudooctahedral configuration, with four (3-R-py) ligands in the equatorial plane and the NCS groups in the axial direction. On heating, they liberate the pyridine ligands in two (R = Cl, Br, CN) or in several steps ($R = NH_2$, ethyl). During the first step of thermal decomposition two (3-R-py) ligands are released according to the equation:

$$Ni(NCS)_2(3\text{-R-py})_4(s) = Ni(NCS)_2(3\text{-R-py})_2(s) + 2\ (3\text{-R-py})(g) + \Delta H \qquad (1)$$

where ΔH represents the heat of decomposition.

The pseudooctahedral configuration remains for the dipyridine complexes formed the sulphur atoms from the NCS groups occupying the free positions in the coordination sphere of the central atom [1, 2].

In the study reported here, a series of five $Ni(NCS)_2(3\text{-R-py})_4$ complexes were decomposed according to Eq. (1) in a thermal analysis apparatus with the objectives of measuring the reaction kinetics and determining the heat of decomposition.

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* Part XX in the series Heterogeneous reactions of solid Ni(II) complexes.

Experimental

Preparation of the complexes

The complexes investigated were prepared by the reaction between $NiCl_6 \cdot 6\,H_2O$, KNCS and 3-R-pyridine in the polycrystalline state as reported previously [1].

Thermoanalytical measurements

A DuPont 990 Thermoanalyzer was used for DSC and isothermal TG measurements. All decompositions of 5–6 mg (DSC) and 15–20 mg (iso TG) samples were carried out under a nitrogen atmosphere ($1\ cm^3 \cdot s^{-1}$). For DSC a constant heating rate of 10 degree/min^{-1} was used. The enthalpy changes were calculated via the relation

$$\Delta H = k\frac{A}{m}$$

where k is the temperature-dependent constant extracted from the phase transformation enthalpies of the standard materials (In, Zn, Sn), A is the DSC peak area, and m is the weight of the analysed sample.

Kinetics

Data from isothermal runs were converted into α (proportion of complex reacted) against $t/t_{0.5}$ (where $t_{0.5}$ = time when $\alpha = 0.5$) plots, and the results were compared with similar plots for models based on diffusion, nucleation or phase-boundary control of the rate-limiting step [3, 4]. For the most probable mechanism the Arrhenius parameters were evaluated.

Results and discussion

The isothermal measurements show the effect of the pyridine substituent on the kinetics of thermal decomposition. Isothermal α *vs.* time curves for (3-Clpy) and ($3\text{-}NH_2py$) complexes were sigmoid and the reaction fitted a first-order equation (random nucleation in the whole volume of the reactant) when $\alpha < 0.2$:

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

Nucleation of the remaining dipyridine products (R = ethyl, Br, CN) occurred instantaneously and the nucleus growth was the rate-determining step, obeying the "contracting-disc" equation:

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

Similar results were obtained by Ball and Pope [5] in an investigation of the decomposition of (triphenylphosphine) Ir complexes.

The activation energies (E) found for the interface advance (nucleus growth) decrease in the sequence (Table 1):

$$\text{3-Clpy} > \text{3-NH}_2\text{py} > \text{3-Brpy} > \text{3-CNpy} > \text{3-Etpy}$$

If the thermal decomposition of the complexes is considered to be a heterogeneous substitution reaction (dissociative or associative mechanism [6]), then the above sequence of activation energies can be explained in terms of the steric properties of the ligands [7, 8]. The increasing steric density around the central atom (the increase in bulk of the ligands or the substituents on the ligands, respectively) will increase the activation energy in the formation of the bonds (associative activation), or decrease (*E*) in breaking bonds during the decomposition reaction (dissociative activation [6]).

For the complexes studied, a decrease of the (*E*) values with the increase of the substituent volume is observed, allowing the assumption that reaction [1] proceeds by dissociative activation. Complexes with the substitutents $R = \mathrm{Cl}$, Br and NH_2 showed higher *E* values as compared with the obtained ΔH values (Table 1). This is in accordance with the requirement for an endothermal one-step reaction. The higher values of ΔH for complexes with $R = \mathrm{CN}$ and ethyl may indicate the occurrence of a several-step reaction with the formation of an intermediate (e.g. $Ni(NCS)_2(3\text{-R-py})_3$). The existence of such intermediates was described previously [9, 10]. In accordance with the dissociative mechanism suggested for the studied compounds, an intermediate may be formed (with a lower coordination number C.N. = 5). The further reorganization of the crystal lattice during decomposition leads to the formation of $Ni(NCS)_2(3\text{-R-py})_2$ with C.N. = 6.

Table 1 Thermochemical and kinetic parameters in thermal decomposition of $Ni(NCS)_2(3\text{-R-py})_4$ complexes (Eq. 1)

	Substituent (R)				
	CN	NH_2	Br	Ethyl	Cl
ΔH, kJ • mol^{-1}	130.6	124.0	115.1	109.6	121.1
Kinetic (Eq. 3):					
Temp. interval, °C	128–136	143–155	100–104	82–91	101–104
Conversion degree	$0 < \alpha < 0.9$	$0.2 < \alpha < 1.0$	$0 < \alpha < 1.0$	$0 < \alpha < 0.9$	$0.2 < \alpha < 0.5$
Rate const. $k \cdot 10^4$, min^{-1}	16–28	46–116	29–44	67–121	53–93
Act. energy, *E* kJ • mol^{-1}	90	128*	126	70	205*
ln *A*, s^{-1}	20.7	31.6	34.9	19.1	60.7

* For the conversion degree $0 < \alpha < 0.2$ the nucleation is rate determining step (Eq. 2). Activation parameters for $Ni(NCS)_2(3\text{-}NH_2\text{-py})_4$: $E = 185$ kJ • mol^{-1}; $k \cdot 10^4$, min^{-1} = 1.6–3.4 (temp. interval 139–145°C); for $Ni(NCS)_2(3\text{-Cl-py})_4$: $E = 207$ kJ • mol^{-1}; $k \cdot 10^4$, min^{-1} = = 26–44 (temp. interval 101–104°C).

Figure 1 shows the dependence $\ln A = f(E)$, obeying the relation $\ln A = aE + b$ (the compensation effect). Different 3-R-py molecules (in particular the steric effects

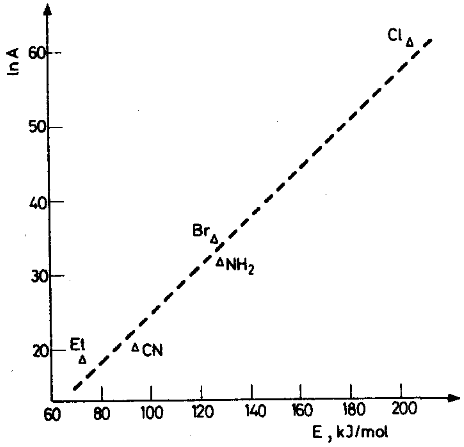

Fig. 1 Compensation plot for decomposition of $Ni(NCS)_2(3\text{-}R\text{-}py)_4$ complexes (R = Cl, Br, CN, NH_2, ethyl)

of the substitutents) influence both the magnitude of the energy barrier (E) and the possibility of formation of an activated complex and its suitable orientation (A) when the reaction product is formed [11].

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