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HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES, V

THERMAL DECOMPOSITION OF COMPOUNDS OF THE TYPE $Ni(NCS)_2L_2$. PART C: KINETIC STUDY OF PSEUDOOCTAHEDRAL COMPLEXES

E. Jóna, V. Jesenák,* T. Šramko and J. Gažo

*Department of Inorganic Chemistry and *Department of Chemical Technology of Silicates, Slovak Technical University, Bratislava, Czechoslovakia*

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The kinetics of the thermal decomposition of solid complexes of the type $Ni(NCS)_2L_2$ (L = pyridine, β-picoline and quinoline), of pseudooctahedral configuration, were studied by using isothermal methods, on the basis of losses of weight, in the temperature range 90–191°. The most suitable reaction order for all the complexes under investigation was found to be $n = 2/3$, i.e. the total decomposition rate is determined by the chemical process proper. The calculated values of E_a (in kcal · mole^{-1}) decrease in the following order: $Ni(NCS)_2py_2$ (29.4) > $Ni(NCS)_2(\beta\text{-pic})_2$ (27.6) > $Ni(NCS)_2Q_2$ (24.3). With increasing volume of the ligand L the reaction rate also increases, and this suggests that the reaction proceeds by dissociative activation. For all the investigated complexes it was found that $\Delta H > E_A$; this may be explained by a several-step mechanism and the complex $Ni(NCS)_2L$ is then considered an intermediate.

Though numerous papers have been published dealing with the thermal decomposition of solid coordination compounds [1], as yet there exists no conclusive experimental information enabling us satisfactorily to sum up all the problems of the kinetics and of the mechanism of thermal decomposition of solid complexes. The reason lies in the complicated characters of these reactions due to transport phenomena occurring in the solid state.

A great number of kinetic measurements of the thermal decomposition of nickel(II) complex have been made by Murgulescu et al. [2–4]. The results obtained are mostly explained by the conception of diffusion of the volatile component through a layer of the decomposed compound. Some authors [5–8] compare the strengths of the Ni-volatile ligand bond by means of the activation energies E_a. More rarely, papers are published using kinetic analysis to study the substitution mechanism (the dissociative or associative mechanism) in the thermal decomposition of solid complexes [9–11].

With respect to the relatively simple experimental techniques and especially to their rapid performance, even though they are less exact, most authors apply non-isothermal methods in the kinetic analysis [12]. In an investigation of the decomposition mechanism the isothermal method appears to be more suitable [13–15]; it has also been applied in our work in studying the kinetics and the mechanism of thermal decomposition of complexes of the type $Ni(NCS)_2L_2$. This paper deals with the pseudo-octahedral complex of this type (L = pyridine, β-picoline or quinoline).

Experimental

The chemicals, analytical methods, preparations and analytical results for the complexes under investigation were reported in a preceding paper of this series [16].

The kinetics of the thermal decomposition of the solid complexes were followed with an OD 102 Derivatograph (MOM, Budapest). The platinum crucibles with profiled bottoms were replaced for the isothermal technique by crucibles of brass, with plane bottoms, placed on a base of the same material. To avoid diffusion hindrances in the sample the thickness of the layer was 1 mm maximum. In place

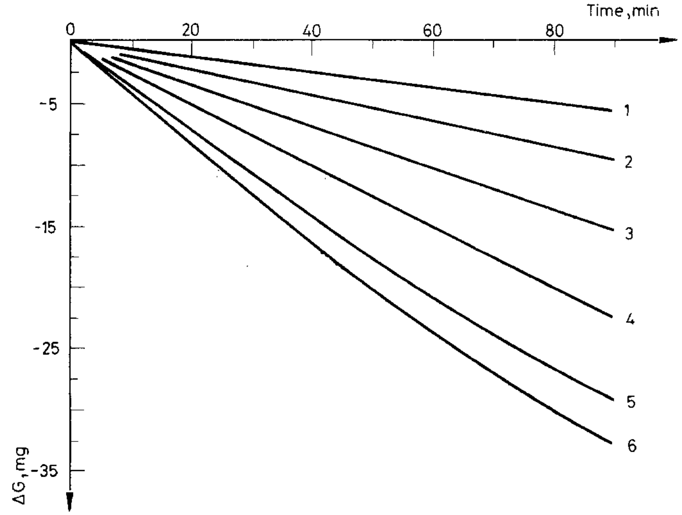

Fig. 1. Change of weight with time for the complex $Ni(NCS)_2py_2$ at constant temperatures: 1 — 162°, 2 — 170°, 3 — 175°, 4 — 181°, 5 — 187°, 6 — 191°

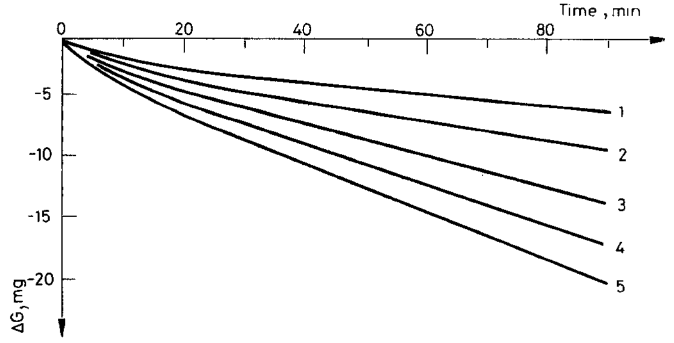

Fig. 2. Change of weight with time for the complex $Ni(NCS)_2(\beta\text{-pic})_2$ at constant temperatures: 1 — 125°, 2 — 132°, 3 — 138°, 4 — 141°, 5 — 144°

of the furnaces supplied with the equipment, we constructed our own furnace for temperatures up to 200°. Constant temperature was maintained by means of a contact thermometer, as already used in studying the kinetics of the reactions of the solid dichlorotetrathioureanickel(II) complex with gaseous ammonia [17]. All samples weighed 100 mg and their grain size was smaller than 0.06 mm. The kinetics were studied by thermogravimetry, by following the loss of weight at given temperatures in a nitrogen atmosphere. The sample was measured into the crucible and the preheated furnace was switched on. The temperature was measured with Pt, Pt-Rh thermocouples with a precision of ±0.5°C. The total time of one measurement was 80 min.

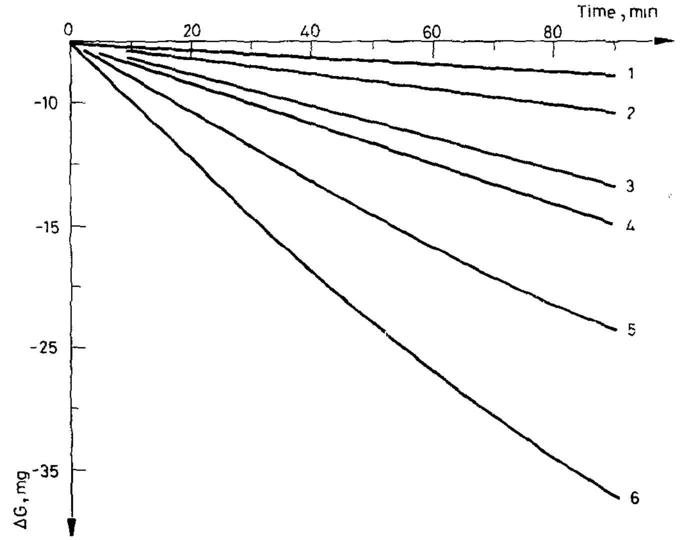

Fig. 3. Change of weight with time for the complex $Ni(NCS)_2Q_2$ (II) at constant temperatures: 1 – 90°, 2 – 98°, 3 – 108°, 4 – 112°, 5 – 116°, 6 – 125°

Figs 1–3 show the experimentally found functions of the weight losses vs. the reaction duration for constant temperatures. These curves yielded the values of the degrees of conversion (α) of the initial solid component. The values obtained were correlated by the kinetic equations

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \tag{1}$$

where k is the rate constant and n the reaction order (0, 1/3, 2/3 and 1). The best agreement was found for the exponent $n = 2/3$. The integrated equation then has the form

$$1 - (1 - \alpha)^{1/3} = k' \cdot t \tag{2}$$

The dependences of $1-(1-\alpha)^{1/3}$ on time are shown in Figs 4–6. From these lines the values of the rate constants were calculated for the given temperatures. The dependence of the rate constants on the temperature corresponds to the Arrhenius equation as can be seen in Fig. 7.

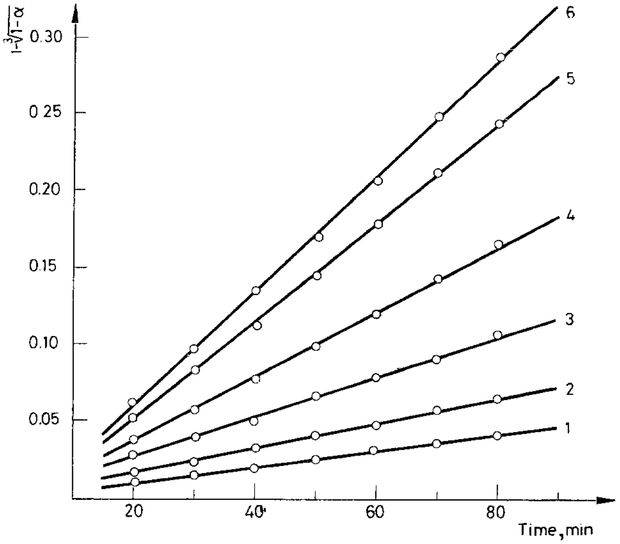

Fig. 4. Change of $1-(1-\alpha)^{1/3}$ with the duration of the decomposition of $Ni(NCS)_2py_2$: 1 – 162°, 2 – 170°, 3 – 175°, 4 – 181°, 5 – 187°, 6 – 191°

The relation

$$\log\frac{k_2'}{k_1'}=\frac{E_a}{2.3R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \tag{3}$$

leads to the apparent activation energy values E_a: 29.4 kcal · mole^{-1} for $Ni(NCS)_2py_2$; 27.6 kcal · mole^{-1} for $Ni(NCS)_2(\beta\text{-pic})_2$ and 24.3 kcal · mole^{-1} for $Ni(NCS)_2Q_2$ (II) (the pseudooctahedral isomer).

Discussion

There are at present general methods for the study of the mechanisms of heterogeneous reactions of the type $A_{(s)} \leftrightarrow B_{(s)} + C_{(g)}$ [13]. In the exact process the mechanisms of the different reactions are expressed by a number of kinetic equations; these are compared with experiment, and the most probable mechanism is selected. These hypothetical equations, however, are usually complicated and we have preferred therefore the simpler method of defining the process kinetics, starting from the general differential equation (1). The process mechanism is then reflected in the reaction order *n*, which is usually between 0 and 1; the cases:

$n = 0$, 1/3; 2/3 and 1, have been physically interpreted [14, 18, 19]. Zero order fits the case when the diffusion of the split-off gaseous component from the free substance surface into the space above it takes place more slowly than the other processes. For regular decomposition, not hindered by diffusion, on an ideal spherical particle surface, when all the other processes are much more rapid than the decomposition proper, the order of 2/3 appears. Reactions of the 1st order may be expected only under special circumstances, since they assume the same probability of decomposition for all the molecules during the whole reaction course. The order of 1/3 is observed according to [18, 19] for the case when the controlling process is represented by the diffusion of the gaseous product from the inside of the crystal to the surface. According to recent sources [20], however, for this case the equation of the kinetics is more complicated.

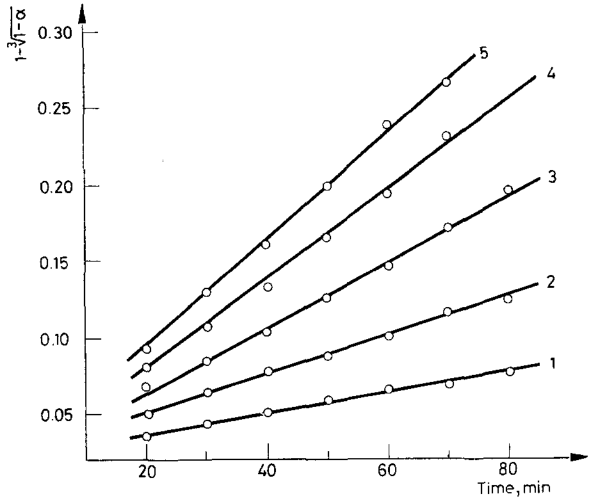

Fig. 5. Change of $1-(1-\alpha)^{1/3}$ with the duration of the decomposition of $Ni(NCS)_2(\beta\text{-pic})_2$: 1 – 125°, 2 – 132°, 3 – 138°, 4 – 141°, 5 – 144°

In the thermal decomposition of pseudooctahedral complexes of the type $Ni(NCS)_2L_2$ by the isothermal method the reaction order 2/3 has been found to fit best, indicating that the decomposition starts on the surface of the crystals and proceeds uniformly to their centers, as also proved by macroscopic investigation. Thus, the total decomposition rate may be considered to be controlled by the chemical process proper [20].

The studied complexes showed fairly considerable differences in their E_a values (and consequently also in the decomposition rates). With respect to the fact that the overall decomposition rates of these compounds are controlled by the same process (the so-called "rough mechanism"), the reasons of these differences have to be looked for in the "fine mechanism", including also the mechanism of ligand substitutions for solid complexes. In the thermal decomposition of the complexes $Ni(NCS)_2L_2$ the substitution of the volatile ligand does not take place by another ligand from the outer coordination sphere, but by the NCS group of the inner sphere. Thus the bond Ni(II)-L is broken and the new bond Ni(II)-S is formed, the S atom becoming more bonded than in the initial compound. The question then arises, however, as to which of the processes is the primary one, this being the basic problem of every substitution reaction of coordination compounds.

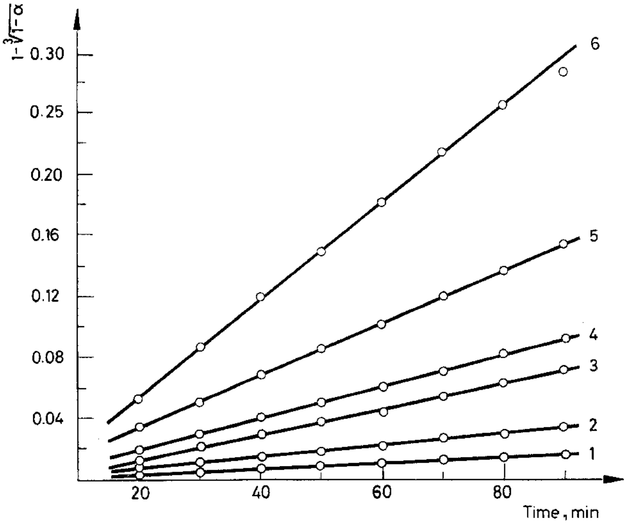

Fig. 6. Change of $1-(1-\alpha)^{1/3}$ with the duration of the decomposition of $Ni(NCS)_2Q_2$ (II): 1 — 90°, 2 — 98°, 3 — 108°, 4 — 112°, 5 — 116°, 6 — 125°

There are different opinions concerning the generalization of the conceptions of substitution reaction mechanisms of coordination compounds. Some authors suggest a rough agreement between the reaction mechanism within groups of analogous complexes. Others think that every reaction has its own mechanism. Both these conceptions may be justified to a certain extent. According to Langford and Gray [21] every group of complexes undergoes substitution of a characteristic activation type (the associative *a* and the dissociative *d*), which may be distinguished by the influence of the entering or leaving groups, on the rates of similar substitutions. These reactions, however, may differ in the so-called stoichiometric mechanism (the associative *A*, dissociative *D* and the "interchange" mechanism *I*). The mechanisms *A* and *D*, when intermediates with higher or reduced coordination number, respectively, are found, are only limiting cases, however, and the actual mechanism is seldom so simple. Often new bonds are formed even before the breaking of the preceding bonds has finished. This is called the "interchange" mechanism (*I*), for which two alternatives are known according to the activation type (I_A, I_D). In our further work we will consequently keep denotations.

In a study of the rates of substitution reactions of analogous complexes in solution, those phenomena connected with spatial effects were found to be explained most easily [21]. Pearson et al. [22] showed that increasing density around the central atom will increase the activation energy in the formation of bonds (associative activation), but can also decrease the E_a value in breaking the bonds (dissociative activation) due to the easier distortability in the intermediate state. Thus, the increasing density of the space around the Ni(II) will considerably decrease the rates of the processes (a) in contrast to the processes (d) which can occur more rapidly.

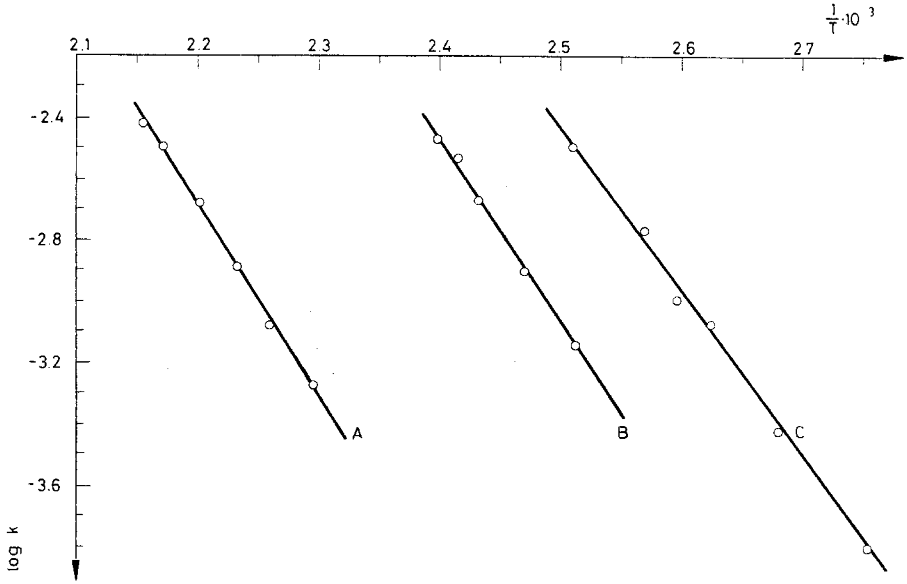

Fig. 7. Change of the logarithm of the rate constant with the reciprocal of the absolute temperature: A — $Ni(NCS)_2py_2$, B — $Ni(NCS)_2(\beta\text{-pic})_2$, C — $Ni(NCS)_2Q$ (II)

As Table 1 shows, the activation energy values appear in the following order: $Ni(NCS)_2py_2 > Ni(NCS)_2(\beta\text{-pic})_2 > Ni(NCS)_2Q_2$ (II).

The rate of decomposition for octahedral complexes increases from $Ni(NCS)_2py_2$ to $Ni(NCS)_2Q_2$ (II). Thus, the reaction course is more rapid for complexes with substituted pyridine molecules than for pyridine complexes. The existence of bulky ligands near the metal atom supports the dissociative activation, because removal of one of the ligands decreases the crowding around the metal atom. The observed increase of the decomposition rate for pseudooctahedral complexes with bulky ligands indicates a reaction course according to the dissociative activation.

Table 1

Kinetic data for pseudooctahedral complexes

Compound	M. W. (L)	Geometric configuration	Isothermal method		
			n	k', sec^{-1}	E_a kcal · mole^{-1}
$Ni(NCS)_2py_2$	79.10	Pseudo-octahedral	2/3	1.96×10^{-5}	29.4
$Ni(NCS)_2(\beta\text{-pic})_2$	93.12		2/3	7.18×10^{-4}	27.6
$Ni(NCS)_2Q_2$ (II)	129.15		2/3	3.18×10^{-3}	24.3

M. W. (L) = molecular weight of ligand, n = order of reaction, k' = rate constant at 398 K, E_a = apparent activation energy.

In comparing the obtained values of E_a with those of the decomposition heats (ΔH) [23], mutual agreement is found in the order. This indicates that the rate-controlling factor is the breaking of the Ni-L bond. In his study of the thermal decomposition of the complexes $NiCl_2L_4$ Beech [7] correlated the values of E_a with those of pK_a. He did not consider, however, that the strength of the M-L bond is influenced not only by the σ-bond, but also by the dative π-bond Ni → L, and by still other factors too [23]. The activation energy although related with the bond breaking energy, need not be equal to the bonding energy. In general, the weakening of the bonds is sufficient to effectuate the reaction. The values of E_a may be the measure of "holding" the ligand in the complex, but it need not be the criterion of the strength of the central atom-ligand bond. The activation energy values may also be influenced by the energy of the lattice [10, 11], but no such information is known for the studied complexes.

All pseudooctahedral complexes under investigation showed higher values of ΔH [23] (by ~ 2 kcal·mol^{-1}) compared with the obtained values of E_a. The same was found for $NiCl_2L_4$ (L = pyridine, β- or γ-picoline) [7] and also for the complexes $M(II)(NCS)_2py_4$ (M = Mn, Fe, Co, Ni and Zn) [24, 25]. This experimental result is contradictory to the requirements of endothermal one-step reactions, yet it is unlikely that all the observed results are due to the imprecise determination of E_a. One possible explanation is based on the suggestion that the reaction takes place in several steps (at least two) and the volatile ligands are released one by one, i.e. the complex $Ni(NCS)_2L$ – one of the intermediates – is formed. For L = β-picoline it has also been isolated. This possibility is supported by other authors [26, 27], who identified the complex $Ni(NCS)_2py$ in the thermal decomposition of $Ni(NCS)_2py_2$. We, however, did not find it in our work [16]; this may be due to the fact that immediately after its formation the decomposition continues and it could therefore not be separated, at least not in a greater amount. Similarly, Kauffman and Beech [25] suggested the existence of $M(II)(NCS)_2py_3$ in the thermal decomposition of the complexes $M(II)(NCS)_2py_4$; however, it was identified only for M = Ni. The reaction mechanism may then be expressed by the following scheme:

$$\begin{tikzcd}
 & \mathrm{Ni(NCS)_2L\,(C.N.5)} \arrow[r, "\mathrm{II}"] \arrow[d, "\mathrm{III}"] & \mathrm{Ni(NCS)_2\,(C.N.6)} \\
\mathrm{Ni(NCS)_2L_2(C.N.6)} \arrow[ur, "\mathrm{I}"] \arrow[dr, "\mathrm{IV}"'] & & \\
 & \mathrm{Ni(NCS)_2L\,(C.N.6)} \arrow[r, "\mathrm{V}"] & \mathrm{Ni(NCS)_2\,(C.N.5)} \arrow[uu, "\mathrm{VI}"']
\end{tikzcd}$$

In accordance with the mechanism of substitutions of reactions for complexes (dissociative activation, suggested by the experimental evidence for the studied complexes), an intermediate may be formed with a lower coordination number (C.N.5), while further reorganization of the crystal lattice leads to the formation of another complex of the same stoichiometric composition, $Ni(NCS)_2L$, but again with C.N.6. This complex may then again pass through an interstage with C.N.5, corresponding to the reactions I, III, V and VI. For the complex $Ni(NCS)_2(\beta\text{-pic})_2$, in the decomposition of which $Ni(SCN)_2 \cdot (\beta\text{-pic})$ was separated in practice, the E_a values correspond only to the reactions I and III.

The intermediate $Ni(NCS)_2L$ may in principle also be formed with C.N.6 [reaction IV, which also occurs for Ni(II) complexes]. Then, however, the reaction does not show the dissociative mechanism *D*. Nor can it be excluded that both ligands L dissociate simultaneously, so that the decomposition takes place according to the scheme:

$$\mathrm{Ni(NCS)_2L_2\,(C.N.6)} \xrightarrow{\mathrm{VII}} \mathrm{Ni(NCS)_2\,(C.N.4)} \xrightarrow{\mathrm{VIII}} \mathrm{Ni(NCS)_2\,(C.N.6)}$$

Based on our experimental results we consider the most probable course of the decomposition to be by reactions I, III, V, and VI.

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Résumé — On a étudié la cinétique de la décomposition thermique des complexes solides du type $Ni(NCS)_2L_2$ (L = pyridine, β-picoline et quinoléine) de configuration pseudo-octaédrique, d'après la perte de poids en régime isotherme entre 90—191°C. L'ordre de la réaction obtenu pour les complexes examinés s'élève à $n = 2/3$, c'est-à-dire que la vitesse de la décomposition totale est déterminée par la réaction chimique elle-même. Les valeurs calculées pour E_a (en $kcal \cdot mol^{-1}$) diminuent suivant l'ordre $Ni(NCS)_2py_2$ (29.4) > $Ni(NCS)_2(\beta\text{-pic})_2$ (27.6) > $Ni(NCS)_2Q_2$ (24.3). La vitesse de réaction croît lorsque le volume des ligands L augmente ce qui permet de suggérer un mécanisme réactionnel avec activation de la dissociation. On a trouvé $\Delta H > E_a$ pour tous les complexes examinés ce qui peut s'expliquer par un mécanisme avec plusieurs étapes, le complexe $Ni(NCS)_2L$ étant alors considéré comme produit intermédiaire.

Zusammenfassung — Die Kinetik der thermischen Zersetzung der festen Komplexe vom Typ $Ni(NCS)_2L_2$ (L = Pyridin, β-Picolin oder Chinolin) und pseudooktaedrischer Konfiguration wurde durch isotherme Methoden auf Grund der Gewichtsverluste zwischen 90—191° untersucht. Die geeignetste Reaktionsordnung wurde für $n = 2/3$ gefunden, d. h. die totale Zersetzungsgeschwindigkeit wird durch den eigentlichen chemischen Vorgang bestimmt. Die errechneten E_a Werte (in $kcal \cdot mol^{-1}$) nehmen in folgender Reihenfolge ab: $Ni(NCS)_2py_2$ (29.4) > $Ni(NCS)_2(\beta\text{-pic})_2$ (27.6) > $Ni(NCS)_2Q_2$ (24.3). Mit zunehmendem Volumen der Liganden nimmt also die Reaktionsgeschwindigkeit zu, der Reaktionsverlauf richtet sich folglich nach der dissoziativen Aktivierung. Für alle untersuchten Komplexe ergab sich $\Delta H > E_a$. Dies läßt sich durch einen Mehrstufenmechanismus erklären, wobei der Komplex $Ni(NCS)_2L$ als Intermediär gilt.

Резюме — Изучена кинетика термораспада твердых комплексов типа $Ni(NCS)_2L_2$ (L = = пиридин, β-пиколин и хинолин) псевдооктаэдрической конфигурации при изотермических условиях на основании потери веса в области температуры 90—191°C. Установлено, что наиболее соответствующий порядок реакции для всех изученных комплексов $n = 2/3$, т. е. общая скорость распада определяется специфическим химическим процессом. Рассчитанные величины E_a(b ккал · $мол^{-1}$) уменьшаются в следующем порядке: $Ni(NCS)_2py_2$ (29.4) > $Ni(NCS)_2(\beta\text{-pic})_2$ (27.6) > $Ni(NCS)_2Q_2$ (24.3). С увеличивающимся объемом лиганда L скорость реакции также увеличивается. Это позволяет предположить, что ход реакции соответствует диссоциативной активации. Найдено, что для всех изученных комплексов $\Delta H > E_a$. Это объясняется многоступенчатым механизмом, при котором комплекс $Ni(NCS)_2L$ промежуточный продукт.