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HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES, VI

THE THERMAL DECOMPOSITION OF COMPLEXES OF THE TYPE $Ni(NCS)_2L_2$

PART D: KINETIC STUDY OF SQUARE-PLANAR COMPLEXES

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The kinetics of the thermal decomposition of square-planar complexes of the type $Ni(NCS)_2L_2$ (L = α-picoline; 2,6-lutidine and quinoline) was studied by following the loss of weight and using the isothermal method, in the temperature range of 72–147°. The reaction order found was $n = 2/3$; this together with macroscopic observations indicates that it is the proper chemical process which is the controlling factor of the total decomposition rate. The values of the activation energies decrease in the following order: $Ni(NCS)_2 Q_2 > Ni(NCS)_2(2,6\text{-lut})_2 > Ni(NCS)_2(\alpha\text{-pic})_2$; this points to the reaction course according to the associative activation. Except for $Ni(NCS)_2Q_2$, ΔH was found to be $> E_a$. This experimental result may be explained by a multi-step mechanism. Possible intermediates are discussed.

The kinetics and the mechanism of the thermal decomposition of solid coordination compounds may be investigated from two points of view, namely with respect to the primary coordination sphere or to the whole lattice. The first stage must be devoted to collecting information of the controlling process in the whole crystal lattice (the so-called "rough" mechanism). Many solid complexes and above all those with heterogeneous coordination sphere and also their heterogeneous reactions represent an interesting subject for the study of the mechanisms of substitution reactions of ligands (the dissociative and associative mechanisms). This is the so-called "fine" mechanism. The difference between the substitution reactions of complexes in solution may be expressively influenced by their geometrical configuration [1]. This is why the decomposition rate of pseudooctahedral [2] and square-planar complexes, respectively, of the type $Ni(NCS)_2L_2$ was studied separately also in the solid state. The present article deals with the study of the decomposition kinetics of square-planar complexes of that type (L = α-picoline, 2,6-lutidine and quinoline) and brings the obtained data in correlation with the thermochemical results.

Experimental

The chemicals, analytical methods, preparations and analysis results of the complexes under investigation are presented in a separate paper [3].

The apparatus, procedure, conditions of measurement for the isothermal technique are given in paper [2].

Figs 1 – 3 show the experimentally found dependences of the loss of weight on the duration of the reaction at constant temperatures. These curves yielded the values of the conversion degree (α) of the initial solid component. The values obtained were correlated by the kinetic equation

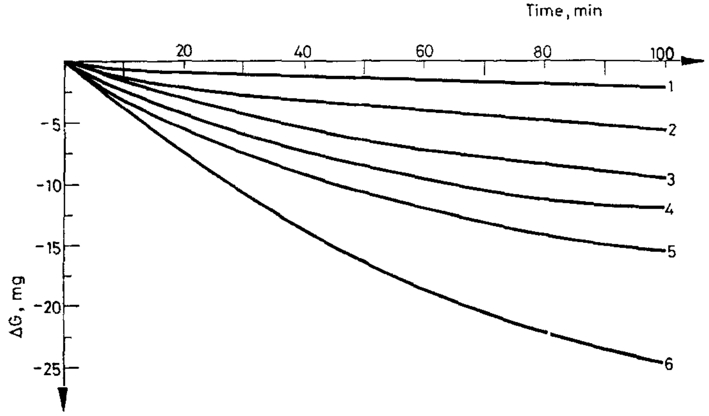

Fig. 1. Plots of loss of weight vs. time for the complex $Ni(NCS)_2(\alpha\text{-pic})_2$ at the constant temperatures: 1. 72°; 2. 85°; 3. 93°; 4. 98°; 5. 100°; 6. 106°

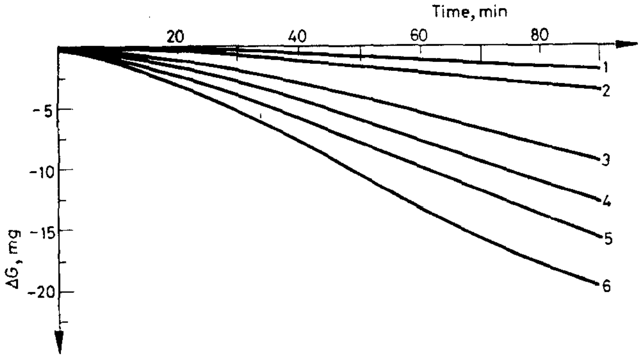

Fig. 2. Plots of loss of weight vs. time for the complex $Ni(NCS)_2(2,6\text{-lut})_2$ at the constant temperatures: 1. 99°; 2. 105°; 3. 112°; 4. 118°; 5. 121°; 6. 125°

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

and the best experimental agreement was achieved for $n = 2/3$. The integrated equation then shows the form

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

The dependences of $1 - (1 - \alpha)^{1/3}$ on the time are plotted in Figs 4–6. We calculated from these plots the values of the rate constants. Their temperature dependence obeys the Arrhenius equation, as it is to be seen in Fig. 7.

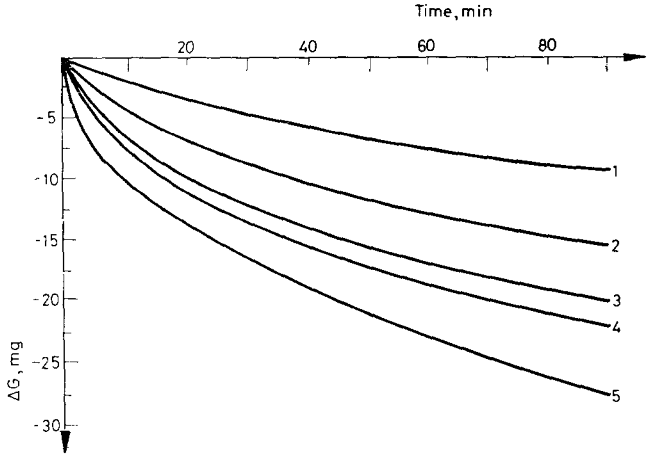

Fig. 3. Plots of loss of weight vs. time for the complex $Ni(NCS)_2Q_2(I)$: at the constant temperatures: 1. 130°; 2. 135°; 3. 141°; 4. 143°; 5. 147°

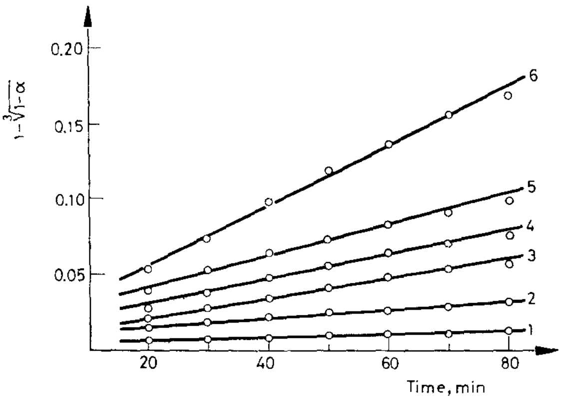

Fig. 4. Plots of $1 - (1 - \alpha)^{1.3}$ vs. duration of the decomposition of $Ni(NCS)_2(\alpha\text{-pic})_2$: 1. 72°; 2. 85°; 3. 93°; 4. 98°; 5. 100°; 6. 106°

The apparent activation energy (E_a) was calculated by the relationship

$$\log \frac{k'_2}{k'_1} = \frac{E_a}{2.3R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3}$$

and yielded the values: 22.8 kcal.mole^{-1} for $Ni(NCS)_2(\alpha\text{-pic})_2$; 27.9 kcal.mole^{-1} for $Ni(NCS)_2(2{,}6\text{-lut})_2$; 30.7 kcal.mole^{-1} for $Ni(NCS)_2Q_2(I)$.

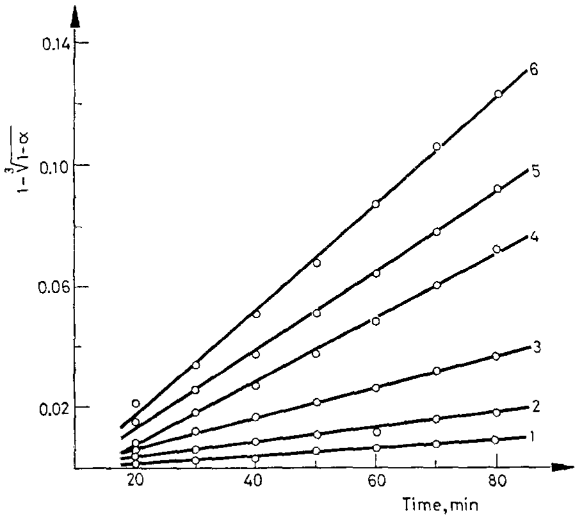

Fig. 5. Plots of $1 - (1 - \alpha)^{1/3}$ vs. duration of the decomposition of $Ni(NCS)_2(2{,}6\text{-lut})_2$: 1. 99°; 2. 105°; 3. 112°; 4. 118°; 5. 121°; 6. 125°

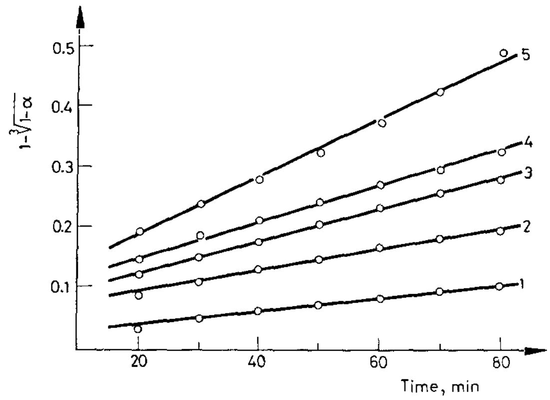

Fig. 6. Plots of $1 - (1 - \alpha)^{1/3}$ vs. duration of the decomposition of $Ni(NCS)_2Q_2(I)$: 1. 130°; 2. 135°; 3. 141°; 4. 143°; 5. 147°

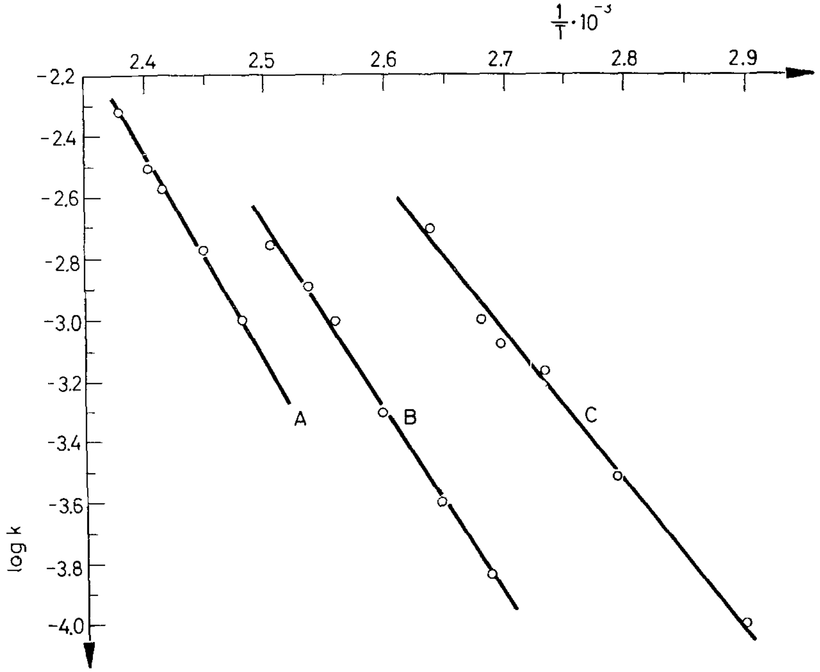

Fig. 7. Plots of the logarithm of rate constants vs. the reciprocal value of the absolute temperature: A) $Ni(NCS)_2Q_2(I)$; B) $Ni(NCS)_2(2,6\text{-lut})_2$; C) $Ni(NCS)_2(\alpha\text{-pic})_2$

Discussion

In studying the mechanism of heterogeneous substitution reactions of coordination compounds in the solid state we start from the knowledge of these reactions in solution [1]. There are, however, essential differences. In the solid state there occur besides the actual chemical reaction still other processes [4, 5] and their rate may not be neglected. In order to study the chemical aspects of heterogeneous reactions such conditions have to be chosen, under which the controlling process is the proper chemical reaction. The necessary information of the controlling process may be obtained by means of kinetic analysis.

In the course of the study of the thermal decomposition kinetics of square-planar complexes of the type $Ni(NCS)_2L_2$ (by isothermal method) a reaction order of $n = 2/3$ was found to fit best the experimental results [6, 7] indicating (analogous to pseudooctahedral complexes of that type) that the decomposition begins on the surface of the crystals and uniformly continues to their centres; this was also evidenced by macroscopic investigation. Consequently the total decomposition rate [2, 8] may be considered to be determined by the chemical process. We have, however, to be aware that a certain order or type of kinetic equation may also be obtained by superposition of several processes. The explanation is that kinetic equations are empirical relations, being adaptable to a certain extent, and by suitably chosen constants we may achieve accordance with any course of the experimental curve. This is why unambiguous conclusions drawn only from the form of the kinetic equation, though this is the conventional way, are in general not justified.

In order to predict the mechanism of ligand substitutions for solid complexes, e.g. in thermal decomposition, it appears to be necessary to know the geometrical configuration of the initial complexes, which should be the same for the whole group of the complexes under investigation. The proper decomposition process may be influenced not only by the primary coordination sphere itself, but also by the outer environment (the volume of the ligands, their ability of coordination and of effecting the coordination sphere). The differences between the substitution reactions of pseudooctahedral and square-planar complexes are in general due to two factors. First, it is the spherical factors, which play an important part for octahedral complexes. These are more "saturated" compared with the square-planar ones and so the repulsion of ligands must be stronger. Secondly, the possibilities to form σ-bonds are for octahedral complexes already exerted; the p_z and d_z^2 orbitals which proved suitable to form σ-bonds in the reactions of square-planar complexes with d^8 electron configuration, are already occupied for octahedral complexes in the ground state. Theoretically at the utmost the probability will decrease that the substitution reactions of the octahedral complexes will run according to the associative activation and those of the square-planar complexes, by the dissociative activation, respectively.

Table 1

Kinetic data of the thermal decomposition of square-planar complexes of the type $Ni(NCS)_2L_2$

Compound	$M_r(L)$	Geometrical configuration	Isothermal method		
			n	k', sec^{-1}	E_a, kcal. mol^{-1}
$Ni(NCS)_2(\alpha\text{-pic})_2$	93.12	Square-planar	2/3	$7.92 \cdot 10^{-3}$	22.8
$Ni(NCS)_2(2,6\text{-lut})_2$	107.16		2/3	$1.75 \cdot 10^{-3}$	27.9
$Ni(NCS)_2Q_2(I)$	129.15		2/3	$7.53 \cdot 10^{-4}$	30.7

$M_r(L)$ is the molecular weight of ligands, n – the reaction order, k' – the rate constant at 398°K, E_a – the apparent activation energy.

As Table 1 shows the values of activation energy for square-planar complexes follow this order: $Ni(NCS)_2(\alpha\text{-pic})_2 < Ni(NCS)_2(2,6\text{-lut})_2 < Ni(NCS)_2Q_2(I)$. Thus the rate constant decreases from the complex with α-picoline to that with quinoline. Increasing the spherical density around the central atom will increase the activation energy in the formation of bonds (the associative activation *a*), but may decrease E_a in the breaking of bonds (the dissociative activation *d*) [1]. The exchange of the hydrogen atoms of the ligand L for methyl increases its volume, thus impeding the interaction of the metal atom with other atoms. The observed decrease of the decomposition rate for square-planar complexes of the type $Ni(NCS)_2L_2$ with more voluminous ligands allows to suggest the reaction course according to the associative activation. No accordance was found for this type of square-planai complexes of the order of E_a (Table 1) with that of ΔH [9]. This may be explained by another activation type as well as with the fact that the final decomposition product shows different geometrical configuration.

For the complexes under investigation, except for $Ni(NCS)_2Q_2$, the values of ΔH were higher (by ~ 2 kcal.mole^{-1}) than those of E_a. This result is in contrast with the requirements of endothermic one-step reactions and its explanation lies in a possible multistep mechanism. Based on the reaction course according to associative activation for the studied square-planar complexes, $Ni(NCS)_2L_2$ an intermediate with the coordination number 5 may be assumed to be present [namely, first the new bond Ni(II) – S is formed] then, in the further decomposition stage the volatile ligand L is split off and the complex $Ni(NCS)_2L$ is formed, which continues to decompose. This complex, however, cannot be always directly identified (as for L = α-picoline and 2,6-lutidine) and apparently undergoes further decomposition right on its formation, analogous to that found for pseudo-octahedral complexes of this type (L = pyridine and quinoline) [2].

In the decomposition of the square-planar complex $Ni(NCS)_2Q_2$ the activation energy corresponds to the reaction course of $Ni(NCS)_2Q_2 \rightarrow Ni(NCS)_2Q + Q$ and since $E_a > \Delta H$, it is a one-step process. With respect to the associative type of activation it is probably an "interchange" mechanism (I_A) that occurs [2].

In studying the mechanism of the thermal decomposition of complexes of the type $Ni(NCS)_2L$ with ligands of π-bonding properties (pyridine and some of its derivatives) we tried to solve this problems by complex method (i.e. to study the stoichiometry, the thermochemical behaviour and the decomposition kinetics). The spatial configuration of the initial complexes was taken into account. The obtained results and the partial conclusions show the possibility and the usefulness of such an approach. Neither this complex study, however, could lead us to unambiguous explanation of all the problems connected with the stepwise character of the thermal decomposition, especially with respect to the substitution reactions occurring in the solid state. We suggest the main reason to be in the circumstance that while in solution the substituent ligand has freedom of motion and can attack the complex in any place, in the solid state it is limited and localized by the lattice energy, the numerical values of which are not known for the complexes under investigation. Besides, the reactions in the solid state are occurring together with the recrystallization process.

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RÉSUMÉ — On a étudié la cinétique de la décomposition thermique des complexes plans carrés du type $Ni(NCS)_2L_2$ (L = α-picoline, lutidine-2,6 et quinoléine) en enregistrant la perte de poids et en opérant en isotherme dans le domaine de température compris entre 72 et 147°. L'ordre de la réaction a été trouvé égal à 2/3; cette valeur et les observations macroscopiques indiquent que le processus chimique lui-même est le facteur principal qui influence la vitesse de la décomposition. Les valeurs des énergies d'activation diminuent dans l'ordre suivant: $Ni(NCS)_2Q_2 > Ni(NCS)_2(lut\text{-}2,6)_2 > Ni(NCS)_2$ $(\alpha\text{-pic})_2$ ce qui apporte la preuve d'une réaction d'activation associative. On a trouvé $\Delta H > E_a$ sauf pour $Ni(NCS)_2Q_2$. On explique ce résultat par un mécanisme avec plusieurs étapes. Discussion des intermédiaires possibles.

ZUSAMMENFASSUNG — Man untersuchte durch Registrieren des Gewichtsverlustes und durch isotherme Methoden die Kinetik der thermischen Zersetzung der quadratischen Komplexe vom Typ $Ni(NCS)_2L_2$ (L = α-Pikolin, 2,6-Luthidin und Chinolin). Man fand die Reaktionsordnung für $n = 2/3$. Hieraus ergibt sich ergänzt durch bestimmende makroskopische Beobachtungen, daß der eigentliche chemische Prozeß der bestimmende Faktor für die totale Zersetzungsgeschwindigkeit ist. Die Aktivierungsenergiewerte vermindern sich in folgender Reihenfolge: $Ni(NCS)_2Q_2 > Ni(NCS)_2(2,6\text{-lut})_2 > Ni(NCS)_2(\alpha\text{-pic})_2$; dies spricht für einen Reaktionsvorgang durch assoziative Aktivierung. Nur bei $Ni(NCS)_2Q_2$ wurde $\Delta H > E_a$ gefunden. Dieser Befund kann durch einen Mehrschrittmechanismus erklärt werden. Mögliche Intermediäre wurden besprochen.

Резюме — Изучена кинетика термораспада комплексов типа $Ni(NCS)_2L_2$ [L = α-пиколин, 2,6 лутидин и хинолин] путем измерения потери веса при использовании изотермического метода в области температур 72—147°C. Рассчитанный порядок реакции равен 2/3, что, наряду с макроскопическими наблюдениями, указывает на собственно химический процесс, являющийся контролирующим фактором скорости полного распада. Величины энергии активации уменьшаются в следующем порядке: $Ni(NCS)_2Q_2 > Ni(NCS)_2$ (2,6-лут.)$_2$ $> Ni(NCS)_2(\alpha\text{-пик})_2$. Найдено отклонение для $Ni(NCS)_2Q_2$ и $\Delta H > E_a$. Этот результат объясняется многоступенчатым механизмом. Возможные промежуточные продукты обсуждаются.