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

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An attempt has been made to apply concepts of complex chemistry in solution to heterogeneous reaction kinetics. A series of solid Ni(II) complexes containing the same anionic ligand and volatile ligands of the same type were investigated under isothermal conditions on the basis of TG curves, and the kinetics of their decompositions were studied. Since the reactions are controlled by the appropriate chemical process, the differences found between the activation energies and the measured values of the standard enthalpies might be explained by substitution processes in the primary coordination sphere. According to the experimental results, the formation of intermediates has to be presumed in all the reactions investigated. A mechanism could be proposed for their formation. No dependence could be detected between the geometrical configuration of the coordination sphere and the stoichiometry of the decomposition process.

The problems of the stoichiometry, kinetics and mechanisms of heterogeneous reactions of solid complexes of the type $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$ are discussed relatively rarely in the literature. The reasons lie in the complexity of the mechanism, due primarily to transport phenomena in the solid state, so that most often only the stoichiometry of these reactions is studied [1].

The kinetics and mechanisms of thermal decomposition of solid complexes can in general be investigated from the point of view of either the primary coordination sphere or the whole lattice. Before studying the problems in the primary coordination sphere, therefore it appears necessary to gain information on the controlling process in the whole sample and in the single particles of the reacting solid, i.e. on the "rough mechanism". The different types of substitution mechanisms (dissociative and associative [2, 3]) occurring in thermal decomposition (i.e. the substitution of volatile ligands by anions) fall into the region of "fine mechanism".

The aim of the present work was to study the mechanisms of thermal decomposition of two configurational isomers of $Ni(NCS)_2(quinoline)_2$ with pseudooctahedral and square-planar structure, respectively, [4–6] and also to investigate the relationship between their structure and the thermal decomposition. For comparative purposes, an analogous study was made of complexes of the same type and similar structure, $Ni(NCS)_2L_2$, where L = heterocyclic nitrogen base, (a) with square-planar configuration (L = α-picoline; 2,6-lutidine), and (b) with pseudooctahedral configuration (L = pyridine; β-picoline) [8].

Table 1

Compound	Geometrical configuration	Stoichiometry	Isothermal method		ΔH° decomp. (kcal · mole^{-1})
			n	E_a (kcal · · mole^{-1})	
$Ni(NCS)_2py_2$	pseudooctahedral	(A)	2/3	29.4	31.6
$Ni(NCS)_2(\beta\text{-pic})_2$		(B)	2/3	27.6	29.3
$Ni(NCS)_2Q_2$(II)		(A)	2/3	24.3	27.8
$Ni(NCS)_2(\alpha\text{-pic})_2$	square-planar	(A)	2/3	22.8	24.4
$Ni(NCS)_2(2,6\text{-lut})_2$		(A)	2/3	27.9	30.1
$Ni(NCS)_2Q_2$(I)		(B)	2/3	30.7	28.5

(A) $Ni(NCS)_2L_{2\,(s)} \rightarrow Ni(NCS)_{2\,(s)} + 2L_{(g)}$

(B) $Ni(NCS)_2L_{2(s)} \rightarrow Ni(NCS)_2L_{(s)} + L_{(g)} \rightarrow Ni(NCS)_{2\,(s)} + 2L_{(g)}$

The TG measurements were made with a Derivatograph under isothermal conditions. The plate-crucible and furnace used were of our own construction [9, 10], and ensured good isothermal conditions and a one-particle layer of the samples. The results are given in Table 1.

The volatile ligands can be released in one-step [L = py; Q(II); α-pic; 2,6-lutidine] (A) or two-step [L = β-pic; Q(I)] (B) processes, corresponding to one-step or two-step decomposition stoichiometry. All these complexes contain the same anionic ligand (NCS) and volatile ligands of the same type. The physical conditions able to affect the stoichiometry of decomposition (sample weight, layer thickness, crystal size and atmosphere) [11, 12] were also the same in our experiments [9]. Should the geometrical configuration influence the stepwise character of the thermal decomposition, different decomposition stoichiometries might be expected for initial complexes of the same type, but with different geometrical configurations in yielding the same final products. Different decomposition stoichiometries were found for the isomers of $Ni(NCS)_2(\text{quinoline})_2$. The decomposition of the pseudooctahedral isomer takes place in one step, and that of $Ni(NCS)_2(\beta\text{-pic})_2$ with the same configuration in two steps. A similar phenomenon is also to be seen for square-planar complexes. This excludes any direct causality between the geometrical configurations of the initial complexes and the stoichiometries of their thermal decompositions.

In the study of the kinetics and mechanism of decomposition the values of the conversion degree (α) of the starting solid were calculated from the thermogravimetric curves. The values obtained were correlated by the kinetic equation

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

where k is the rate constant, and n the order of reaction. The best experimental agreement was found for $n = 2/3$. The dependences of the rate constants on the temperature correspond with the Arrhenius equation. The apparent activation energy values E_a in Table 1 were determined from this equation.

The most suitable $n = 2/3$ for the isothermal decomposition of these complexes indicates that the decomposition begins on the surface of the crystals and proceeds uniformly towards their centers. This has also been confirmed by microscopic investigation. Thus, it can be suggested that the total decomposition rate is determined by the appropriate chemical process. It is necessary to remember, however, that a certain order or type of kinetic equation may also be obtained by superposition of several processes. Unambiguous conclusions based only on the form of the kinetic equation are in general not justified therefore. With regard to the fact that the overall decomposition rates of all the studied complexes are defined by the same controlling process (rough mechanism), the reasons for the differences in their decomposition rates (and also in their E_a values) have to be sought in their fine mechanisms.

In the study of the rate of substitution reactions of a number of analogous complexes in solution, those phenomena have been found to be elucidated most easily which show some relation to space effects. Pearson et al. [15] showed that increasing steric density around the central atom increases the activation energy E_a in the formation of bonds (associative activation); it can also decrease E_a, however, in the rupture of bonds (dissociative activation) due to easier distortion in the intermediate state. As Table 1 shows, the values of E_a decrease in the following order: (a) for pseudooctahedral complexes: $Ni(NCS)_2py_2 > Ni(NCS)_2(\beta\text{-pic})_2 > Ni(NCS)_2Q_2(II)$; and (b) for square-planar complexes: $Ni(NCS)_2Q_2(I) > Ni(NCS)_2(2,6\text{-lut})_2 > Ni(NCS)_2(\alpha\text{-pic})_2$. The reaction rate increases in the same order. The observed increase in reaction rate for pseudooctahedral complexes with more voluminous ligands permits the suggestion that the course of the reaction corresponds to the dissociative activation. For square-planar complexes the contrary was found, indicating associative activation.

The standard enthalpies of the studied reactions were also investigated by differential scanning calorimetry. The values found are shown in Table 1. With the exception of $Ni(NCS)_2Q(II)_2$, the decomposition enthalpy is higher than the activation energy in all cases and it has to be assumed that intermediates were formed in all reactions, even in those where only a one-step stoichiometry was found. In accordance with the proposed mechanisms these intermediates might be complexes with coordination number 5. They are formed in the case of pseudooctahedral compounds by release of one of the organic ligands, while in the case of the square-planar complexes new bonds may be formed before the release of the organic ligand.

References

1. W. W. WENDLANDT and J. P. SMITH, The Thermal Properties of Transition Metal Aminocomplexes, Elsevier, Amsterdam, 1967.
2. F. BASOLO and F. G. PEARSON, Mechanism of Inorganic Reactions. 2nd edition. Wiley, New York, London, 1967.

3. C. H. Langford and H. B. Gray, Ligand Substitution Processes, Benjamin, New York, Amsterdam, 1965.
4. T. Šramko, E. Jóna and A. Sirota, Proceedings of the 2nd Conference on Coordination Chemistry. Smolenice, Bratislava, ČSSR, 1969, p. 239.
5. J. Kohout, M. Kohutová and E. Jóna, Z. Naturforsch., 25 (1970) 1054.
6. E. Jóna, T. Šramko, J. Kohout, A. Sirota and J. Gažo, Chem. Zvesti 25 (1971) 241.
7. H. C. A. King, E. Körös and S. M. Nelson, J. Chem. Soc. (1963) 5449.
8. S. M. Nelson and T. M. Shepherd, Inorg. Chem., 4 (1965) 813.
9. E. Jóna, T. Šramko and J. Gažo, J. Thermal. Anal. 4 (1972) 61.
10. E. Jóna, V. Jesenák and T. Šramko, Chem. Zvesti, 23 (1969) 420.
11. D. Young, Decomposition of Solids. Russian translation "Kinetika razlozhenija tvjerdych veshchestv". Izdat. "Mir" Moscow, 1969., p. 97.
12. S. Škramovský, R. Forster and G. F. Hüttig, Z. Phys. Chem., 25 (1934) 1.
13. G. F. Hüttig, Mh. Chem., 85 (1954) 376.
14. I. Proks, Chem. Zvesti, 20 (1966) 697.
15. R. G. Pearson, C. R. Boston and F. Basolo, J. Amer. Chem. Soc., 75 (1953) 3089.
16. E. Jóna, T. Šramko, P. Ambrovič and J. Gažo, J. Thermal Anal., 4 (1972) 153.

Résumé — On a étudié la cinétique de la décomposition d'une série de composés solides du Ni(II) avec le même ligand anionique et avec des ligands volatils du même type en utilisant les résultats de la thermogravimétrie isotherme. Comme les réactions sont contrôlées par leur processus chimique propre, les différences qui ont été observées entre l'énergie d'activation et les valeurs mesurées des enthalpies standard peuvent s'expliquer par des processus de substitution dans la sphère de coordination primaire. Les résultats expérimentaux laissent présumer l'existence d'étapes intermédiaires pour toutes les réactions étudiées. Le mécanisme de leur formation a pu être proposé. On n'a pas pu déceler de rapport entre la configuration géométrique de la sphère de coordination et la stoechiométrie du processus de décomposition.

Zusammenfassung — Es wurde ein Versuch gemacht, komplexchemische Vorstellungen in Lösungen auf die Kinetik heterogener Reaktionen zu übertragen. Eine Reihe fester Ni(II)-Komplexe mit demselben anionischen Liganden und mit flüchtigen Liganden desselben Typs wurde aufgrund der TG-Kurve unter isothermen Bedingungen untersucht und die Kinetik ihrer Zersetzung studiert. Da die Reaktionen durch den entsprechenden chemischen Vorgang gesteuert werden, können die zwischen den Aktivierungsenergien und den gemessenen Werten der Standardenthalpien gefundenen Unterschiede durch Substitutionsvorgänge in der primären Koordinationssphäre erklärt werden. Den Versuchsergebnissen gemäß muß bei sämtlichen untersuchten Reaktionen die Bildung von Zwischenprodukten angenommen werden. Eine Erklärung ihres Bildungsmechanismus wird vorgeschlagen. Es wurde kein Zusammenhang zwischen der geometrischen Konfiguration der Koordinationssphären und der Stöchiometrie des Zersetzungsvorganges gefunden.

Резюме — Сделана попытка приложить понятия химии комплексов в ростворох к кинетике гетерогенных реакций. Исследован в изотормических условиях на основании кривых ТГ ряд твердых комплексов Ni(II), содержащих одинаковый анионный лиганд и летучие лиганды одного типа, и изучена кинетика их распада. В связи с тем, что реакции контролируются соответствующим химическим процессом, обнаруженная разница между энергиями активации и измеренными величинами стандартных энтальпий может быть объяснена процессами замещения в первичной координационной сфере. Согласно результатам эксперимента во всех исследованных реакциях предполагается образование промежуточных продуктов. Предложен механизм их образования. Зависимость между геометрической конфигурацией координационной сферы и стехиометрией процесса распада установить не удалось.