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HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES, XI

THE INFLUENCE OF DIFFERENT EXPERIMENTAL CONDITIONS ON THE STOICHIOMETRY OF THERMAL DECOMPOSITION OF THE COMPLEX $Ni(NCS)_2(\beta\text{-picoline})_4$

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The influence of factors caused by different experimental conditions on the stoichiometry of thermal decomposition of the complex $Ni(NCS)_2(\beta\text{-picoline})_4$ was studied. By means of TG it was found that the release of β-picoline was shown by the derivatograph (air atmosphere, sample of 50—500 mg, rate of temperature increase 1—6°/min, crucible with a hole in the bottom) in three steps (−2, −1, −1), by the micro-balance (sample of 2.59 mg) in two steps (−2, −2), and by the vacuum thermobalance in one step (−4). Under quasi-isothermal and quasi isobaric conditions in a special crucible β-picoline was released in three steps (−1, −2, −1). An analogous result was obtained with the derivatograph using a crucible with a lid. The reasons for these differences are discussed.

Different experimental conditions considerably influence not only the course of thermogravimetric curves and the decomposition temperatures, but also the stepwise character of thermal decomposition (number of steps corresponding to defined intermediates and their compositions) [1, 2]. In previous work [3, 4] we showed that the physical properties of the compounds under investigation (such as the particle size or the mode of preparation) had an influence on the decomposition stoichiometry (number of steps of the process) of nickel(II) complexes with some monodentate nitrogen ligands. These factors are the cause that different authors have found different stoichiometries of decomposition for a given complex with a high number of volatile ligands [e.g. for $Ni(NCS)_2(\beta\text{-pic})_4$ (pic = picoline)] [5—8]. Their results, however, are not always reproducible because of their insufficient description of the experimental conditions used.

In the present work we have aimed at the study of the decomposition stoichiometry of one compound only, the complex $Ni(NCS)_2(\beta\text{-pic})_4$ (of constant grain size) under different experimental conditions. The present development of experimental techniques (micro-balance, working in vacuo, use of different crucibles) allows change in the experimental conditions over a wide range, and consequently it may be expected that the number of differing data on the decomposition stoichiometry for the same substance will further increase. The aim of this study was to show that the different number of steps of thermal decomposition for a given compound (under different conditions) is a physical reality that will be encountered many times in the field of coordination compounds.

Experimental

The chemicals and analytical methods are as published earlier [9].

The complex $Ni(NCS)_2(\beta\text{-pic})_4$ was prepared in the following way: 0.04 mole $NiCl_2 \cdot 6\,H_2O$ was dissolved under stirring in 80 ml ethanol. On dissolution, 0.08 mole pulverized solid KNCS was added. The precipitated KCl was filtered off and 20 ml β-picoline was added to the clear solution of $Ni(NCS)_2$. The crystalline precipitate was filtered off, washed with ethanol and ether and dried in the air (grain size less than 0.06 mm).

Analysis results for $Ni(NCS)_2(\beta\text{-pic})_4$:

Calculated:	%Ni = 10.72,	N = 15.35,	C = 57.05,	H = 5.16.
Found:	%Ni = 10.65,	N = 15.11,	C = 56.20,	H = 5.09.

Results and discussion

The literature data show that complexes of the type MX_2A_4 (M = transition metal; X = Cl, Br, I or NCS; A = volatile monodentate ligand) can exhibit rather different decomposition stoichiometries [11, 12]. Likewise, different authors did not find the same decomposition stoichiometry, even for a given complex, e.g. $Ni(NCS)_2(\beta\text{-pic})_4$ [5–8]. Though the experimental conditions do not differ considerably, the results obtained by the various authors are different. It follows from this fact that for every determination of the decomposition stoichiometry the experimental conditions must be precisely presented (sample weight, rate of temperature increase, atmosphere, type of apparatus, shape of crucible, method of complex preparation, particle size), since otherwise the published data cannot be used for a more detailed interpretation.

These differing results of the various authors gave us the impulse to carry out a complex study of the stoichiometry of thermal decomposition of $Ni(NCS)_2(\beta\text{-pic})_4$ under ten sets of experimental conditions (see Table 1). The experiments were performed with three apparatuses: a derivatograph [10] with the standard crucible (having a hole in its bottom) with an upper diameter of 14 mm (without a lid), for different sample weights and rates of temperature increase, using a standard crucible with a lid, a polyplate crucible and a special crucible under quasi-isothermal and quasi-isobaric conditions [13]; a Du Pont micro-balance; and a Sartorius vacuum thermobalance.

Commercially available apparatuses usually allow recording of TG, DTG, and DTA curves.

Even all these methods together cannot determine the true decomposition stoichiometry (number of defined intermediates), but only the instrumental stoichiometry of decomposition [8, 14] that is recorded by the apparatus. For the determination of the true stoichiometry it is necessary to apply phase analysis and perhaps also to supplement this method by spectral investigation [8, 14]. For the determination of the decomposition stoichiometry the weight changes of the compounds under investigation as found by means of the apparatuses used here are essential. Therefore, for the determination of the instrumental stoichiometries of thermal decomposition, in this work we started from the inflection points on the TG curves.

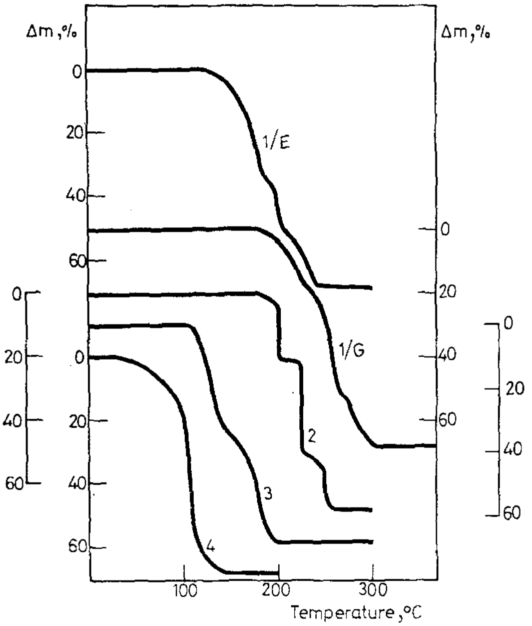

Fig. 1. Decomposition of $Ni(NCS)_2(\beta\text{-pic})_4$ complex

The experimental data indicated four different instrumental stoichiometries of thermal decomposition (Table 1, Fig. 1):

a) The initial complex releases β-picoline in three steps: $Ni(NCS)_2(\beta\text{-pic})_4$: 4 → 2; 2 → 1; 1 → 0.

b) The initial complex releases β-picoline in three steps; $Ni(NCS)_2(\beta\text{-pic})_4$: 4 → 3; 3 → 1; 1 → 0.

c) The initial complex releases β-picoline in two steps: $Ni(NCS)_2(\beta\text{-pic})_4$: 4 → 2; 2 → 0.

d) The initial complex releases β-picoline in one step: $Ni(NCS)_2(\beta\text{-pic})_4$: 4 → 0.

TG curve 1/*E* corresponds to common conditions used in our previous work [4, 14]. TG curves 1/*A*, *B*, *C*, *D* and *F* are analogous (therefore they are not shown in Fig 1), and thus neither the changes of the weighed portion or of the rate of temperature increase under the reported conditions, nor the use of the polyplate crucible, influenced the instrumental stoichiometry of decomposition. TG curves 1/*G* and 2 show an analogous course of stoichiometry, in spite of the different conditions. Both kinds of decomposition, however, yielded conditions such that the decomposition took place in an atmosphere of β-picoline. TG curves 3 and 4 are obtained with small sample amounts and a low ligand concentration in the gaseous phase.

With respect to the experimental data, the applied conditions may be divided into those that do not affect the decomposition stoichiometry and that do influence it. Now let us discuss the experimental conditions and possible causes that have an influence on the decomposition stoichiometry.

Though the thermal decompositions of solid complex compounds of the type NiX_2L_4 with monodentate nitrogen ligands are stepwise processes, e.g. for the complex $Ni(NCS)_2(\beta\text{-pic})_4$ (−1, −1, −1, −1) [7], it is not always possible to identify all the expected intermediates. For example, in the decomposition of the complex $NiCl_2(NH_3)_6$ we obtain $NiCl_2(NH_3)_2$ directly [13, 15, 16] and the missing intermediates remain unknown. In such a case the compounds corresponding to the missing intermediates are thermodynamically unstable for structural reasons [17], so that they cannot be prepared, even be another method. With a linearly increasing temperature, however, the thermal decomposition reactions take place under thermodynamically non-equilibrium conditions. It is possible that some

Table 1

The stoichiometry of thermal decomposition of the complex $Ni(NCS)_2(\beta\text{-picoline})_4$ (taken from TG curves) in dependence of experimental conditions

Decomposition		Apparatus	Sample weight, mg	Rate of temperature increase, °C/min⁻¹	Crucible	Atmosphere	Decomposition stoichiometry
1	A	derivatograph	50	2	platinum	air	−2, −1, −1
	B	derivatograph	50	5	platinum	air	−2, −1, −1
	C	derivatograph	500	1	platinum	air	−2, −1, −1
	D	derivatograph	300	6	platinum	air	−2, −1, −1
	E	derivatograph	100	3	platinum	air (or nitrogen)	−2, −1, −1
	F	derivatograph	486.7	5	platinum polyplate	air	−2, −1, −1
	G	derivatograph	500	6	platinum with a lid	ligand	−1, −2, −1
2		derivatograph	500	(5)	labyrinth*	ligand	−1, −2, −1
3		micro-balance	2.59	0.5	platinum	air	−2, −2
4		vacuum thermo-balance	10.6	2.5	platinum	vacuum	−4

* Measurements made in quasi-isothermal and quasi-isobaric conditions [13].

of the intermediates are not observed only for the reason that they are unstable under the given conditions of the thermal process, since the partial pressure of the ligand in the gaseous phase is not sufficient (Fig. 1, curve 4). This latter circumstance may be the cause why a lower number of intermediates may be expected for small samples (Fig. 1, curve 3). A larger sample, or a static air atmosphere, produce the conditions for a higher partial pressure of the ligand in the gaseous phase, and this can result in a higher number of intermediates (Fig. 1, curve 1/*E*). Under analogous conditions, by suitable choice of the sample and the rate of temperature increase, a four-step process of decomposition of the investigated complex has been observed (−1, −1, −1, −1) [8]. The absence of the intermediate $Ni(NCS)_2(\beta\text{-pic})_3$ for the cases 1/*A* to 1/*F* (Table 1) need not be caused by thermodynamic factors only. An important part may also be played by the crystallization kinetics of the intermediates; it may be influenced by the temperature at which the initial complex decomposes. Under dynamic conditions of thermal decomposition only a small amount of the first intermediate can arise, so that it is not recorded in the TG curve in the thermal decomposition process; it may be identified, however, in the DTG curve, or by phase analysis [8].

The thermal decomposition 1/*G* approaches the quasi-equilibrium conditions obtained in thermal decomposition 2, using a labyrinth crucible. As Fig. 1, curve 2 shows, the initial complex undergoes spontaneous decomposition at 200°. The intermediate $Ni(NCS)_2(\beta\text{-pic})_3$ formed is stable in weight up to 221°; at 223° it undergoes spontaneous decomposition to $Ni(NCS)_2(\beta\text{-pic})$, that is stable up to 245°, and at 250° spontaneous decomposition occurs to $Ni(NCS)_2$.

Under quasi-isothermal and quasi-isobaric, i.e. quasi-equilibrium conditions, the decomposition stoichiometry differs markedly from that in a non-equilibrium state. This unexpected experimental result can be explained by a greater rate of decomposition of the complex $Ni(NCS)_2(\beta\text{-pic})_2$ than that for $Ni(NCS)_2(\beta\text{-pic})_3$.

It is also possible, however, that under the given experimental conditions the complex $Ni(NCS)_2(\beta\text{-pic})_2$ is really thermodynamically unstable and disproportionates to $Ni(NCS)_2(\beta\text{-pic})_3$ and $Ni(NCS)_2(\beta\text{-pic})$.

Though we could not explain all the experimental results unambiguously, it has been proved that the stoichiometry of thermal decomposition of the solid complex $Ni(NCS)_2(\beta\text{-pic})_4$ can be markedly influenced by changes in the experimental conditions. This result may be used in the study of decomposition kinetics (a minimum sample, or vacuum, are applicable, thereby decreasing the number of steps), and also for purposes of synthesis. It makes possible the preparation of complexes of the type $Ni(NCS)_2(\beta\text{-pic})_3$, that cannot be obtained from solution and are not formed under common conditions of thermal decomposition in a thermodynamic non-equilibrium state.

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RÉSUMÉ — On a étudié l'influence des facteurs en relation avec des conditions d'expérience différentes, sur la stoechiométrie de la décomposition thermique du complexe $Ni(SCN)_2$ $(\beta\text{-picoline})_4$. On a établi que le dégagement de la β-picoline s'effectue en trois étapes (−2, −1, −1) si l'expérience TG est réalisée à l'aide d'un Derivatograph (atmosphère d'air, échantillon de 50−500 mg, vitesse d'échauffement 1—6 °C/min, creuset avec fond percé d'un trou), en deux étapes (−2, −2) avec une microbalance (prélèvement de 2.59 mg) et en une étape (−4) si l'expérience TG est réalisée sous vide. En conditions quasi-isothermes et quasi-isobares, dans un creuset de forme spéciale, la β-picoline se dégage en trois étapes (−1, −2, −1). On parvient à un résultat analogue avec un Derivatograph en utilisant un creuset muni d'un couvercle. On discute les causes de ces différences.

ZUSAMMENFASSUNG — Der Einfluß verschiedener Versuchsbedingungen auf die Stöchiometrie der thermischen Zersetzung des Komplexes $Ni(NCS)_2(\beta\text{-Pikolin})_4$ wurde untersucht. Mittels TG wurde festgestellt, daß der Derivatograph (Luft-Atmosphäre, 50−500 mg Probe, Geschwindigkeit des Temperaturanstiegs 1 bis 6 °C/min., Tiegel mit Loch im Boden) die Freisetzung des β-Pikolins in drei Stufen (−2, −1, −1), die Mikrowaage (Probe von 2.59 mg) in zwei Stufen (−2, −2) und die Vakuumthermowaage in einer Stufe (−4) angibt. Bei quasi-isothermen und quasi-isobaren Bedingungen in einem besonderen Tiegel wurde β-Pikolin in drei Stufen (−1, −2, −1) freigesetzt. Ein ähnliches Ergebnis wurde mit dem Derivatographen bei Verwendung eines Tiegels mit Deckel erhalten. Die Ursachen dieser Unterschiede werden erörtert.

Резюме — Было изучено влияние факторов, обусловленных различными экспериментальными условиями, на стехиометрию термического разложения комплекса $Ni(NCS)_2$ $(\beta\text{-пиколин})_4$. С помощью ТГ было найдено, что дериватограф (воздушная атмосфера, вес образца 50—500 мг, скорость повышения температуры 1—6 °С/мин, тигель с углубленным дном) показал выделение пиколина в три стадии (—2, —1, —1), микровесовой (вес образца 2.59 мг) — в две стадии (—2, —2) и вакуумно-термовесовой — в одну стадию (—4). При квази-изобарных условиях в специальном тигле выделение β-пиколина происходило в три стадии (—1, —2, —1). Аналогичный результат был получен на дериватографе, используя тигель с крышкой. Обсуждены причины этих различий.