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STUDY OF THE THERMAL DECOMPOSITION PROCESSES OF CLATHRATE COMPOUNDS

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The decompositions of the clathrate compounds $[M(NCS)_2(4\text{-MePy})_4]\cdot nG$ (where M = Mn, Co, Ni or Cd; G = 4-methylpyridine (4-MePy), benzene or xylenes) were studied on a Q-derivatograph under quasi-equilibrium conditions and with linear heating. These clathrates can be divided into two groups, in which the loss of guest is either (I) accompanied by destruction of the host complex, or (II) occurs before decomposition of the host complex. Kinetic parameters were obtained.

Due to their structures clathrate compounds are interesting subjects for the research of heterogeneous thermal reactions of the type $A_s \rightarrow B_s + C_{gas}$. In this work we have studied the features of the decompositions of the clathrate compounds $M(NCS)_2(4\text{-MePy})_4\cdot nG$, where M = Mn(II), Co(II), Ni(II) or Cd(II), and G = 4-methylpyridine (4-MePy), benzene or xylenes.

Experimental

Synthesis of the host coordination complexes was carried out by a known method [1]. The clathrate compounds were sysnthesized through the reaction between the host coordination complex (crystal compound) and the guest in the vapour state at room temperature.

The thermal decomposition processes were studied on a Q-derivatograph under quasi-equilibrium conditions [2] using different sample holders and with linear heating. The temperatures of decomposition under quasi-equilibrium conditions were used for qualitative estimation of the thermodynamic stabilities of the compounds investigated.

The kinetic curves of gas evolution were obtained by means of a continuous reactor [3] under non-isothermal conditions. The samples had a mass of 5–10 mg; the heating rate was 4–6 deg min^{-1}; the helium flow rate was 60 cm^3 min^{-1}; a conductometric detector was used. Experimental data were processed on a computer with the program TA IB [4]. For the compounds studied, the equation of a contracting sphere was the equation best describing the process. The values of E and A were calculated from 5 experiments; experimental errors were found with a confidence level of 95%.

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Results and discussion

A simple general description cannot be given for the course of thermal decomposition of host coordination complexes and clathrates,

$Mn(NCS)_2(4\text{-}MePy)_4 \cdot 0.67(4\text{-}MePy)$.

Decomposition of the Mn(II) clathrate occurs in three steps (Fig. 1). Loss of the volatile guest component is accompanied by the chemical dectruction of the host complex. The first stage is

$$[Mn(NCS)_2(4\text{-}MePy)_4] \cdot 0.67(4\text{-}MePy) \rightleftarrows$$
$$\rightleftarrows [Mn(NCS)_2(4\text{-}MePy)_2] + 2.67\,(4\text{-}MePy)\uparrow \qquad (1)$$

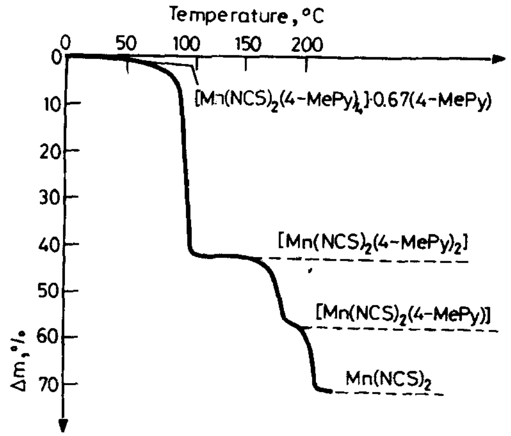

Fig. 1 Thermal decomposition of the clathrate $[Mn(NCS)_2(4\text{-}MePy)_4] \cdot 0.67(4\text{-}MePy)$. Sample holder: covered crucible ($p = 0.2$ atm). Heating program: quasi-isothermal; sample mass: 200 mg, atmosphere: air.

The decomposition temperature is 113°. The kinetics of this process was studied: $E = 135 \pm 9$ kJ/mol; $\log A = 15.5 \pm 1.1$.

$[Co(NCS)_2(4\text{-}MePy)_4] \cdot 1.07(4\text{-}MePy)$ and $[Co(NCS)_2(4\text{-}MePy)_4] \cdot$

The thermal decomposition of the clathrate and the host complex under quasi-equilibrium conditions proceeds at once to the complex containing 3 molecules of 4-methylpyridine (Eq. (2), Fig. 2)

$$[Co(NCS)_2(4\text{-}MePy)_4] \rightarrow [Co(NCS)_2(4\text{-}MePy)_3] + (4\text{-}MePy)\uparrow \quad (2)$$

The decomposition temperatures are 163 and 165°, respectively. In this case the clathrate is stable up to the decomposition temperature of the host complex.

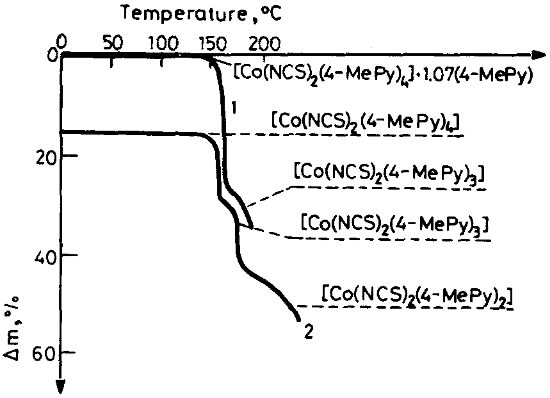

Fig. 2 Thermal decomposition of the clathrate $[Co(NCS)_2(4\text{-}MePy)_4]\cdot 1.07(4\text{-}MePy)$ (1) and complex $[Co(NCS)_2(4\text{-}MePy)_4]$ (2). Sample holder: labyrinth (p = 1atm). Heating program: quasi-isothermal; sample mass: 200 mg, atmosphere: air.)

The kinetic parameters are: $E = 147$ kJ/mol; $\log A = 17.4$; $t_{\text{init}} = 76°$.

The kinetics of the clathrate decomposition cannot be studied in this manner since the stages are not separated.

$[Cd(NCS)_2(4\text{-}MePy)_4]\cdot 0.67(4\text{-}MePy)$ and $[Cd(NCS)_2(4\text{-}MePy)_4]\cdot$

The TG curves for the clathrate and the host complex under quasi-equilibrium conditions are presented in Fig. 3. Both compounds decompose to the complex containing 2 molecules of 4-MePy:

$$[Cd(NCS)_2(4\text{-}MePy)_4]\cdot 0.67(4\text{-}MePy) \rightleftarrows$$
$$\rightleftarrows [Cd(NCS)_2(4\text{-}MePy)_2] + 2.67\,(4\text{-}MePy)\uparrow \quad (3)$$
$$[Cd(NCS)_2(4\text{-}MePy)_4] \rightleftarrows [Cd(NCS)_2(4\text{-}MePy)_2] + 2\,(4\text{-}MePy)\uparrow \quad (4)$$

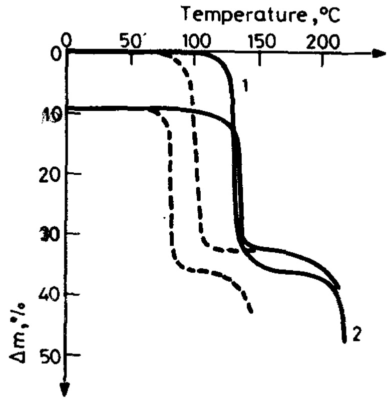

Fig.3 Thermal decomposition of the clathrate $[Cd(NCS)_2(4\text{-}MePy)_4]\cdot 0.67(4\text{-}MePy)$ (1) and complex $[Cd(NCS)_2(4\text{-}MePy)_4]$ (2). Sample holder: labyrinth (unbroken line), open crucible (dotted line p = 0.05atm). Heating program: quasi-isothermal; sample mass: 200mg, atmosphere: air.

It is interesting to note that in an open crucible (p_{guest} = 0.05 atm) the clathrate is more stable than the host complex (100° and 80°, respectively). In a labyrinth crucible (p_{guest} = 1 atm), the two compounds decompose at practically the same temperature, ~140°. It is known [5, 6] that the host Cd(II) complex disproportionates at 134.0 ± 0.5°:

$$4\,[CdX_2A_4] \rightleftarrows 3\,[CdX_2A_4]\cdot 0.67A + [CdX_2A_2] \qquad (5)$$

At 140°, therefore, in both cases we observe the decomposition of the same compound, the clathrate.

The decomposition of the host complex was studied on linear heating (Fig. 4). In this case the decomposition of the complex proceeds according to the parallel reactions (4) and (5) and is accompanied by the evolution of gaseous 4-MePy (weight loss beginning at 127°) and the formation of the clathrate by reaction (5). When all the initial complex is spent, the clathrate formed by reaction (5) begins to decompose (147°). The decomposition of the complex in an open crucible proceeds by reaction (4).

The kinetic parameters were obtained for reaction (3): $E = 112 \pm 2$ kJ/mol; $\log A = 13.4 \pm 0.2$; $t_{\text{init}} = 50°$; and for reaction (4): $E = 102 \pm 8$ kJ/mol; $\log A = 12.2 \pm 1.4$; $t_{\text{init}} = 37°$. The kinetic stabilities of the clathrate and the host complex are practically the same. They seem to be determined by the stability of the structural framework of the host complex.

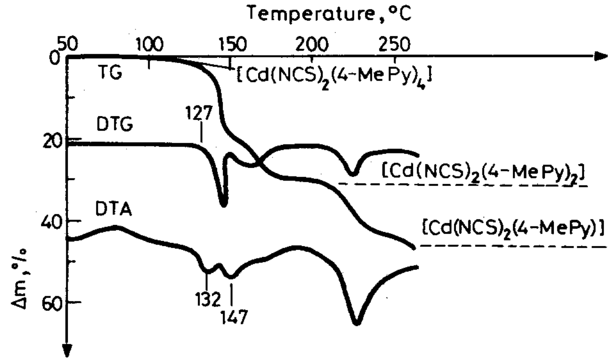

Fig. 4 Thermal decomposition of the complex [Cd(NCS)$_2$(4-MePy)$_4$]. Sample holder: labyrinth. Heating program: 2.5 deg/min; sample mass: 200.6mg, atmosphere: air.

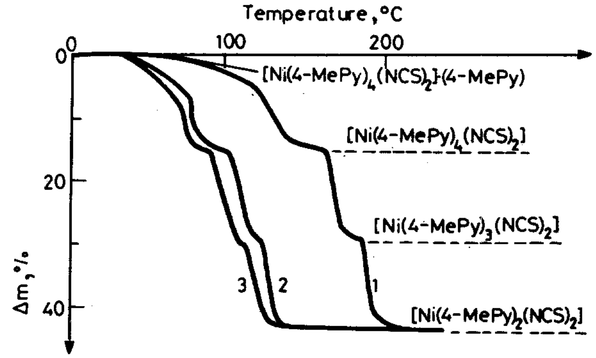

Fig. 5 Thermal decomposition of the clathrate [Ni(NCS)$_2$(4-MePy)$_4$]·1.05(4-MePy). Sample holder: labyrinth (1), covered (2) and open crucible (3). Heating program: quasi-isothermal; sample mass: 200mg, atmospere: air.

[Ni(NCS)$_2$(4-MePy)$_4$]·1.05(4-MePy) and [Ni(NCS)$_2$(4-MePy)$_4$]·

The clathrate decomposes to the host complex, the removal of the guest occurring in 2 steps (Fig. 5). Both on linear heating and under quasi-equilibrium conditions, the two-stage character of the process is retained. It is known [7] that the decomposition of the clathrate at room temperature proceeds wholly according to reaction (6), the guest being lost up to $y = 0$ without change of structure:

$$\beta\text{–}[\mathrm{Ni(NCS)_2(4\text{-}MePy)_4}]\cdot(\mathrm{4\text{-}MePy}) \rightleftharpoons$$
$$\rightleftharpoons \beta\text{–}[\mathrm{Ni(NCS)_2(4\text{-}MePy)_4}]\cdot y(\mathrm{4\text{-}MePy}) + (1-y)(\mathrm{4\text{-}MePy})\uparrow \qquad (6)$$

$$\beta\text{–}[\mathrm{Ni(NCS)_2(4\text{-}MePy)_4}]\cdot(\mathrm{4\text{-}MePy}) \rightleftharpoons$$
$$\rightleftharpoons \alpha\text{–}[\mathrm{Ni(NCS)_2(4\text{-}MePy)_4}] + (\mathrm{4\text{-}MePy})\uparrow \quad (7)$$

The authors presumed that the change in the mechanism from (6) to (7) takes place in some stage of the thermal decomposition. This is caused by (I) the collapse of vacant parts of the clathrate canals when their degree of occupation by guest molecules is less than 60% ($0 \leqslant y \leqslant 0.6$), and (II) disproportionation of the clathrate phase of varying composition into the clathrate with $y = 1$ and the host α-modification, followed by clathrate decomposition according to reaction (7). This is confirmed by cooling the sample after the inflection point is reached, and re-heating. The two-stage character of the process is retained. One can therefore conclude that the two-step mechanism of guest loss is peculiar to the Ni(II) clathrate. The clathrate decomposes during the first stage into a solid solution (with retention of the initial structure and gradual loss of the guest in the temperature interval 100–130 °) and during the second one into a compound with constant composition, namely the host α-modification, at 130°.

This latter complex dissociates in 4 steps. Under quasi-equilibrium conditions the decomposition temperature for the 1st stage is 165°.

$$[\mathrm{Ni(NCS)_2(4\text{-}MePy)_4}] \rightarrow [\mathrm{Ni(NCS)_2(4\text{-}MePy)_3}] + \mathrm{4\text{-}MePy}\uparrow \quad (8)$$

In this case, the clathrate decomposes to the host complex and the guest molecule before the host complex begins to decompose.

The kinetic parameters obtained for reaction (6) were $E = 123 \pm 6$ kJ/mol and $\log A = 16.4 \pm 0.9$, and for reaction (7) $E = 93$ kJ/mol and $\log A = 10.1$.

The kinetic parameters for reaction (8) were $E = 151 \pm 5$ kJ/mol; $\log A = 16.5 \pm 0.8$.

The difference in kinetic stability of the clathrate and the host complex is due only to the energy barrier, since their decomposition processes are isoentropic.

The thermal decompositions of the clathrates $[\mathrm{Ni(NCS)_2(4\text{-}MePy)_4}]\cdot n\mathrm{G}$, where the guest G = benzene or xylenes, were studied. For these clathrates the following scheme of decomposition is observed:
$[\mathrm{Ni(NCS)_2(4\text{-}MePy)_4}]\cdot n\mathrm{G} \rightleftarrows \mathrm{Ni(NCS)_2(4\text{-}MePy)_4} \rightleftarrows$ following stable phase. According to the temperatures of decomposition under quasi-equilibrium conditions, the following series of thermodynamic stability was obtained: G; benzene < o-xylene < m-xylene < p-xylene

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Zusammenfassung — Die Zersetzung von Clathrat-Verbindungen der Zusammensetzung $[M(NCS)_2(4\text{-}MePy)_4]\cdot nG$ (M = Mn, Co, Ni, Cd; G = 4-Methylpyridin (4-MePy), Benzen, *o*-, *m*-, *p*-Xylen) wurde mittels Q-Derivatograph unter Quasi-Gleichgewichtsbedingungen und bei linearer Aufheizung untersucht.
Die studierten Clathrate lassen sich in zwei Gruppen einteilen, je nachdem ob die Abgabe des Gastmoleküls G entweder vor oder unter Gleichzeitiger Zerstörung des Wirtskomplexes erfolgt. Kinetische Parameter wurden ermittelt.

РЕЗЮМЕ — С помощью Q-дериватографа в квазиравновесных условиях и в условиях линейного нагрева изучено разложение клатратных соединений состава $[M(NCS)_2(4\text{-}MePy)_2]\cdot nG$, где M — двухвалентные марганец, кобальт, никель и кадмий, а G — 4-метилпиридин, бензол и ксилолы. Изученные клатраты могут быть разделены по тому признаку, что потеря молекул внедрения сопровождается разложением комплекса или же процесс выделения таких молекул происходит перед разложением комплекса. Установлены кинетические параметры происходящих реакций.