

PROCESSES OF THERMAL DISSOCIATION OF CLATHRATES ON THE BASE OF COORDINATION COMPOUNDS

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Abstract

Inclusion compounds are very interesting materials for thermoanalytical investigations. Stable guest molecules are packed in the cages, channels or layers in the host matrix, thermal dissociation reactions are reversible and have the clear-cut stoichiometry. The clathrates with a matrix of coordination compounds (of the type $[MA_4X_2] \cdot nA$) were synthesized (M —transition metals; A —Py, 4-MePy; X — NO_3 , NCS, NCO; $n=0.67$ or 1 or 2). Four Py or MePy molecules are tightly bound in the coordination sphere by $M-N$ bonds and others are confined in the matrix cavities by van der Waals forces.

Processes of thermal dissociation of the clathrates were studied. Q-thermogravimetry (for checking the stable intermediate phases) and the home-made gas-flow reactor (as EGA-device for kinetic studies) were used. The compensation dependence ($\lg A_i = aE_i + b$) was observed for the most of clathrates series, it was explained by the identity of the reaction mechanism.

Keywords: coordination compounds, inclusion compounds, kinetic lability, Q-thermogravimetry, solid-state

Introduction

Such inclusion compounds as clathrates [1] are the important representative of supramolecular systems. A big group of them are Werner clathrates on the base of the matrix of coordination compounds $[MA_4X_2] \cdot nA$ [2] (usually A —molecules of pyridine and its derivatives, M^{2+} —transition metal cations, X^{1-} —anion ligands). Four pyridine (Py) or 4-methylpyridine (MePy) molecules are tightly bound in the coordination sphere by $M-N$ bonds and others are confined in the matrix cavities by van der Waals forces.

The thermal decomposition of these inclusion compounds are studied in lesser degree than thermal transformation of the well-known matrix substances. As an example there are some thoroughly performed works on the study of the thermal dissociation of complexes $[MPy_4X_2]$ and $[M(MePy)_4X_2]$ [3–6].

Experimental

In this work we summarize our data on studying thermal behaviour in four series; each series consists of isostructural clathrates with different metal in host complex (references presented below are related to the clathrates preparation):

- | | |
|---|--|
| 1 [M(MePy) ₄ (NCS) ₂]-MePy | (M=Fe, Co, Ni, Zn; MePy=4-methylpyridine) [7-10] |
| 2 [M(MePy) ₄ (NCS) ₂]-2/3MePy | (M=Mn, Fe, Cu, Zn, Cd) [7, 10-13, 14] |
| 3 [MPy ₄ (NCO) ₂]-2Py | (M=Mn, Fe, Co, Ni, Cu, Cd; Py=pyridine) [15] |
| 4 [MPy ₄ (NO ₃) ₂]-2Py | (M=Co, Ni, Zn, Cd) [16-18]. |

Derivatograph Q-1500-D and Derivatograph-C (MOM, Hungary) were used for the study of the step-wise character of thermal dissociation reactions [19]. Special set of sample holders allows to run the experiment in quasi-isobaric conditions; the maintenance of the small and constant decomposition rate (0.3 mg min⁻¹) creates the temperature stabilization. For the reactions with easy reversibility it means the quasi-equilibrium conditions of the reaction, therefore the intermediate compounds are the thermodynamically stable phases. Sample mass was 150 mg, atmosphere: static air.

Home-made gas-flowing reactor (with conductometric detector) was used as EGA-device for the non-isothermal kinetic experiments [20] (sample mass was in limits of several mg, the fraction of grains with size distribution $d_{\max}/d_{\min} \leq 5$, the rate of helium flow through the sample was 60-120 cm³ min⁻¹, the heating rate 5°C min⁻¹).

The recorded gas evolution curves ($d\alpha/dt$ vs. T) were used for kinetic analysis. The experimental data were processed with computer programs TA 1B (by Šesták and Skvara [21]). The selection of the kinetic equation was carried out by linearity of the function $\lg g(\alpha)$ vs. $1/T$ (integral method); the search was made amongst 13 equations (describing nucleation, nuclei growth, diffusion and reactions on the interface of different dimension).

In all cases the rate controlling process was the chemical reaction on the interface, $d\alpha/dt = k(1-\alpha)^{2/3}$, in the beginning of thermal dissociation ($0.05 \leq \alpha \leq 0.55$, approximately) and the process of evolved gas diffusion through the product layer formed on the grain surface ($0.55 \leq \alpha \leq 0.95$, approximately). The values of E and A were calculated from 5-6 experiments; the experimental errors were found with a confidence level of 95% and as usual did not exceed 5-7%.

Results and discussion

Thermal dissociation under the quasi-equilibrium conditions

The [M(MePy)₄(NCS)₂]-MePy clathrates

Structurally, these clathrates refer to the class known as tetragonal β -phases [22-23]. There are zigzag intersecting channels in this structural type where guest species are located. The size and geometry of the channels make easy movement of guest molecules possible through the structure. The Ni-clathrate is well studied; the host matrix in this case is kinetically quite stable making the partial or complete

guest removing possible. The empty matrix may be repeatedly refilled with a great number of guest types of suitable size. Due to these properties β -[Ni(MePy)₄(NCS)₂] matrix was referred to as 'organic zeolite' [24].

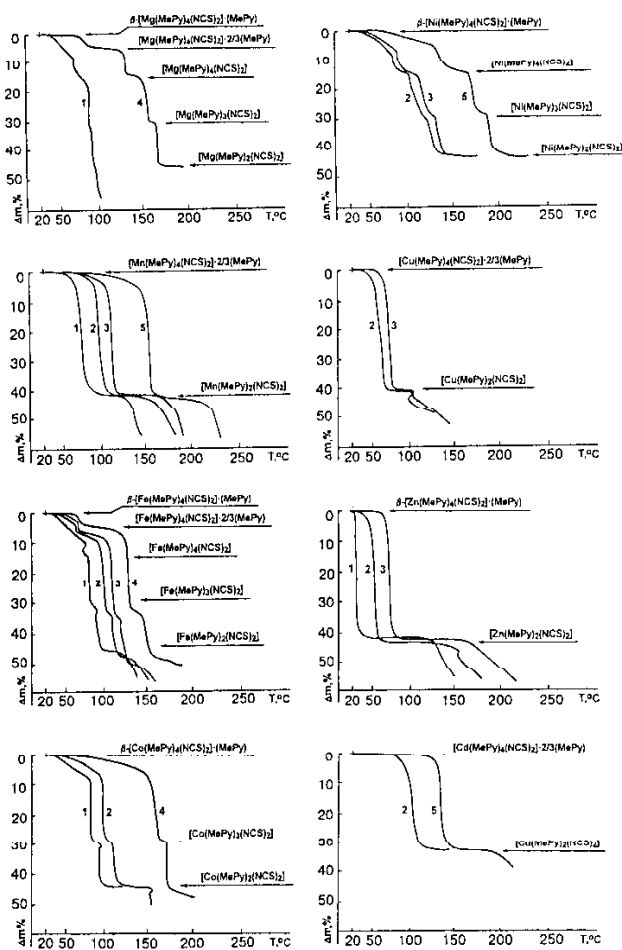
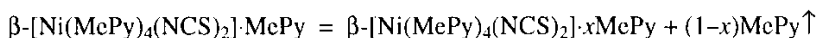
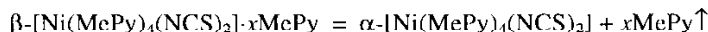


Fig. 1 Thermal decomposition of clathrates $[M(4\text{-MePy})_4(\text{NCS})_2] \cdot n(4\text{-MePy})$. Quasi-isothermal heating program ($q=0.3 \text{ mg min}^{-1}$). Sample holders: 1 – plate-like, 2 – open crucible, 3 – crucible with lid, 4 – conical type, 5 – labyrinth holder

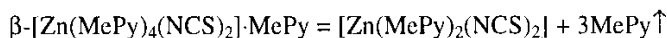
The thermoanalytical data for the studied β -clathrates are shown in Fig. 1. For the Ni-clathrate the first decomposition step may be attributed to the guest escape from the β -matrix without destruction of the matrix:



while the second one occurs with formation of a non clathrate α form of the host complex:



In spite of structural similarity, the Zn-clathrate reveals essentially different dissociation mechanism decomposing to bis(MePy)-complex in one step:



This may be explained by the instability of the $[\text{Zn}(\text{MePy})_4(\text{NCS})_2]$ matrix by it self, so as the respective complex does not exist as individual compound [10] (the complex may exist only inside clathrate, due to 'contact stabilization phenomenon' [25-26]). Dissociation of the Co-compound represents an intermediate case, and dissociation of Mg- and Fe-clathrates is more complicated. Thus, structural similarity of the clathrates does not result in their similar dissociation behaviour.

The $[\text{M}(\text{MePy})_4(\text{NCS})_2]\cdot 2/3\text{MePy}$ clathrates

These clathrates are also isomorphous representing another, trigonal structural type. This host matrix has isolated straight channels stretching along the c crystallographic axis. The channels are of special geometry, large parts containing two guest molecules are connected with narrow isthmuses. If available, water fills these isthmuses to give structurally limited stoichiometry $[\text{M}(\text{MePy})_4(\text{NCS})_2]\cdot 2/3\text{MePy}\cdot 1/3\text{H}_2\text{O}$. This water is not critical for the clathrates stability or their other properties [7] and will be not further discussed. For this structural type, one hardly might expect guest moving through the channel without serious phase distortions. The thermal curves are similar qualitatively (Fig. 1). It is worth to say, that the stabilized temperatures of the thermal dissociation under quasi-equilibrium (in labyrinth sample holder) are practically equal for the existed matrix complex and clathrate (for instance, 163 and 165°C for Co-compounds, 140 and 140°C for Cd-compounds). So the stability of these clathrates in the decomposition reaction depends mainly upon the stability of the host complex matrix.

The $[\text{MPy}_4(\text{NCO})_2]\cdot 2\text{Py}$ clathrates

The compounds belong to the third, orthorhombic structural type [27]. Guest pyridine species are located inside cages connected to each other to form straight rectangular-prismatic channels stretching along the α crystallographic axis. Host molecules have too little contacts to each other. The series may be divided into two qualitatively different groups (Fig. 2). In the Mn-, Fe-, Co- and Ni-systems host complex forms as the first product of the clathrate dissociation; thermodynamic stability of both clathrate and host phases increase in this row. In the Cu- and Cd-systems only the guest molecules prevent the whole structure of collapsing. This results

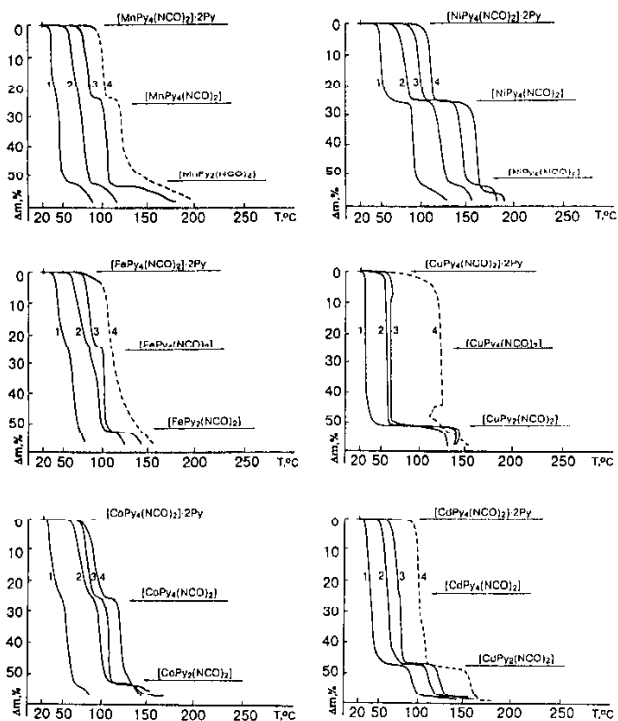


Fig. 2 Thermal decomposition of clathrates $[MPy_4(NO_3)_2] \cdot 2Py$. The processes with liquid phase formation are marked with dashes. The destinations are in Fig. 1

in significant decreasing in the thermodynamic stability of the clathrates as compared to the members of the first group.

The $[MPy_4(NO_3)_2] \cdot 2Py$ clathrates

The compounds also belong to the orthorhombic structural type. This series represents an extreme case of host instability: for all four clathrates the respective host complexes do not form as individual phases. This problem was carefully investigated before by full determination of the $Py-[M(Py)_3(NO_3)_2]$ phase diagrams ($M=Zn$ [17, 26]; Cd [18, 26]) and/or by strain method ($M=Co, Ni$ [16]; Zn [28]; Cd [18]). In accordance to this, as Fig. 3 shows, the dissociation goes directly to high stable tripyridine complexes with removing one of bonded pyridine along with guest ones.

Kinetic stability studies

The clathrates $[M(4-MePy)_4(NCS)_2] \cdot 2/3(4-MePy)$ ($M=Mn, Co, Cd, Cu$) decompose instantaneously to the complex $[M(4-MePy)_2(NCS)_2]$ (or $[Co(4-MePy)_3(NCS)_2]$), al-

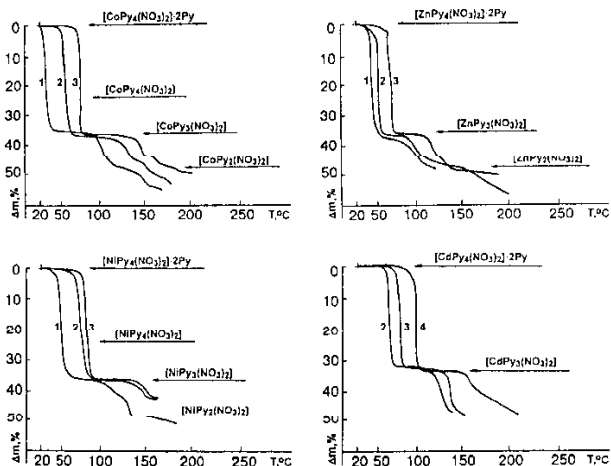


Fig. 3 Thermal decomposition of clathrates $[MPy_4(NO_3)_2] \cdot 2Py$. The destinations are in Fig. 1

though the stable matrix complex exists for Mn-, Co- and Cd-systems ($M(NCS)_2(solid) - (4-McPy)_{liquid}$). Such a matrix complex does not exist at all only for Cu-system.

The kinetic parameters in the series correlate with the length of the metal–ligand bonds in the coordination spheres within the clathrates ($L_{Cu-N}=2.51 \text{ \AA}$, $L_{Cd-N}=2.49 \text{ \AA}$, $L_{Mn-N}=2.34 \text{ \AA}$). Therefore we can conclude that the kinetic stability of these clathrates in the decomposition reaction depends mainly upon the stability of the host complex matrix (only partially modified by clathrates framework for Co, Mn, Cd-compounds and created for Cu-compound). The including guest molecules are removed because of the matrix destruction. The change in the length of the metal–ligand bonds explains why $[Mn(4-McPy)_4(NCS)_2]$ exists as a stable phase and $[Cu(4-McPy)_4(NCS)_2]$ does not. The analogy in reaction mechanism for all four clathrates is supported by the existed compensation dependence (Fig. 4).

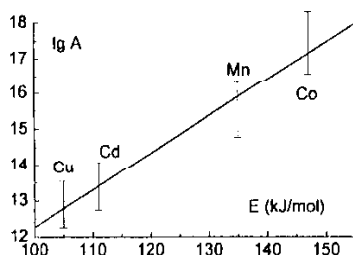
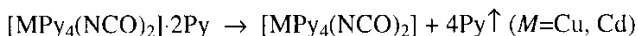
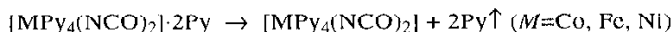


Fig. 4 Kinetics of thermal dissociation of clathrates $\{M(4-McPy)_4(NCS)_2\} \cdot 2/3(4-McPy)$

The clathrates $[\text{MPy}_4(\text{NCO})_2] \cdot 2\text{Py}$ have different decomposition reactions:



The analogy in reaction mechanism for Fe, Co and Ni compounds is supported too by the compensation dependence, and it is clear that Cu compound is not included in the series (Fig. 5).

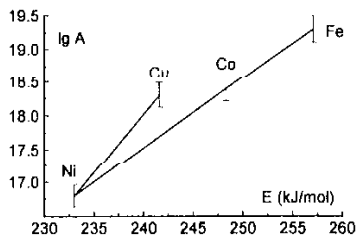


Fig. 5 Kinetics of thermal dissociation of clathrates $[\text{MPy}_4(\text{NCO})_2] \cdot 2\text{Py}$

The replacement NCS-anion by NCO-anion increases the kinetic stability both of the clathrates, and matrix compounds, changes the composition and the stability of the intermediate phases, although this does not result in the stabilization of Cu- and Cd-complex matrix. The stability of the Fe-, Co- and Ni-clathrates is not connected with the matrix stability by itself, the clathrates can decompose to the stable matrix.

The thermoanalytical study of inclusion compounds gives the possibility to investigate the step-wise processes of thermal dissociation, to recognize real intermediate phases, to analyze quantitatively the kinetic stability of the clathrates (including matrix compound stability), to discuss the possible mechanism of decomposition.

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