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THE STABILITY OF INCLUSION COMPOUNDS UNDER HEATING
Part I. Inclusion compounds of microporous manganese formate with included dioxane {$Mn(HCOO)_2 \cdot 1/3C_4H_8O_2$} and tetrahydrofurane {$Mn(HCOO)_2 \cdot 1/3C_4H_8O$}

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The thermal decomposition of two inclusion compounds $Mn(HCOO)_2 \cdot 1/3C_4H_8O_2$ and $Mn(HCOO)_2 \cdot 1/3C_4H_8O$ was studied in the inert atmosphere. The process of both dioxane, and tetrahydrofurane removal has two steps; the intermediate phase is unstable and kinetically hindered. Manganese formate is stable up to 330°C. Thermogravimetric data (obtained at different rates of linear heating) were processed with computer program (with 'Model free' approach). Kinetic parameters were calculated for the first decomposition step, and the process is described by equation of *n*-order reaction with autocatalysis.

Keywords: *coordination compounds, inclusion compounds, 'model free' kinetics*

Introduction

Inclusion compounds are important representatives of supramolecular systems and so are very interesting and favored materials for the study of thermal stability by thermoanalytical methods. Their synthesis (and the existence in itself) are based on their high enough kinetic (and thermodynamic) stability at room temperature in the processes of thermal dissociation with the breakdown to the host matrix and the guest compound. There are no direct connections between the detailed structure of the inclusion compounds (such as strong and week bonds, etc.) and compounds thermal stability, their steps of decomposition, stability of capable intermediate phases, and so on. However, their thermodynamic stability in thermal dissociation process is essentially connected with entropy contribution in more important way, than with energetic factor [1].

Regular porous materials such as zeolytes or coordination polymers (metal-organic frameworks) are well-known host matrices, which are able to incapsulate smaller guests into the interlattice voids to form host-guest inclusion compounds. Recently we reported a guest-templated synthesis of new manganese (II) formate framework, which has permanently porous structure and possesses highly selective gas sorption properties [2]. At the same time this microporous metal-organic host framework was shown to undergo a long-range magnetic ordering with guest-modulated critical temperature [3].

Herein we report the study of thermal decomposition of two inclusion compounds of the microporous Mn(II) formate host structure with 1,4-dioxane and tetrahydrofurane (THF) guest molecules.

Experimental

Synthesis

Slightly modified procedure was used to prepare Mn(II) formate inclusion complexes [2]. The mixture of $Mn(NO_3)_2 \cdot 6H_2O$ (580 mg, 2.0 mmol) and formic acid (184 mg, 4.0 mmol) was dissolved in a mixture of dimethylformamide (DMF, 8.0 mL) with guest solvent (4.0 mL, guest=dioxane or THF) and heated at 120–125°C in sealed glass tube. After 2 days the colorless polyhedral crystals were filtered out, washed with DMF/*G* mixture and dried in air for 1 h to give inclusion compound $Mn_3(HCOO)_6 \cdot G$ (where *G*=guest) (c.a. 200 mg, 55–60%) The phase purity of the corresponding $Mn_3(HCOO)_6 \cdot G$ host-guest compounds were checked by powder X-ray analysis.

Thermal analysis

TG measurements were carried out on a Netzsch thermal analyzer TG 209. The experiments were performed in argon flow (100 $cm^3 \ min^{-1}$), at heating rates of 4, 8 and 12 grad $min^{-1,}$ the sample mass was kept 7.00±0.02 mg. The DSC measurement was carried

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out on a Mettler analyzer DSC822e/700 in argon flow (60 cm^3 min^{-1}) at a heating rate 10 grad min^{-1}, the sample mass was 33.5 mg.

Kinetic analysis under non-isothermal conditions

Thermogravimetric data were processed with the computer program NETZSCH Thermokinetics 2 (Version 2004.05). Special program module 'Model free' allows processing several thermogravimetric curves, obtained with different heating rates, without the information about the kinetic topochemical equations. Program 'ASTM E698' [4] enables to calculate the averaged values of activation energy according to temperatures of maximum decomposition rate. Programs 'Friedman Analysis' [5] and 'Ozawa–Flynn–Wall Analysis' [6–8] allow calculating the activation energies, and preexponential factors (assuming a first-order reaction) for the every experimental point of fractional conversion (in the interval $0.02<\alpha<0.98$). 'Ozawa–Flynn–Wall Analysis' is based on the dependence between the heating rate and inverted temperature; 'Friedman Analysis' is based on the dependence between the rate of conversion degree and inverted temperature. The same set of experimental data is used further for searching the topochemical equation (the selection from 16 equations: chemical reaction on the interface, nucleation, and diffusion). This calculation is made by the improved differential method of Borchardt–Daniels, with multiple linear regression method [9]. It is very important, that the interval of conversion degree (α) for this calculation can be chosen on the base of the relative constancy of the calculated kinetic parameters from 'Friedman Analysis' or 'Ozawa–Flynn–Wall Analysis'. F-test is used for the search of the best kinetic description [10]. If the calculation results in two or three kinetic equations with near values of correlation coefficients and F-test, but with noticeably different values of kinetics parameters, it is rationally to choose the equation with activation energy values near to data of 'Model free' module programs.

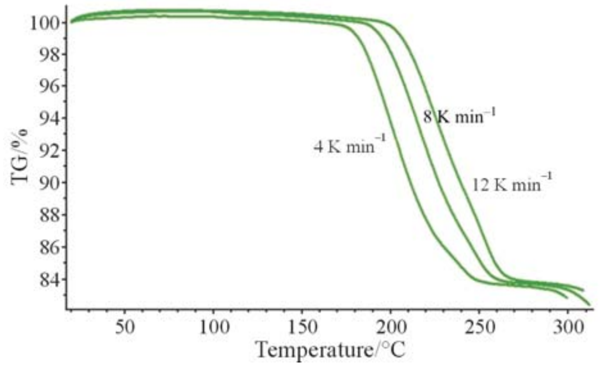

Fig. 1 TG-curves for $Mn(HCOO)_2 \cdot 1/3C_4H_8O_2$ decomposition (dioxane removal), m=7.00±0.02 mg, argon flow 100 cm^3 min^{-1}, heating rates 4, 8 and 12 K min^{-1}

Results and discussion

$Mn(HCOO)_2 \cdot 1/3C_4H_8O_2$

TG curves of the thermal decomposition of $Mn(HCOO)_2 \cdot 1/3C_4H_8O_2$ at three heating rates are shown in Fig. 1. The mass loss corresponds to the reaction:

$$Mn(HCOO)_2 \cdot 1/3C_4H_8O_2 \rightarrow Mn(HCOO)_2 + 1/3C_4H_8O_2 \uparrow$$

The curves show that the thermal decomposition occurs (rather unexpectedly) in two steps, the proportion between them being distinctly dependable on the heating rate (Figs 2, 3): the second mass loss step decreases with heating rate (both temperature interval) decreasing. Such second step behavior can be connected with the existence of different (both porous and non-porous) structures of manganese formate $Mn(HCOO)_2$ [2]; the assumption of the porous matrix framework collapse at elevated temperatures is fairly reasonable.

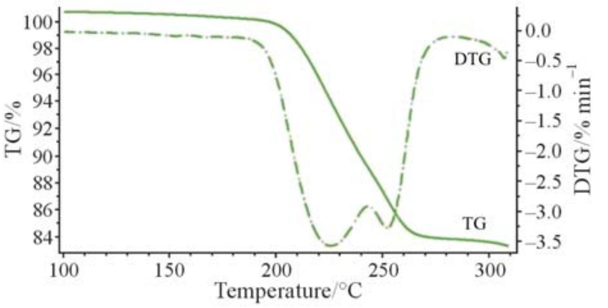

Fig. 2 Thermal decomposition curves: TG and DTG for $Mn(HCOO)_2 \cdot 1/3C_4H_8O_2$ decomposition (dioxane removal), m=7.00±0.02 mg, argon flow 100 cm^3 min^{-1}, heating rate 12 K min^{-1}

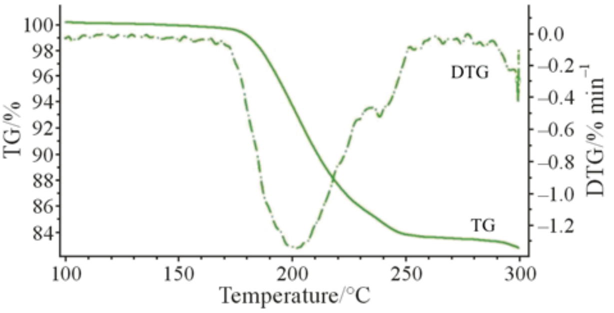

Fig. 3 Thermal decomposition curves: TG and DTG for $Mn(HCOO)_2 \cdot 1/3C_4H_8O_2$ decomposition (dioxane removal), m=7.00±0.02 mg, argon flow 100 cm^3 min^{-1}, heating rate 4 K min^{-1}

Three thermogravimetric curves (obtained under linear heating: 4, 8 and 12 grad min^{-1}) were processed by 'Friedman Analysis' and 'Ozawa–Flynn–Wall Analysis' programs. Program 'ASTM E698' (using temperatures of maximum decomposition rate) results in incorrect data for multi-step reactions.

Energy of activation is constant enough in the region of α=0.10–0.80, according to both calculations (E=74.7–78.2 kJ mol^{-1} in OFW Analysis), values increase to 180 kJ mol^{-1} in the region of α=0.80–0.90 in Friedman Analysis (Fig. 4), which indicates the existence of the second step of the reaction. So we simply recalculate these data, utilized only the original interval α=0.01–0.80 as the 100% conversion for the first step. These recalculated data are shown on Fig. 5 (with minor change of the activation energy: E_a=75.0–78.2 kJ mol^{-1} for α=0.05–0.95 of the first step).

Kinetic parameters were calculated by Borchardt–Daniels method for the selected region of conversion (0.05<α<0.95 for the first decomposition step). The checking equations: Bna, CnB, Fn, D3, A3 (Table 1).

It is important that here is no diffusion complication for the gas evolving during the decomposition. In accordance with F-test the best topochemical equations for the decomposition process are Bna or CnB:

$$f(\alpha)=(1-\alpha)^{1.17}\alpha^{0.49} \quad E_a=77.9 \text{ kJ mol}^{-1}, \log A= 6.3$$

$$f(\alpha)=(1-\alpha)^{1.15}(1+16\alpha) \quad E_a=77.8 \text{ kJ mol}^{-1}, \log A= 5.4$$

The obtained values of activation energy fully agree with the calculated ones by 'Free model' approach (E_a=75.0–78.2 kJ mol^{-1}).

We study the decomposition of this compound by DSC method (Fig. 6). The first complex endothermic peak (200–330°C) is connected with dioxane removal, the second one (330–420°C) – with the decomposition of manganese formate. The estimate of the thermal effect of dioxane removal $\{Mn(HCOO)_2\cdot 1/3C_4H_8O_2 \rightarrow Mn(HCOO)_2 + 1/3C_4H_8O_2\uparrow\}$ is 48 kJ mol^{-1}.

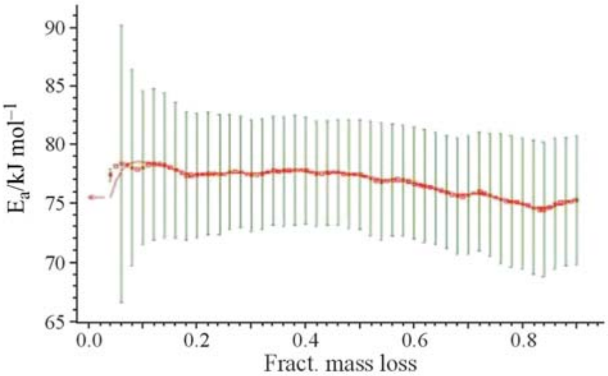

Fig. 5 $Mn(HCOO)_2\cdot 1/3C_4H_8O_2$. Dependence E_a=$f(\alpha)$, calculated by Ozawa–Flynn–Wall method (the first step of decomposition)

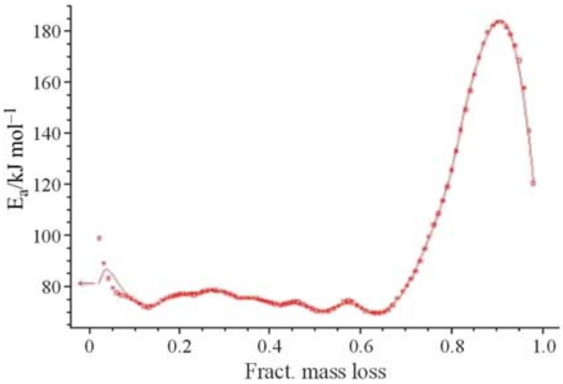

Fig. 4 $Mn(HCOO)_2\cdot 1/3C_4H_8O_2$. Dependence E_a=$f(\alpha)$, calculated by Friedman method (100% of dioxane removal)

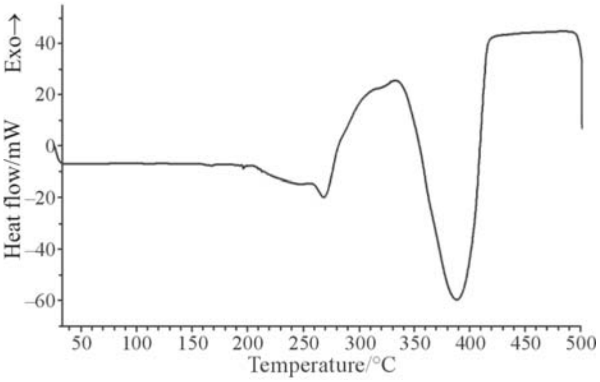

Fig. 6 DSC-curve for dioxane removal (200–330°C) and $Mn(HCOO)_2$ decomposition (330–420°C)

Table 1 Inclusion compound $Mn(HCOO)_2\cdot 1/3C_4H_8O_2$
Data of F-test on fit-quality (for the search of the best kinetic description, α=0.05–0.95)

#	Code	Type	f-act	F exp	F crit (0.95)	Correlation coefficient
1	S	Bna	131	1.00	1.34	0.99817
2	S	CnB	131	1.48	1.34	0.99728
3	S	Fn	132	7.77	1.34	0.98558
4	S	A3	133	30.04	1.33	0.94263
5	S	D3	133	48.78	1.33	0.90506

$Mn(HCOO)_2 \cdot 1/3C_4H_8O$

TG curves of the thermal decomposition of $Mn(HCOO)_2 \cdot 1/3C_4H_8O$ at three heating rates are shown in Fig.7.

The curves show (Figs 7, 8) that the thermal decomposition occurs in three steps. We believe that the first decomposition step is connected with the admixture of the water inclusive compound. At present time we did not succeed in the pure thf-compound isolation. The mass loss for the second and the third steps corresponds to the reaction:

$$Mn(HCOO)_2 \cdot 1/3C_4H_8O \rightarrow Mn(HCOO)_2 + 1/3C_4H_8O \uparrow$$

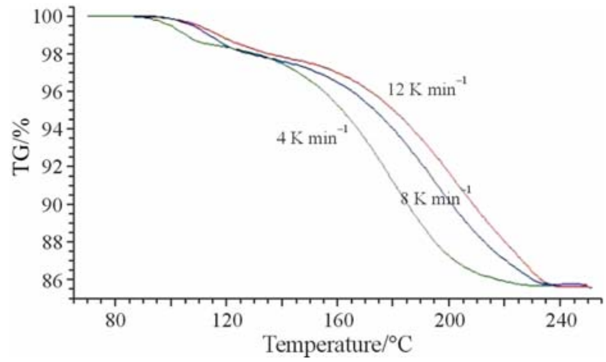

Fig. 7 TG-curves for $Mn(HCOO)_2 \cdot 1/3$ THF decomposition (THF removal), m=7.00±0.02 mg, argon flow 100 cm^3 min^{-1}, m=7.00 ±0.02 mg, heating rates 4, 8 and 12 K min^{-1}

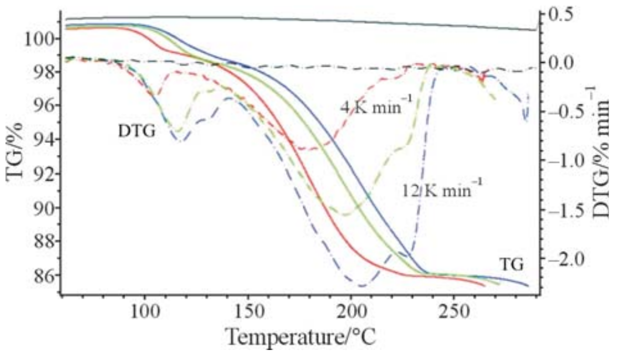

Fig. 8 Thermal decomposition curves: TG (solid line) and DTG (dotted line) for $Mn(HCOO)_2 \cdot 1/3$ THF decomposition (THF removal), m=7.00±0.02 mg, argon flow 100 cm^3 min^{-1}, heating rates 4 and 12 K min^{-1}

So we used for kinetic study the TG-curves only after 120°C.

It turned out that the second and the third decomposition steps are identical to the double-step decomposition curves of the compound with dioxane (compare DTG curves on Figs 2, 3 and 8). The proportion between them is again distinctly dependable on the heating rate: the second mass loss step decreases with heating rate (both temperature interval) decreasing. So we believe again that such second step behavior can be connected with the existence of different (both porous and non-porous) structures of manganese formate $Mn(HCOO)_2$ [2].

Three thermogravimetric curves (obtained under linear heating: 4, 8 and 12 grad min^{-1}) were processed by Friedman Analysis and Ozawa–Flynn–Wall Analysis Programs. Program 'ASTM E698' (using temperatures of maximum decomposition rate) results in incorrect data for multi-step reactions.

Energy of activation values are constant enough in the region of α=0.35–0.80, according to both calculations (E=69.7–70.0 kJ mol^{-1} in Friedman Analysis), values increase to 190 kJ mol^{-1} in the region of α=0.80–0.95 in 'Friedman Analysis', which indicates the second step of the reaction. So we simply recalculates these data, utilized only the original interval α=0.01–0.80 as the 100% conversion for the first step. These recalculated data are shown on Fig. 5 (E_a=69–75 kJ mol^{-1} for α=0.40–0.95).

Kinetic parameters for the first decomposition step were calculated by Borchardt–Daniels method for the selected region of conversion ($0.40<\alpha<0.95$). The checking equations: Fn, Bna, CnB, D3 (Table 2).

There is no diffusion complication for the gas evolving during the decomposition. In accordance with F-test the best topochemical equations for the decomposition process are Fn, Bna or CnB, the contribution of the second term is negligible:

$$f(\alpha)=(1-\alpha)^{0.63}\ E_a=76.6\text{ kJ mol}^{-1},\ \log A=6.4$$

$$f(\alpha)=(1-\alpha)^{0.63}\alpha^{0.000025}\ E_a=76.6\text{ kJ mol}^{-1},\ \log A=6.4$$

$$f(\alpha)=(1-\alpha)^{0.63}(1+0.0001\alpha)$$
$$E=76.6\text{ kJ mol}^{-1},\ \log A=6.4$$

The obtained value of activation energy agrees with the calculated ones by 'Free model' approach (E=69–75 kJ mol^{-1}).

Table 2 Inclusion compound $Mn(HCOO)_2 \cdot 1/3C_4H_8O$
Data of F-test on fit-quality (for the search of the best kinetic description, α=0.40–0.95)

#	Code	Type	f-act	F exp	F crit (0.95)	Correlation coefficient
1	S	Fn	74	1.00	1.47	0.98712
2	S	Bna	73	1.01	1.47	0.98712
3	S	CnB	73	1.01	1.47	0.98712
4	S	D3	75	6.94	1.47	0.91318

Conclusions

It can be expected that the simple porous structure of the host matrix with identical cages leads to one-step decomposition process; but real decomposition is more complex, which is clear from TG-, DTG- and DSC-curves (Figs 2, 3, 6 and 8). We associate this with the principal existence of several different structures of the pure manganese(II) formate (including non-porous phases) [2], therefore partial collapse of porous structure may take place along with guest molecules release from the host channels at elevated temperatures.

The stability of such inclusion compound can be connected with the stability of the matrix structure itself. For example, it is worth to note, that the well known inclusion compound (clathrate) $[Zn(Py)_4(NO_3)_2]\cdot 2Py$ can be synthesized in the system '$Zn(NO_3)_2$–Py', although the host compound $[Zn(Py)_4(NO_3)_2]$ itself does not exist in the system (stable crystal phases are $[Zn(Py)_3(NO_3)_2]$ and $[Zn(Py)_2(NO_3)_2]$). The guest-free matrix is unstable, and so the clathrate decomposes right away to the $[Zn(Py)_3(NO_3)_2]$ [11, 12].

The obtained values of activation energy, being calculated by two different methods is reliable; these values (78 and 77 kJ mol^{-1}) are identical for both compounds. It is worth to note that their boiling temperatures are noticeably different (101.3 and 65.6°C). We believe that the equality of compounds kinetic stability depends on the uniform output hindrance for guest molecules through channels of the host porous structure.

Further pre-arranged investigation of decomposition processes for other inclusion compounds with $Mn(HCOO)_2$ matrix will give the possibility to compare the thermal stability in the longer series.

The quantitative studies of inclusion compounds stability are the essential contribution to present-day works, dealing with such type of compounds (e.g. [13–22]).

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