

THE STUDY OF THE THERMAL DISSOCIATION PROCESSES OF COMPOUNDS OF THE TYPE $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_{2.n}\text{A}$.

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Thermal dissociation processes of compounds with the composition $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_{2.n}\text{A}$ (A-polar organic solvent: alcohols, aldehydes, ketones, organic acids) were investigated. Kinetics of dissociation was studied in a flow reactor, the values of activation energy and preexponential factor were calculated. The influence of a solvent nature, of the length of included molecules and of the type of crystalline lattice was studied. The sequence of kinetic stability was obtained. It corresponds to the sequence of solvent activity with respect to H-binding up with the complex. For the series of alcohols non-monotonous dependence of kinetic parameters on the length of chain (with the division into two groups: with even and odd n) was obtained. For all the compounds studied a compensation relationship is observed ($\lg A = aE + b$).

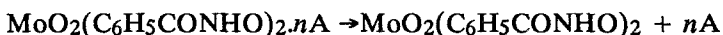
The study of the chemistry of crystal solvates is of great interest since so far only a part of these compounds, namely hydrates, has been investigated in depth. The hydrates have been convenient models for studying kinetics of topochemical processes of thermal dissociation (dehydration). For them there was carried out the analysis of the state of water molecules in solid substances [1, 2].

Molybdenum(VI) dioxobisbenzhydroxamate is known to have the ability to combine with polar organic solvents and form the compounds of the type $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_{2.n}\text{A}$ (A - alcohols, ketones, organic acids, aldehydes, etc; n - the quantity of solvent molecules) [3 - 5].

When heated to $t = 200^\circ$ the solvate crystals $\text{MoO}_2\text{R}_{2.n}\text{A}$ dissociate stepwise into starting complex compound MoO_2R_2 and gaseous product $n\text{A}$. The decomposition with the explosion of nonsolvated

$\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2$ occurs under the heating over a temperature range 170 - 200° [5].

The study of kinetics of the first stage of topochemical dissociation is of interest:



In the paper the following sequences of compounds are chosen as the objects investigated:

$\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_{2.n}$ alcohol (methyl, ethyl, propyl, *n*-butyl, amyl);

$\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_{2.n}$ ketone (acetone, ethyl-methyl ketone);

$\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_{2.n}$ organic acid (1/2 formic, 3/4 acetic, 1/2 propionic);

$\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_{2.n}$ aldehyde (1/3 salicyl).

It is interesting to follow the influence of the solvent nature on the stability of the above compounds in the thermal dissociation reactions, to study the influence of the length of solvent molecules included, as well as the change of dipole moment values and the type of crystalline lattice on the kinetic parameters of decomposition.

The experiment was carried out with a flow reactor [6]; the sample (10 mg) was heated linearly at a rate of 4-5 deg/min, the helium flow through the sample was 60 cm³/min; the gas evolution curve was recorded with a conductometric detector.

For processing gas evolution kinetic curves we used the integral method of Šestak and Šatava realized in the computer program TA IV [6]. After going through 13 kinetic equations (diffusion, nucleus formation, nucleus growth, chemical reaction on the interphase boundary) we selected the best equation for describing the process on linearity of the function $\lg g(\alpha)$ vs. $1/T$. For compounds studied the best equation over a conversion range $\alpha \approx 5-50\%$ was the equation of the shrinking sphere [$1 - (1 - \alpha)^{1/3}$] (the chemical reaction on the interphase boundary).

The search of the most suitable formal description of experimental data by one of the kinetic equations (with the use of linearization) is known not to guarantee uniqueness of the solution of the inverse task. That is why, we consider that when analyzing the patterns of kinetic stability the behaviour of kinetic parameters in series is important but not their absolute magnitude. This is the way we discuss the data obtained.

The calculated values of the activation energy and preexponential factor are in Table 1. We failed to calculate the kinetic parameters for adducts with organic acids because of the inseparability of gas evolution peaks.

Table 1 Kinetic parameters of the thermal dissociation reaction $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2 \cdot nA \rightarrow \text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2 + nA$

<i>A</i> solvent	E_a , kJ/mol	$\lg Z$	Temp. range of the decomp., °C	* α , %
CH ₃ OH	139±11	15.4±1.4	95-146	8-80
C ₂ H ₅ OH	451±37	49.8±4.6	159-190	0.5-78
C ₃ H ₇ OH	233±27	28.8±3.4	80-140	0.5-70
C ₄ H ₉ OH	423±12	48.2±1.5	146-173	20-80
C ₅ H ₁₁ OH	489±25	55.4±3.1	155-178	30-80
CH ₃ COCH ₃	414	47.9	144-169	36-88
CH ₃ COC ₂ H ₅	403±36	47.3±4.3	130-160	0.5-81
HOC ₆ H ₄ COH	103	12.6	46-99	5.5-42

* the conversion range (α) used for the calculation of kinetic parameters.

The error values for kinetic parameters are listed at the confidence coefficient of 95%

Let us now consider the influence of organic solvent nature on the stability of compounds in the thermal decomposition reactions (Table 1). The adduct $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2$ with salicyl aldehyde has the lowest decomposition temperature and kinetic parameters (E_a and $\lg Z$). The adduct with amyl alcohol has the highest ones. The structural investigations [7] showed that the character of given compounds depends on a relative capacity of the complex and solvent molecules to forming intermolecular hydrogen bonds and on the geometry of the fragments formed. The series of solvent activity with respect to H-binding with $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2$ complex: methyl formamide > butyl alcohol > ethyl-methyl ketone > salicyl aldehyde > propionic acid is given in the article [7]. Series is constructed in comparison to structural fragments of the crystals.

The presence of hydrogen bonds of complex molecule (*CM*)... solvent (*A*) depends on the quantity and the character of functional groups in the solvent molecules. So, the carboxy group -COOH can independently form three hydrogen bonds in the acid molecule: C=O group forms one and -OH group - two bonds. Since propionic acid is able to selfassociation, it uses these H-active groups in intermolecular hydrogen bonds of *PA...PA* but bonds of *CM...PA* are not formed at all. The crystal is constructed as the clathrate type. The solvent in crystal $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2 \cdot 1/3$ salicyl aldehyde uses H-active groups in the intramolecular bonds. The bonds of *CM...SA* occur not with whole the complex molecules but only with 1/3 of all the *CM*. The frameworks of *CM...CM* are the base of these structures [7]. The transition to ethyl-methyl ketone and butyl alcohol having active proton-acceptor carboxy and hydroxyl groups is accompanied by the change

of the character of the structure: every complex molecule is connected by intermolecular hydrogen bond with its solvent. Finally, there are no bonds of $CM...CM$ in the case of methyl formamide being both the acceptor and the donor of protons. The molecules of methyl formamide play an important structural role owing to the net of H-bonds of $CM...A$.

The experimental series of kinetic stability of crystal solvates (according to the activation energy values) obtained by us is the following: butyl alcohol \geq ethyl-methyl ketone $>$ salicyl aldehyde. It coincides with the series of solvent activity with respect to H-binding with complex $MoO_2(C_6H_5CONHO)_2$ [7]. The thermal stability is determined by the structural features and the solvent nature.

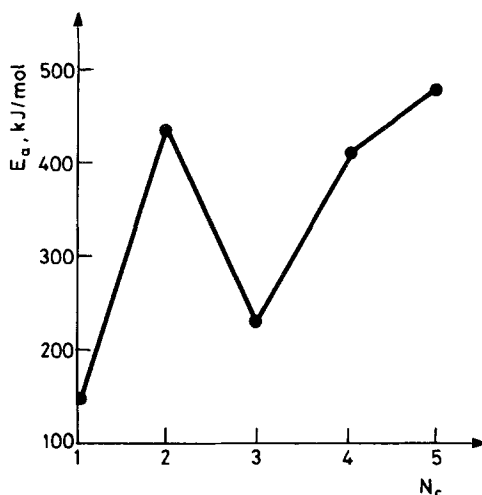


Fig. 1 The dependence of activation energy values on the quantity of carbon atoms in the chain of alcohols

The series of crystal solvates with alcohols of $C_nH_{2n-1}OH$ ($n = 1-5$) is the largest from the series of compounds investigated. Evident non-monotonous dependence of kinetic parameters on the length of hydrocarbon chain (Fig. 1) can be hardly connected only with power characteristics of bond of alcohol molecules in the crystalline framework. The existence of two groups - with even and odd quantity of carbon atoms in molecule - is traced in this dependence. It seems to be connected with the different character of interaction of two groups of molecules with the complex framework. This difference in the interaction of alcohol molecules with surrounding matrix being really showed only in solid state is distinctly seen from the comparison

of boiling temperatures and heats of evaporation and the temperatures and heats of melting alcohols (Table 2). Monotonous dependences are observed for liquid phases and essentially nonmonotonous ones are for the solid state. The dependence of heat of melting alcohols on the quantity of carbon atoms (Fig. 2) is nearly analogous to that of activation energy values (Fig. 1).

Table 2 The boiling and melting temperatures and heats of evaporation and melting of alcohols [10]

<i>A</i> solvent	$T_{\text{boil.}}$ °C	$\Delta H_{\text{evap.}}$ kJ/mol	$T_{\text{melt.}}$ °C	$\Delta H_{\text{melt.}}$ kJ/mol
CH ₃ OH	64.6	37.5	-97.8	3.16
C ₂ H ₅ OH	78.4	42.1	-117.3	5.02
C ₃ H ₇ OH	97.8	47.0	-127.0	5.18
C ₄ H ₉ OH	117.5	51.3	-79.9	9.36
C ₅ H ₁₁ OH	138.0	55.1	-78.5	9.82

It is interesting to note that similar nonmonotonous dependence of kinetic parameters on the length of chain (with the division into two groups: with even and odd n) was observed for thermal dissociation processes of the inclusion compounds of carbamide with hydrocarbons C_nH_{2n+2} ($n = 8-12$) [6].

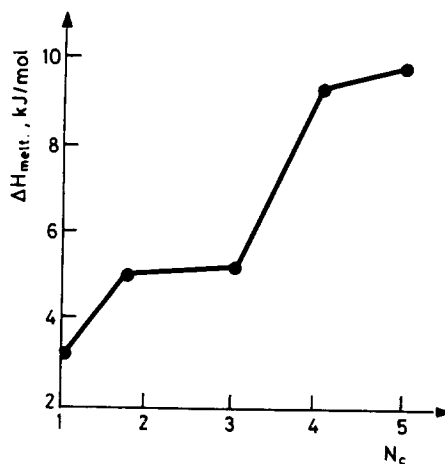


Fig. 2 The dependence of heats of melting on the quantity of carbon atoms in the chain of alcohols

It is known that for the widely investigated hydrates the thermal stability (usually used in the literature the determination of kinetic stability in the thermal decomposition processes) can be determined not by bond energy of water molecules but sooner by the conditions of destruction of the crystalline framework with the isolation of water molecules combined (owing to heat motions of structure-forming elements of a crystal) [1].

The same conclusion seems to be likely to be made for solvates investigated, the kinetic stability of compounds with alcohols considerably depending not only on the quantity of carbon atoms (the length of hydrocarbon chain) but also on if this quantity is even or odd.

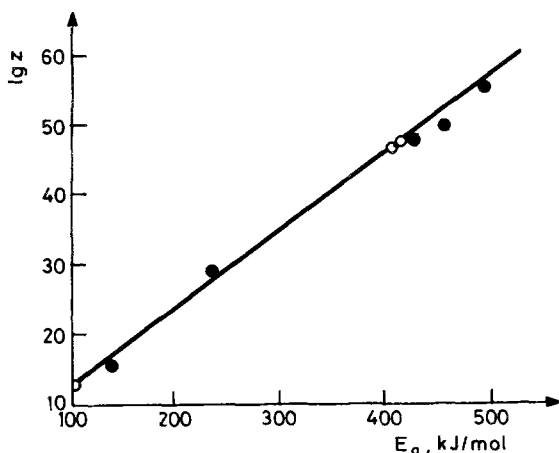


Fig. 3 Compensation effect in the thermal dissociation reaction $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2n\text{A} \rightarrow \text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2+n\text{A}$
 ● - alcohols; ○ - ketones, aldehyde

The compensation relationship $\lg A = aE + b$ is observed for all the compounds studied (Fig. 3). There is the point of view in literature that the presence of such dependences indicates on the analogy in the mechanisms of chemical reactions [8]. As a rule, such dependence in thermal dissociation processes is observed for a number of isostructural or similarly constructed coordination compounds (the rows are formed either by the change of central atom or by that of a intra-spherical volatile ligand) [6]. It is noteworthy that such a dependence for example is also observed for all the compounds in studying thermal dissociation reactions of platinum complexes with different S-donor and N-donor ligands. The community of mechanism of the process is more dependent on the analogy in the structure of complexes than on the identity of donor atoms of removing ligand [9].

of the process is more dependent on the analogy in the structure of complexes than on the identity of donor atoms of removing ligand [9].

The analogy in the structure of the compounds seems also to ensure the similar mechanism of chemical reaction in the thermal decomposition processes of solvates studied.

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Zusammenfassung — Es wurden thermische Dissoziationsvorgänge von Verbindungen der Zusammensetzung $\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_{2n}\text{A}$ (mit A = polares organisches Lösungsmittel: Alkohole, Aldehyde, Ketone, organische Säuren) untersucht. Die Dissoziationskinetik wurde in einem Durchlaufreaktor untersucht, die Werte für Aktivierungsenergie und präexponentiellen Faktor berechnet. Es wurde weiterhin der Einfluß von der Art des Lösungsmittels, von der Länge der beteiligten Moleküle und vom Kristallgittertyp untersucht sowie eine Reihenfolge bezüglich der kinetischen Stabilität ermittelt. Diese stimmt mit der Reihenfolge der Lösungsmittelaktivität bezüglich der H-Bindung zum Komplex überein. Für die Alkoholreihen (zwei Reihen: mit geradem bzw. ungeradem n) wurde keine sich monoton mit der analogen Reihe verändernde Abhängigkeit der kinetischen Parameter von der Kettenlänge beobachtet. Für alle untersuchten Verbindungen wurde eine Kompensationsgleichung ($\lg A = aE + b$) beobachtet.