THE STUDY OF THE THERMAL DISSOCIATION PROCESSES OF COMPOUNDS OF THE TYPE MoO$_2$(C$_6$H$_5$CONHO)$_2$.nA.

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Thermal dissociation processes of compounds with the composition MoO$_2$(C$_6$H$_5$CONHO)$_2$.nA (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 MoO$_2$(C$_6$H$_5$CONHO)$_2$.nA ($A$ - alcohols, ketones, organic acids, aldehydes, etc; $n$ - the quantity of solvent molecules ) [3 - 5].

When heated to $t = 200^\circ$ the solvate crystals MoO$_2$R$_2$.nA dissociate stepwise into starting complex compound MoO$_2$R$_2$ and gaseous product nA. The decomposition with the explosion of nonsolvated
MoO$_2$(C$_6$H$_5$CONHO)$_2$ occurs under the heating over a temperature range 170 - 200$^\circ$ [5].

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

$$\text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2 \cdot n\text{A} \rightarrow \text{MoO}_2(\text{C}_6\text{H}_5\text{CONHO})_2 + n\text{A}$$

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

- MoO$_2$(C$_6$H$_5$CONHO)$_2$.alcohol (methyl, ethyl, propyl, n-butyl, amyl);
- MoO$_2$(C$_6$H$_5$CONHO)$_2$.ketone (acetone, ethyl-methyl ketone);
- MoO$_2$(C$_6$H$_5$CONHO)$_2$.n organic acid (1/2 formic, 3/4 acetic, 1/2 propionic);
- MoO$_2$(C$_6$H$_5$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 cm$^3$/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 $\lg g(\alpha) \text{ vs.} 1/T$.

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.