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STUDY OF THE THERMAL DISSOCIATION OF PROCESSES OF NICKEL(II) AND COBALT(II) β-DIKETONATE ADDUCTS

V. A. Logvinenko, N. E. Fedotova, I. K. Igumenov
and *G. V. Gavrilova*

INSTITUTE OF INORGANIC CHEMISTRY, SIBERIAN DEPARTMENT
OF THE ACADEMY OF SCIENCES OF THE U.S.S.R., NOVOSIBIRSK,
U.S.S.R.

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Thermal dissociation processes of β-diketonate adducts with the composition $ML_2 \cdot 2B$ (L = acetylacetone and its substituted derivatives; M = Ni, Co; B = H_2O, $BuNH_2CH_3OH$, Py, NH_3) were investigated. Kinetics of dissociation were studied in a flow reactor. For dehydration processes a compensation relationship is observed ($\lg A = aE+b$), demonstrating analogous mechanisms.

A semi-quantitative series of the thermodynamic stabilities of the dihydrates is obtained from experimental data at quasi-equilibrium conditions (Q-derivatograph).

Many nickel(II) and cobalt(II) β-diketonates exist in the crystalline state as oligomers, substantially reducing the volatility of the compounds. One of the ways allowing to obtain monomer molecules capable to pass into the gaseous state without decomposition at relatively low temperatures is adduct formation. A defined set of partners allows to obtain complexes with the general formula $ML_2 \cdot nB$, with given properties (thermal stability determined as the starting temperature of decomposition, volatility, low melting temperature etc.). Generalized the data in the literature one may state that among the factors defining volatility and thermal behaviour of the adducts of the metal chelates the most important are: the nature of the metal, the substituent in the ligand and the Lewis base; these are jointly responsible for the properties of the complex formed. The effect of these factors on the thermal stability of similar compounds has been studied by numerous researchers.

On the example of Zn(II), Mn(II), Co(II), Ni(II) and Cu(II) β-diketonate dihydrates, with acetylacetone (HAA), trifluoroacetylacetone (HTFA) and hexafluoroacetylacetone (HGFA) serving as ligands, it has been demonstrated that the particularities of the thermal decomposition of the hydrates is caused by the

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tendency of the M(β-diketona)$_2$ molecules to oligomerization, since the most favourable configuration for manganese(II), nickel(II) and cobalt(II) is the octahedron, for zinc the tetrahedron [1, 2].

Fluorine substitution in the ligand leads to reduced thermal stability of the metal β-diketonates [1–4], decreasing with increasing numbers of trifluoromethyl groups in the ligand, while thermal stability increase of their adducts with Lewis bases is observed. Both the temperature of the start of dehydration and that of sublimation change in the following way:

$$M(AA)_2 > M(TFA)_2 \geqslant M(GFA)_2 \qquad [2, 3].$$

The study of the thermal behaviour of a number of Ni(II) and Co(II) β-diketonates formed with alkyl derivatives of acetylacetone demonstrated that the thermal stability increases both with the length of the hydrocarbon chain in the ligand and with the volume of the end group [5]:

$$AA < DNPM < DNBM < DIVM < DPM < DNCM$$

$$R = —CH_3;\ —CH_2—CH_3;\ —CH(CH_3)_2;\ —CH_2—CH(CH_3)_2;$$

$$—C(CH_3)_3;\ —(CH_2)_5—CH_3.$$

Simultaneously, however, the beginning of dehydration changes in the opposite direction [6], that is, the complexes formed by stable chelates are usually unstable. A similar result was found when copper(II) β-diketonate adducts with γ-picoline were studied regarding their thermal behaviour [4].

Changes of the thermal behaviour of adducts depending on the donor utilized were studied for numerous β-diketonate complexes with oxygen- and nitrogen-containing Lewis bases [7–9, 10–14, 4, 15]. Obviously the general conclusion might be that the stronger the Lewis base, the more stable the adducts being formed.

A comparison of the results in the above-cited papers leads to the conclusion that the strength of the Lewis base affects the strength of the M–L bond [4].

However, the majority of the papers dealing with the behaviour of metal β-diketonates at changes of temperature only describe the phenomena and do not contain quantitative evaluation of the kinetic or thermodynamic stability in thermal dissociation processes. We therefore investigated the thermal dissociation processes of numerous nickel(II) and cobalt(II) β-diketonate adducts, utilizing thermoanalytical methods allowing to obtain quantitative (kinetic) and semi-quantitative (thermodynamic) information.

Experimental

Synthesis, purification and analysis of the compounds

The cobalt and nickel β-diketonate dihydrates with the general formula $ML_2 \cdot 2H_2O$ were obtained by letting saturated ML_2 solutions in benzene or chloroform stand in a closed vessel saturated with water vapour. The precipitate formed within 24 hours was filtered, carefully washed with cold heptane, and dried in air till constant weight. Accurate stoichiometric compounds were obtained by hydration (dehydration) of previously analyzed $ML_2 \cdot nH_2O$. $ML_2 \cdot 2NH_3$ was obtained by adding a saturated alcoholic ammonia solution to the metal β-diketonate solution in hot benzene. The precipitate was filtered, washed with cold heptane and dried to constant weight. $ML_2 \cdot 2BuNH_2$ and $ML_2 \cdot 2Py$ were obtained by adding $BuNH_2$ or Py in excess to the solution in benzene of the metal chelate. The precipitate formed after boiling for 30 min and subsequent cooling was filtered, carefully washed with cooled benzene and dried in air to constant weight. $ML_2 \cdot 2CH_3OH$ was obtained by recrystallizing the metal β-diketonate from absolute methanol. The precipitate was filtered, washed with cooled heptane and dried in air.

All compounds obtained were analyzed for metal, C, H, F and N content.

Thermogravimetry at quasi-equilibrium conditions

To investigate the thermodynamic stability of the compounds, the Q-derivatograph under quasi-isobaric quasi-isothermal conditions [16, 17] was utilized. In this regime of the apparatus, temperature of the specimen increases linearly only till no mass loss occurs. When mass loss begins, a special control mechanism maintains a very small difference between sample temperature and oven temperature, and hence thermolysis proceeds at a constant low rate (0.16 mg/min). For reactions where equilibrium is readily established, this procedure results in stabilization of the decomposition temperature, i.e. the experiment takes place under quasi-isothermal conditions.

By using various sample holder shapes, it is possible to keep the pressure of the gases evolved almost constant (labyrinth crucible: ~1 atm, crucible with cover: ~0.2 atm, open crucible: ~0.05 atm, multiplate holder: ~0.01 atm).

The temperatures of quasi-isothermal thermolysis are the temperatures for reaching one and the same equilibrium constants of the thermal dissociation process, and hence are suited to set up a qualitative sequence of the thermodynamic stabilities of the compounds in identical-type thermal decomposition processes [18].

We used plate-like sample holders, since at high vapour pressure (water, pyridine or other volatile ligands) the degree of thermal dissociation and the degree of pyrolysis of the metal acetylacetonate will not be separated.

Experimental conditions for studying the macrokinetics of thermal dissociation processes

For studying the kinetics of thermal dissociation processes (splitting off water, pyridine and other volatile ligands) we used a flow reactor [18]; the sample (10 mg) was heated linearly at a rate of 4–5 deg/min; helium flow through the sample was 60 cm^3/min; the gas evolution curve was recorded with a conductometric detector. This arrangement eliminates retardation of the process by diffusion and reduces concentration and temperature gradients in the sample. We used a narrow grain size fraction (0.1–0.4 mm). Helium flow through the sample placed on a porous support will bring about decomposition conditions close to dynamic vacuum conditions, allowing to exclude the participation of the reverse reaction (pressure of the gas evolved <0.1 Torr).

Usually the necessary requirements for investigating the kinetics of thermal dissociation cannot be satisfied by using the thermogravimetric-system derivatograph.

Method of processing kinetic parameters

For processing the kinetic curves of gas evolution, we used a FORTRAN computer program [18, 19], we used integral processing of the kinetic parameters linearizing the function $\lg g(\alpha)$ *vs.* $1/T$. After going through 13 kinetic equations (diffusion, nucleus formation, nucleus growth, chemical reaction on the interphase boundary) we selected the equation best describing the process.

For all studied compounds, the kinetics of the process were best described by the equation of the shrinking sphere corresponding to the chemical reaction on the interphase boundary.

Part of the experimental data was processed in a more simple manner, without selecting the best-suited equation, using the method of Horowitz and Metzger (the shrinking sphere equation) [20].

Results and discussion

In the studied series of compounds, thermal dissociation processes were found to belong to different types (cf. e.g. Fig. 1). This fact does not allow to formulate general thermodynamic and kinetic stability relationships for thermal dissociation processes.

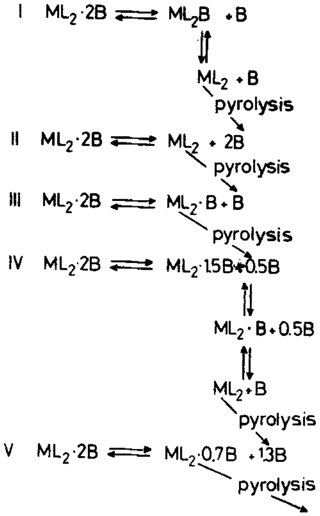

Fig. 1 Schematic representation of thermal dissociation processes of metal β-diketonate adducts

Based on thermogravimetric data at linear temperature rise the decomposition processes proceed along the following stages:

1. $Ni(BA)_2 \cdot 2H_2O \rightarrow Ni(BA)_2 \cdot H_2O \rightarrow Ni(BA)_2$
2. $Ni(DBM)_2 \cdot 2H_2O \rightarrow Ni(DBM)_2 \cdot H_2O \rightarrow Ni(DBM)_2$
3. $Ni(DPM)_2 \cdot 2H_2O \rightarrow Ni(DPM)_2$
4. $Ni(TFA)_2 \cdot 2H_2O \rightarrow Ni(TFA)_2 \cdot 1.5H_2O \rightarrow Ni(TFA)_2 \cdot H_2O \rightarrow$ $\rightarrow Ni(TFA)_2$
5. $Ni(PTA)_2 \cdot 2H_2O \rightarrow Ni(PTA)_2$
6. $Ni(GFA)_2 \cdot 2H_2O \rightarrow Ni(GFA)_2 \cdot H_2O$ $\downarrow$ decomposition
7. $Ni(AA)_2 \cdot 2NH_3 \rightarrow Ni(AA)_2$
8. $Ni(BA)_2 \cdot 2Py \rightarrow Ni(BA)_2 \cdot Py$
9. $Co(AA)_2 \cdot 2H_2O \rightarrow Co(AA)_2 \cdot 0.7H_2O$

In quasi-equilibrium experiments the following differences were observed: for instance, in reaction (2) the monohydrate $Ni(DBM)_2 \cdot H_2O$ is observed only under quasi-equilibrium conditions, while in reaction (4), the formation of the sesquihydrate is not observed.

Table 1 Macrokinetic parameters of the thermal dissociation of some metal β-diketonate adducts (mean values of two experiments)

Reaction	E, kJ/mol	lg A
$Ni(BA)_2 \cdot 2H_2O \rightarrow Ni(BA)_2 \cdot H_2O + H_2O$	65	5.8
$Ni(DBM)_2 \cdot 2H_2O \rightarrow Ni(DBM)_2 + 2H_2O$	90	9.9
$Ni(DPM)_2 \cdot 2H_2O \rightarrow Ni(DPM)_2 + 2H_2O$	122	16.3
$Ni(TFA)_2 \cdot H_2O \rightarrow Ni(TFA)_2 + H_2O$	369	40.9
$Ni(PTA)_2 \cdot 2H_2O \rightarrow Ni(PTA)_2 + 2H_2O$	63.5	6.8
$Ni(GFA)_2 \cdot 2H_2O \rightarrow Ni(GFA)_2 \cdot 1.5H_2O + 0.5H_2O$	247	35.6
$Ni(AA)_2 \cdot 2NH_3 \rightarrow Ni(AA)_2 + 2NH_3$	111	11.1
$Ni(BA)_2 \cdot 2Py \rightarrow Ni(BA)_2 \cdot Py + Py$	181	20.6
$Co(AA)_2 \cdot 2H_2O \rightarrow Co(AA)_2 \cdot 0.7H_2O + 1.3H_2O$	132	17.6

In Table 1, the macrokinetic parameters of those thermal dissociation processes are listed, for which the individual stages of thermal dissociation were sharply distinguishable; in some cases this was impossible (cf. Fig. 2).

For five processes, the kinetic parameters are ruled by the compensation effect, demonstrating their analogy with the mechanism of dehydration processes [18]. For $Ni(TFA)_2 \cdot 2H_2O$ (Fig. 3) (since the dehydration peaks for $0.5H_2O$ and $0.5H_2O$ mass losses are not separated) we studied the kinetics of dehydration of the

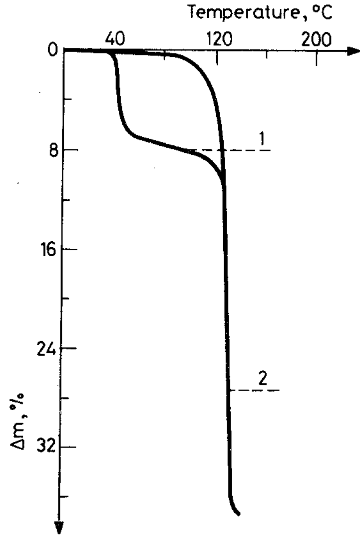

Fig. 2 Thermal dissociation of the adducts $Ni(DPM)_2 \cdot 2H_2O$ (1) and $Ni(DPM)_2 \cdot 2Py$ (2). Multiplate-shaped sample holder, quasi-isothermal heating program, sample mass 150 mg, helium atmosphere

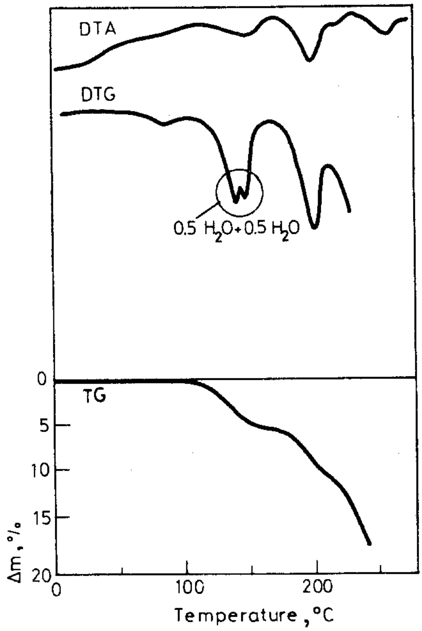

Fig. 3 Thermal dissociation of the $Ni(TFA)_2 \cdot 2H_2O$ adduct. Sample mass 150 mg, heating rate 5 deg/min, helium atmosphere

intermediate monohydrate, for this reason these kinetic parameters do not lie on the plot of the compensation effect (Fig. 4).

From the quasi-equilibrium experimental data, the following sequence of thermodynamic stability was obtained for thermal dehydration of $ML_2 \cdot 2H_2O$ compounds:

$$\mathrm{DPM} < \mathrm{BA} < \mathrm{GFA} < \mathrm{DBM}\ (\approx (\mathrm{TFA}) \qquad \text{(Fig. 5)}$$

This sequence corresponds to the sequence of M–L bond energies [21–23], i.e. the stronger the M–L bond, the weaker the M–OH_2 bond.

However, another sequence of kinetic stability follows from the activation energies of the dehydration processes (and the temperatures when dehydration begins):

$$\mathrm{PTA} \leqslant \mathrm{BA} < \mathrm{DBM} < \mathrm{DPM} < \mathrm{GFA}$$

A possible explanation would be that dehydration rates are defined not only by the splitting of the M–OH_2 bond, but also by a polymerization process in which the M–L bond is remodelled.

The attempt to construct complete sequences of thermodynamic and kinetic

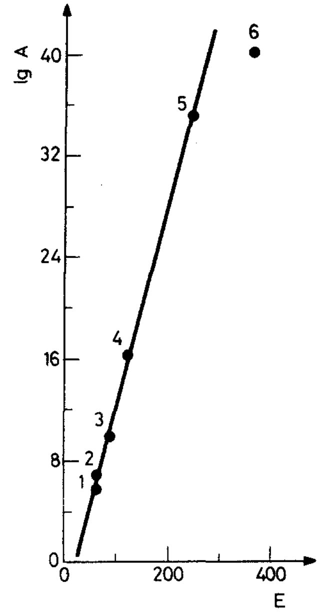

Fig. 4 Compensation effect in the dehydration processes of metal(II) β-diketonate dihydrates ($NiL_2 \cdot 2H_2O$), where L is *(1)* – 2,2-dimethyl-6,6,6-trifluoroheptane-3,5-dione (PTA), *(2)* – 1-phenylbutanedione-1,3 (BA), *(3)* – 1,3-diphenylpropanedione-1,3 (DBM), *(4)* – 2,2,6,6-tetramethylheptane-3,5-dione (DPM), *(5)* – 1,1,1,5,5,5-hexafluoropentane-2,4-dione (GFA), *(6)* – 1,1,1-trifluoropentane-2,4-dione (TFA) corresponding to the monohydrate $Ni(TFA)_2 \cdot H_2O$

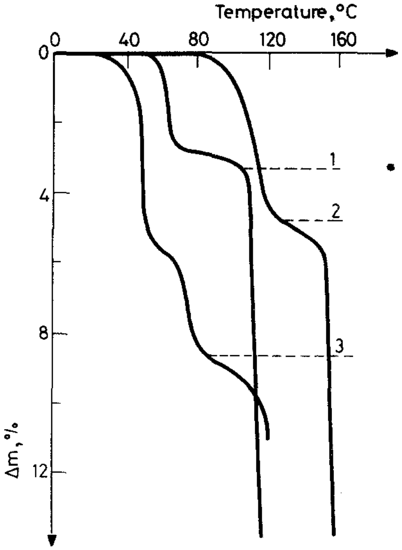

Fig. 5 Thermal dissociation of $NiL_2 \cdot 2H_2O$ adducts. Multiplate-shaped sample holder, quasi-isothermal heating program, sample mass 150 mg, helium atmosphere. (1) – $Ni(GFA)_2 \cdot H_2O$; (2) – $Ni(TFA)_2 \cdot H_2O$; (3) – $Ni(BA)_2$

stability for all compounds investigated could not be realized owing to the differences of the intermediate phases in thermal dissociation. Thus, varying the ligand L and B leads not only to the expected specific sequence regarding the strength of the M–L and M–B bonds, but also to a sharp change in thermodynamic and kinetic stability of the intermediate phases $ML_2 \cdot (2-x)B$.

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Zusammenfassung — Es wurden die thermischen Dissoziationsprozesse von β-Diketonataddukten der Zusammensetzung $ML_2 \cdot 2B$ (L = Azetylazeton und dessen substituierte Abkömmlinge; M = Ni, Co; $B = H_2O$, $BuNH_2$, CH_3OH, Py, NH_3) untersucht. Die Kinetik der Dissoziation wurde in einem Flowreaktor untersucht. Als Beweis für die Ähnlichkeit der Mechanismen der Dehydrierungsprozesse konnte eine $\lg A = aE+b$ Beziehung festgestellt werden. Von unter Quasi-Gleichgewichtsbedingungen gewonnenen Daten konnte eine semiquantitative Serie der thermodynamischen Stabilitäten der Dihydrate abgeleitet werden (Q-Derivatograph).

Резюме — Изучены процессы термической диссоциации аддуктов β-дикетонатов состава $ML_2 \cdot 2B$ (L = ацетилацетон и его замещенные производные; M = Ni, Co; $B = H_2O$, $BuNH_2$, CH_3OH, Py, NH_3). Кинетика диссоциации исследована в проточном реакторе; для процессов дегидратации наблюдается компенсационная зависимость ($\lg A = aE+b$) свидетельствующая об аналогии в механизме. Полуколичественный ряд термодинамической устойчивости дигидратов получен по данным эксперимента в квазиравновесных условиях (Q-дериватограф).