Thermochimica Acta, 93 (1985) 69-71
Elsevier Science Publishers B.V., Amsterdam

THERMODYNAMIC STABILITY IN THE SERIES OF THRINUCLEAR μ_3-OXOACETATES $Fe_2^{III}M^{II}O(CH_3COO)_6(H_2O)_3\ 2H_2O$, WHERE M = Mn, Fe, Co, Ni IN THE PROCESS OF THEIR THERMOLYSIS

Yakubov Kh. M., Nasonova T. A., Abdullaev Sh. Kh.
Tadjik State University, Dushanbe, USSR

The results of derivatographic investigations of thrinuclear heterovalent acetate μ_3-oxoclusters with the general formula

$$Fe_2^{III}M^{II}O(CH_3COO)_6(H_2O)_3\ 2H_2O,$$

where M = Mn, Fe, Co or Ni in quasi isothermal conditions are presented in the report. It has been shown, that thermal decomposition of the investigated compounds exists in the temperature interval 60 – 350 °C and consists of a few steps. Endothermal process existing in the interval 155 – 195 °C has been studied in detailes. The series of thermodynamic stability Mn Fe Co Ni has been constructed on this decomposition step thermolysis temperatures of the studied clusters.

The interest for thrinuclear carboxilate clusters of transition elements combines with their original physico-chemical properties, conditioned by their internal molecular exchange interactions betwen metal ions. The variation in the complexes $Fe_2MO(CH_3COO)_6(H_2O)_3\ 2H_2O$ of 3d-metal makes it possible construct the series of thermodynamic stability.

The report is devoted to the investigation of metal nature influence on thermodynamic parameters of thermal decomposition processes of heteronuclear acetates with the general formula $Fe_2^{III}M^{II}O(CH_3COO)_6(H_2O)_3\ 2H_2O$, where M^{II} = Mn, Fe, Co, Ni.

Heteronuclear μ_3-oxoacetates of 3d-elements have been synthesized by chloride mixtures of Fe(III) and M(II) in the ratio 2 : 1, with calcium acetate surplus in aqueous solution of acetic acid /1/. Element analysis results of the synthesized complexes are represented in the table.

Table - The results of element analysis of the synthesized heteronuclear acetate complexes x)

No.	Compound	C	H	Fe^{3+}	M^{2+}
1.	$Fe_2^{III}Mn^{II}O(CH_3COO)_6(H_2O)_3\ 2H_2O$	$\frac{22.8}{23.0}$	$\frac{4.51}{4.47}$	$\frac{8.30}{7.8}$	$\frac{8.6}{8.8}$
2.	$Fe_2^{III}Fe^{II}O(CH_3COO)_6(H_2O)_3\ 2H_2O$	$\frac{22.6}{22.9}$	$\frac{4.58}{4\text{-}46}$	$\frac{17.7}{17.8}$	$\frac{8.6}{8.8}$
3.	$Fe_2^{III}Co^{II}O(CH_3COO)_6(H_2O)_6\ 2H_2O$	$\frac{22.1}{22.8}$	$\frac{4.46}{4\text{-}41}$	$\frac{17.9}{17.7}$	$\frac{8.9}{9.3}$
4.	$Fe_2^{III}Ni^{II}O(CH_3COO)_6(H_2O)_3\ 2H_2O$	$\frac{23.3}{22.9}$	$\frac{4.51}{4.41}$	$\frac{19.0}{17.7}$	$\frac{9.0}{9.2}$

x) over the line is found (%) under the line is calculated (%)

Proceedings of ICTA 85, Bratislava

Thermal analysis has been carried out on derivatograph "Q-1500d" of the system Paulik-Paulik-Erday in quasiisothermal regime with the use of quasiisobar crucible (P = 0.7 atm). The weight of the investigated sample was 200 mg. The sample was heating with the rate corresponding to the programmator regime I.

Acetate clusters' decomposition in quasiisothermal isobar regime is shown in the Figure. As you can see in the Figure, the process of complex decomposition in quasiequilibrium conditions in the temperature interval 0 – 250 °C proceeds on three linear laws. Thermolysis of the studied compounds under the higher temperatures is complex, that is, probably, combined with the change of internal heat content of the samples under their decomposition.

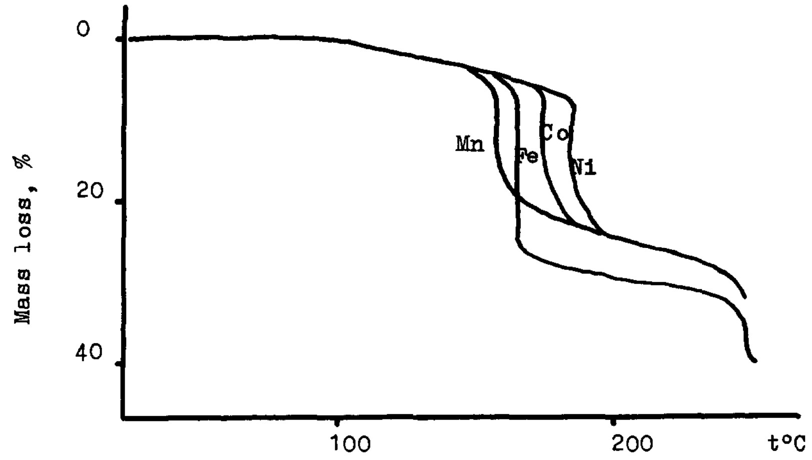

Fig. Thermolysis of the clusters $Fe_2^{III}M^{II}O(CH_3COO)_6(H_2O)_3\ 2H_2O$ under quasiisobar-isothermal conditions (P = 0.7 atm). Decomposition rate is 0.4 mg/min.

Preparative and mass-spectrometry analysis of fugitive and solid products of the first thermolysis step of the complexes (the first line section in the Fig.) has shown, that it may be described by the scheme:

$$Fe_2MO(CH_3COO)_6(H_2O)_3\ 2H_2O \text{ — } Fe_2MO(CH_3COO)_6(H_2O)_3 + 2H_2O \quad (I)$$

Experimentally found values of mass loss (5.3 – 6.0 % for the complexes with different M) are in well agreement with theoretically calculated (5.8 %). Coincidence of the thermolysis curves of this step for the complexes with different M is well explained by the suggested scheme (I). Supersphere water molecules don't form coordinated bonds with the complexforming metal, that is why their removal from the complex does not depend on metal nature.

Mass-spectrometry analysis of gaseous thermolysis products of the acetates in the temperature interval corresponding to the second destruction step has shown, that a considerable quantity of steam and acetic acid are in the gaseous phase, moreover, concentration dependences of the lasts on temperature have been found to be cophase. It makes it possible suggest, that H_2O and CH_3COOH are formed at the same process result, namely:

$$Fe_2MO(CH_3COO)_6(H_2O)_3 \text{ —— } Fe_2MO(CH_3COO)_5(OH)(H_2O)_{2-n} + nH_2O + CH_3COOH \qquad (II)$$

The last reaction is confirmed by the element analysis data of solid thermolysis products.

It is known, that indirect estimation of thermodynamic stability (for the construction of stability series) may be done on the data of thermal experiment in quasiequilibrium conditions /2/. Constructed on thermolysis temperatures the series of thermodynamic stability of the compounds coincides with the stability series constructed on equilibrium constant values under the standard temperature.

On thermolysis temperatures of the second decomposition step of the our investigated clusters you can construct the next series of thermodynamic stability: Ni Co Fe Mn.

The strength of the bond metal-ligand is growing from manganese to nikel. This stability series correlates with the series of the energy of extrastabilisation by crystal field (ESCF) for highspin octahedric 3d-ions.

It must be pointed out, that thermodynamic stability series found by us and constructed on the temperatures of the second thermolysis step of the studied oxoacetate clusters coincides with the series of the change of exchange integrals /3/ and quadrupole splittings in gamma-resonance spectra /4/ of these compounds that indicates in favour of the same influence of heterometal nature M on physico-chemical properties of the clusters.

Comparative thermodynamic stability of the clusters with the general formula $Fe_2^{III}M^{II}O(CH_3COO)_6(H_2O)_3$ in the dependence on heterometal M nature: Ni Co Fe Mn, has been studied by the method of thermal analysis.

REFERENCES

1 Yakubov Kh. M., Zhemchuzhnikova T. A., Zelentsov V. V., Abdullaev Sh. Kh., Fisher V. R. - In: The 9th International conference on organometal chemistry: Abstracts of papers, Dijon (France), 1979, p. 58.

2 Logvinenko V. A., Thermal analysis of coordination compounds and clusters. Novosibirsk: Nayuka, 1982, s. 25-34.

3 Yakubov Kh. M., Zelentsov V. V., Zhemchuzhnikova T. A., Abdullaev Sh. Kh., Fisher V. R. - Dokl. AN SSSR, 1980, t. 250, s. 402-405.

4 Yakubov Kh. M., Turta K. I., Zhemchuzhnikova T. A., Abdullaev Sh. Kh., Stukan R. A. - Dokl. AN TadjSSR, 1982, t. 25, s. 734-737.