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ANALYSIS OF THERMODYNAMIC AND KINETIC STABILITIES IN THE THERMAL DECOMPOSITION OF THE TRINUCLEAR μ-OXOACETATES $Fe_2^{III}M^{II}O(CH_3OO)_6(H_2O)_5$, WITH M = Mn, Fe, Co OR Ni

Kh. M. Yakubov, V. A. Logvinenko**, T. A. Zhemchuzhnikova*, Sh. Kh. Abdullaev*, G. V. Gavrilova*** and *A. N. Mikheev***

*TADZHIK STATE UNIVERSITY, DUSHANBE;
**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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The thermal analysis of acetate clusters of general formula $[Fe_2^{III}M^{II}O(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$, with M = Mn, Fe, Co or Ni, was performed in dynamic and quasi-isothermal regimes. The thermal decompositions of these compounds proceed in the interval 40–310° and consist of two endothermic and three exothermic stages. Dependence on the nature of the transition metal M is evidenced most explicitly in the parameters of the second stage, proceeding in the interval 103–170°. For this stage the sequences of thermodynamic stability and kinetic stability were established. The effect of the nature of the metal on the thermodynamic and kinetic parameters of the thermal decomposition processes involving the heteronuclear acetates was analyzed. Mechanisms for the first two stages of thermal decomposition are suggested.

Interest in trinuclear carboxylate clusters of transition metals is due to their unusual physico-chemical properties by virtue of the intramolecular exchange interaction between the metal ions. Through variation of the 3*d* metal in the complexes $Fe_2MO(CH_3COO)_6(H_2O)_3\cdot 2H_2O$, attractive possibilities open up for establishing thermodynamic and kinetic stability sequences. Although several references to the thermal analysis of iron acetate complexes are to be found in the literature [1–3], only in [3] has an attempt been made to investigate the kinetic stabilities of three compounds $Fe_2^{III}Fe^{II}O(CH_3COO)_6\cdot nL$, containing various ligands L.

This paper deals with the effect of the nature of the metal M on the thermodynamic and kinetic parameters of the thermal decomposition of heteronuclear acetates of the general formula $[Fe_2MO(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$, with M = Mn, Fe, Co or Ni.

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Experimental

The complexes were synthesized by the reaction of a mixture of Fe(III) and M(II) chlorides in the ratio 2 : 1 with excess calcium acetate, in aqueous acetic acid solution [4]. The results of elemental analysis of the synthesized compounds are listed in Table 1.

Table 1 Results of elemental analysis of the synthesized heteronuclear acetate complexes

Compound	C, %	H, %	Fe^{3+}, %	M^{2+}, %
$[Fe_2^{3+}Mn^{2+}O(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$	Found 22.8	4.51	18.3	8.6
	Calcd. 23.0	4.47	17.8	8.8
$[Fe_2^{3+}Fe^{2+}O(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$	Found 22.6	4.58	17.7	8.6
	Calcd. 22.9	4.46	17.8	8.9
$[Fe_2^{3+}Co^{2+}O(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$	Found 22.1	4.46	17.9	8.9
	Calcd. 22.8	4.41	17.7	9.3
$[Fe_2^{3+}Ni^{2+}O(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$	Found 23.3	4.51	18.0	9.0
	Calcd. 22.8	4.41	17.7	9.3

A derivatograph G–1500 D, system Paulik–Paulik–Erdey, was used for thermal analysis in the dynamic and quasi-isothermal regimes, in air. Al_2O_3 was used as reference material. The sample mass was 100 mg in dynamic, and 200 mg in quasi-isothermal experiments. The heating rate in the dynamic regime was 2.5 deg/min.

For mass spectrometry of the volatile reaction products, the apparatus described in [5] was used. The experimental conditions were: pressure 6.7 Pa, sample heating rate 9 deg/min.

Overall evolved gas curves were obtained with a gas flow reactor [6], using a conductometric detector. The flow rate of helium through a 2–3 mm thick sample layer was 50 ml/min. A narrow fraction of particles (100–400 μm diam.) was used in all thermoanalytical experiments.

The kinetic parameters and the topochemical mechanisms of the thermal decompositions of the complexes studied were calculated with the program TAIB [7] on an EC 10–33 computer.

Results and discussion

The thermoanalytical experiments demonstrated that the thermal decompositions of the synthesized heteronuclear clusters proceed in several stages in the temperature interval from 40 to 310°. The thermal curves for all compounds are in general similar, but each compound has its individual features. The parameters of the observed decomposition stages for the compounds studied are listed in Table 2, and Fig. 1 presents by way of example the thermal curves for $[Fe_2CoO(CH_3COO)_6(H_2O)_3] \cdot 2H_2O$.

The thermal decomposition was found to consist of five stages, the first two absorbing heat, and the other three evolving heat.

Preparative and mass-spectrometric analysis of the volatile and solid products in the first stage, accompanied by an endothermic effect, demonstrated that the process is decribed by

$$\begin{aligned}&[Fe_2MO(CH_3COO)_6(H_2O)_3] \cdot 2H_2O \rightarrow \\ &\rightarrow [Fe_2MO(CH_3COO)_6(H_2O)_3] + 2H_2O\end{aligned} \tag{1}$$

Table 2 Thermoanalytical data on the complexes investigated (ceramic crucible, heating rate 2.5 deg/min, air)

Stage	Thermal effect	Temperature parameters, °C $T_{init.}$	T_{max}	T_{end}	Δm, %
		(i) $[Fe_2^{3+}Mn^{2+}O(CH_3COO)_6(H_2O)_3] \cdot 2H_2O$			
1.	endothermic	41	76	103	5.3
2.	endothermic	103	140	160	18.2
3.	exothermic	160	—	247	33.2
4.	exothermic	247	253	270	49.5
5.	exothermic	270	—	293	62.3
		(ii) $[Fe_2^{3+}Fe^{2+}O(CH_3COO)_6(H_2O)_3] \cdot 2H_2O$			
1.	endothermic	40	81	103	6.0
2.	endothermic	103	133	157	20.4
3.	exothermic	157	259	265	55.0
4.	exothermic	265	—	279	60.0
5.	exothermic	279	—	285	62.1
		(iii) $[Fe_2^{3+}Co^{2+}O(CH_3COO)_6(H_2O)_3] \cdot 2H_2O$			
1.	endothermic	42	83	111	5.7
2.	endothermic	111	153	170	20.1
3.	exothermic	170	240	249	37.0
4.	exothermic	249	262	274	53.0
5.	exothermic	274	289	303	62.5
		(iv) $[Fe_2^{3+}Ni^{2+}O(CH_3COO)_6(H_2O)_3] \cdot 2H_2O$			
1.	endothermic	40	78	107	5.7
2.	endothermic	111	155	171	20.3
3.	exothermic	171	—	267	39.5
4.	exothermic	267	276	295	57.5
5.	exothermic	295	—	300	62.7

Accuracy: temperature parameters ±4°; mass loss: ±1.0%

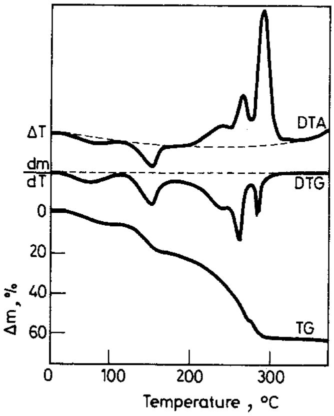


Fig. 1 Thermoanalytical curves of the complex $[FeCoO(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$. Sample mass: 100 mg

The experimentally found mass loss values (5.3 to 6.0% for complexes with different metals M) agree well with the theoretical value (5.8%). The independence of the parameters from the nature of the heterometal M in the first decomposition stage is readily explained by Eq. (1), since the outer sphere water molecules do not form coordinate bonds with the complex-forming metal.

Decomposition of the inner coordination sphere starts at temperatures above 110°. Table 2 demonstrates that the temperature parameters of the second decomposition stage differ significantly for the individual acetate complexes; they may thus be utilized for their identification.

The parameters of the subsequent stages (3 to 5) are also sensitive to the nature of the metal M; however, the relationship is difficult to establish, mainly because the temperature intervals of these stages are so close to one another that they overlap. We therefore refrain from giving an interpretation, but note that acetone and substantial amounts of CO_2 were detected by mass spectrometry in the gas phase evolved in the decomposition of the heteronuclear acetates between 170 and 300°.

In the temperature interval from 110 to 170°, corresponding to the second thermal decomposition stage, mass spectroscopy indicated that the gas phase contains significant amounts of water and acetic acid vapour, and also that the variations in their concentrations with temperature proceed in parallel. This finding allows the assumption that H_2O and CH_3COOH are formed in the same reaction:

$$[Fe_2MO(CH_3COO)_6(H_2O)_3] \rightarrow Fe_2MO(CH_3COO)_5(OH)(H_2O)_{2-n} + \\ + nH_2O + CH_3COOH \qquad (2)$$

This reaction is confirmed by the results of elemental analysis of the solid decomposition products. The experimentally determined mass loss values (from the TG curves) in the interval 110–170° also agree well with those calculated for Eq. (2) (Table 3).

Table 3 Experimental and calculated sample mass losses in process II

M	n	m_{calcd}, %	m_{found}, %
Mn	1	18.2	18.2
Fe	2	20.9	20.4
Co	2	20.9	20.1
Ni	2	20.9	20.3

The second stage of thermal decomposition appears informative primarily for study of the relative stabilities of the complexes in the sequence of 3*d* metals. Two aspects of stability are usually distinguished: thermodynamic stability and kinetic stability. For topochemical reactions, the thermodynamic stability is comparable to the metal-ligand bond energy, and the kinetic stability to the instability of these bonds.

It is known that (for establishing stability sequences) thermodynamic stability can be estimated indirectly via thermal analysis data on thermal decompositions under quasi-equilibrium conditions [6]. This sequence is identical with the sequence established from the equilibrium constants at standard temperature.

In Fig. 2, the decomposition of acetate clusters under quasi-isothermal–quasi-isobaric conditions is presented. The shift of the decomposition stages towards higher temperatures is due to the utilization of a quasi-isobaric crucible ($p = 0.7$ bar) in these experiments. The Figure reveals that thermal decomposition starts along three linear portions of the curves.

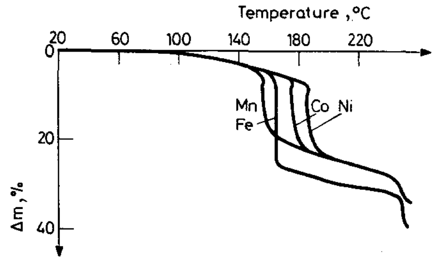


Fig. 2 Thermolysis of the clusters $[Fe_2MO(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$ with M = Mn, Fe, Co or Ni, under quasi-isobaric–quasi-isothermal conditions ($p = 0.7$ bar). Sample mass 200 mg, rate of decomposition <0.4 mg/min

An analysis of the decomposition curves in the quasi-equilibrium regime indicates that the second decomposition stage of $[Fe_2FeO(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$—in contrast to the other clusters—proceeds with zero slope and with high mass loss. The latter is obviously due to the thermodynamic instability of the solid product of the second decomposition stage (process II) at 165° for the compounds with $M = Fe$; it decomposes with breakdown of the inner sphere.

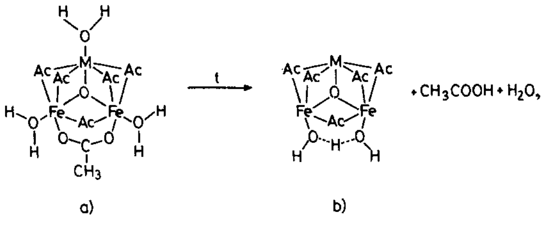
From the temperatures of the second stages of thermal decomposition (Fig. 2), the following sequence of thermodynamic stability can be established:

$$Ni > Co > Fe > Mn$$

i.e. the metal-ligand bond strength increases from manganese to nickel.

It can readily be recognized that this stability sequence is identical with the sequence of the energy of stabilization by the crystal field for high-spin octahedral $3d$ ions. From the aspect of crystal field theory, the stability increase of the metal-ligand bond from manganese (d^5) to nickel (d^8) may be explained in the following manner. Additional electrons in the t_{2p} orbital lead to a concentration of negative charge in the space between the ligands. Due to this negative charge, the metal ion attracts the ligands with greater force, since filling of the t_{2p} orbital reduces the screening of the nucleus as the nuclear charge increases.

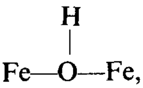
The characteristic correlation between the thermal decomposition parameters of the heteronuclear compounds and the stabilization energy of the heteroion by the crystal field allows the assumption that the start of process II is controlled by the splitting of the most labile $M—H_2O$ bond. As soon as this bond is broken, redistribution of electron density will presumably take place; as a result, one bridging ligand CH_3COO^- connecting two Fe(III) ions will be protonated and split off from the complex *A*, so that the intermediate molecule *B* will be formed:

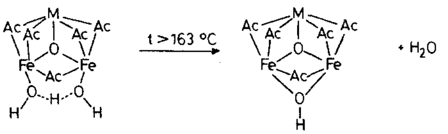


(3)

were Ac is the ion CH_3COO^-

The strength of the bridge $Fe-\overset{H}{\overset{|}{O}}\cdots H\cdots\overset{H}{\overset{|}{O}}-Fe$ is apparently practically independent of the nature of the metal M. Its rearrangement, with splitting-off of

H_2O and formation of the bridge  $\mathrm{Fe{-}\overset{\overset{\displaystyle H}{|}}{O}{-}Fe}$, proceeds at higher temperatures ($t > 163°$ at $p = 0.7$ bar):



(4)

Since the second decomposition stage of the cluster with M = Mn ends at temperatures below 163°, it should be described by Eq. (3) only.

For investigations of the kinetic stability of the acetate clusters, the second stage (110–170°) described by Eq. (2) again appears best suited. Since the quantitative processing of the DTA, DTG and TG curves obtained with commercial thermoanalytical instruments is known to be incorrect, we used a special experimental arrangement for our kinetic investigations: we determined the parameters based on the data of overall gas evolution obtained in the gas flow reactor described in [6].

Processing of the experimental results with the program TAIB [7] demonstrated that the gas evolution curves are described by the kinetic equation for contracting spheres, i.e. the kinetic parameters may be related to the rate of the chemical reaction on the phase boundary.

The values of the activation energy E_a and of the frequency factor $\log A$ of the kinetic equation, calculated for each complex as mean values of five independent experiments (for random error values with a confidence coefficient of 95%), and the degree of transformation intervals α for which the calculations were performed, are listed in Table 4.

Table 4 Kinetic parameters of the process $[\mathrm{Fe_2^{3+}M^{2+}O(CH_3COO)_6(H_2O)_3}] \to$ $\to \mathrm{Fe_2^{3+}M^{2+}O(CH_3COO)_5(OH)(H_2O)_{2-n}} + n\ \mathrm{H_2O} + \mathrm{CH_3COOH}$

M	T_{init}, °C	T_{end}, °C	E_a, kJ/mol	$\log A$	Interval of α, %
Ni	103 ± 3	153 ± 4	177.1 ± 10	19.8 ± 1.0	8–81
Co	87 ± 1	140 ± 2	167.4 ± 1.6	18.95 ± 0.05	5–53
Mn	92 ± 3	147 ± 5	131.0 ± 9.2	14.2 ± 1.0	16–90
Fe	90 ± 4	151 ± 7	129.0 ± 1.6	13.9 ± 0.4	9–96

As indicated by these data, the sequence of kinetic stability for the clusters investigated, established from both the activation energy values and the frequency factor values, is Ni > Co > Mn > Fe.

The clusters with M = Fe and Mn are very close to one another in kinetic stability and are more labile than the complexes containing cobalt and nickel.

A comparison of the sequences of thermodynamic and kinetic stabilities for the clusters studied demonstrates that they agree for iron, cobalt and nickel. The finding that manganese does not fit into this relationship may be caused by a different thermal decomposition mechanism. This is in agreement with our assumption that in contrast to the other compounds, the cluster with the triad Fe_2Mn loses only one inner sphere water molecule in the second stage of decomposition (process III).

It is of interest to note that the sequence of thermodynamic stability established from the thermal decomposition temperatures is in agreement with the sequences of exchange integrals [8] and quadrupole splitting in the gamma resonance spectra [9]. Thus, three independent physical methods: thermal analysis, magnetic susceptibility and gamma resonance spectroscopy provide results in conformity as regards the effect of the nature of the heterometal on the physico-chemical properties of clusters with the general formula $[Fe_2^{III}M^{II}O(RCOO)_6(H_2O)_3]$.

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Zusammenfassung — Die thermische Analyse von Acetatclustern der allgemeinen Formel $[Fe_2^{III}M^{II}O(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$ (M = Mn, Fe, Co, Ni) wurde unter dynamischen und quasi-isothermen Bedingungen ausgeführt. Die thermische Zersetzung dieser Verbindungen verläuft im Bereich von 40–310 °C in zwei endothermen und drei exothermen Schritten. Die Abhängigkeit von der Natur des Übergangsmetalls M ist bei den Parametern des zwischen 103 und 170 °C verlaufenden zweiten Schrittes am ausgeprägtesten. Für diesen Schritt wurde die Reihenfolge der thermodynamischen und kinetischen Stabilität festgestellt. Der Effekt der Natur des Metalls auf die thermodynamischen und kinetischen Parameters der Zersetzungsprozesse von heteronuklearen Acetaten wurde analysiert. Für die ersten zwei Schritte der Thermolyse werden Mechanismen in Vorschlag gebracht.

Резюме — В динамическом и квазиизотермическом режимах проведен термический анализ ацетатных кластеров общей формулы $[\mathrm{Fe}_2^{\mathrm{III}}\mathrm{M}^{\mathrm{II}}\mathrm{O}(\mathrm{CH}_3\mathrm{COO})_6(\mathrm{H}_2\mathrm{O})_3]\cdot 2\mathrm{H}_2\mathrm{O}$, где $\mathrm{M} = \mathrm{Mn}$, Fe, Co, Ni. Процесс термолиза этих соединений протекает в интервале 40–310 °C и состоит из двух эндотермических и трех экзотермических стадий. Наиболее явная зависимость от свойств центрального атома переходного металла M обнаруживается для параметров второй стадии термолиза, протекающей в интервале 130–170°. Для этой стадии построены ряды термодинамической устойчивости и кинетической лабильности. Проанализировано влияние природы металла на термодинамические и кинетические параметры процессов термической деструкции гетероядерных ацетатов. Предложен механизм двух первых стадий термолиза.