Reactivity of metal-containing monomers
48.* Thermal transformations of cobalt(II) maleate

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Thermal conversion of cobalt(II) maleate, $CoC_4H_2O_4 \cdot 2H_2O$, (1) at 340—370 °C was studied. The composition of the products of pyrolysis was determined. The major solid-phase product of decomposition consists of nano-sized particles of CoO (sizes vary within narrow limits) stabilized by the polymeric matrix. Thermal conversions of Co^{II} maleate involve dehydration, polymerization of dehydrated monomers, and decarboxylation of the resulting polymer.

Key words: metal carboxylates, thermolysis, solid-phase polymerization, nano-sized particles, stabilization.

It was demonstrated that the final solid-phase products of thermolysis of crystal hydrates of transition metal acrylates are highly disperse metal-containing phases, namely, metals and/or their oxides, which are uniformly distributed over the decarboxylated polymeric matrix that formed in the course of this multistage process.[2—5] Depending on the nature of the metal-containing phase, its concentration in the products of pyrolysis vary within 55.0—59.0 wt.% (17.0—27.0 vol.%). The resulting concentrations are smaller than the values that are of practical interest for micromagnetonics.

One of the most promising ways of increasing the portion of the metal-containing phase in products of thermal conversion of monomers of metal carboxylates involves a search for chemical systems with a rather high specific concentration of metal and studies of such systems. In this respect, polycarboxylates of unsaturated acids, in particular, maleates and fumarates of transition metals, are of obvious interest. Studies of the kinetics and mechanism of thermal conversions of these dicarboxylates are also of scientific interest with respect to studies of their reactivity[6—8] and mechanisms of decarboxylation of complexes, which contain acido ligands in spatial proximity to each other.

In this work, we studied quantitatively thermolysis of cobalt(II) maleate, $Co(OCOHC=CHOCO) \cdot 2H_2O$, (1).

Experimental

Complex 1 was prepared by the reaction of Co^{II} carbonate with an excess of acid according to a known procedure.[1] Freshly prepared maleate has the

$Co(OCOCH=CHOCO) \cdot 3H_2O$ composition. However, according to the data of elemental analysis, it was partially dehydrated to $Co(OCOCH=CHOCO) \cdot 2H_2O$ with time. Found (%): C, 21.50; H, 2.23; Co, 28.52. $C_4H_6O_6Co$. Calculated (%): (%): C, 22.97; H, 2.87; Co, 28.19. IR, v/cm^{-1}: 1638 ($v(C=C)$); 1435, 1366 ($v_s(COO)$); 1544 ($v_{as}(COO)$); 3407 ($v_{OH}(H_2O)$).

Pyrolysis of complex 1 was carried out under static isothermal conditions at T_{exp} = 340—380 °C in a self-generated atmosphere (before the experiment, the samples were evacuated at room temperature (T_r) for 30 min). The kinetics of conversion was monitored taking into account gas evolution with the use of a membrane null-manometer. Thermolysis of samples was carried out in a nonisothermal reaction vessel. The volume heated to T_{exp} was ~0.05 V (V is the volume of the reaction vessel). After completion of thermolysis, the amount of gases evolved at T_r was determined, samples were taken for mass-spectrometric analysis, the weight loss of the sample was determined, and low-temperature fractionation (77 K) of the gaseous products was carried out.

Pyrolysis of complex 1 in the mode of thermal analysis was performed on a C derivatograph (MOM, Hungary) in air with heating at a rate of 5—10 K min^{-1} in the temperature range of 20—600 °C (the weight of the sample was 0.0637 g).

Mass-spectrometric studies of gaseous products of conversion were performed on an MS-3702 mass spectrometer. The IR absorption spectra of complex 1 and condensed and gaseous products of its conversion were recorded on a Specord IR-75 instrument in the 600—4000 cm^{-1} region.

The specific surfaces ($S_{sp}/m^2 g^{-1}$) of complex 1 and solid-phase conversion products were determined from the low-temperature absorption of nitrogen (according to a procedure reported in Ref. 9, the accuracy was ~5%).

The topological characteristics of thermolysis of 1 were studied by optical and electron microscopy. Optical studies were carried out on an MBI-6 instrument using transmitted polarized and nonpolarized light. Samples were prepared as suspensions in mineral oil.
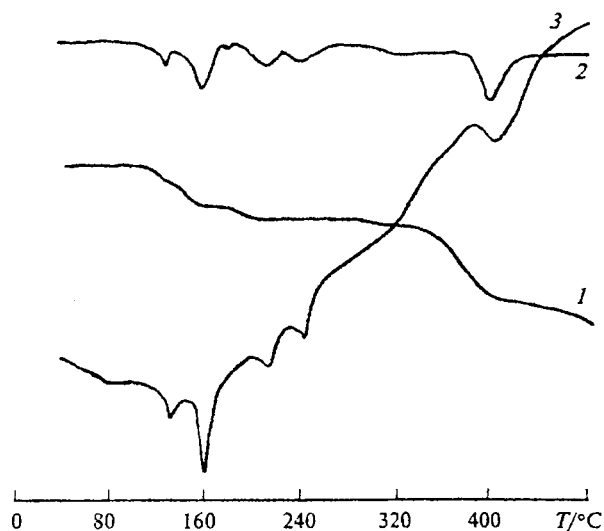
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* For Part 47, see Ref. 1

Fig. 1. Thermal analysis curves of pyrolysis of Co(OCOCH=CHCOO)·2H₂O: *1*; TGA; *2*, DTGA; and *3*, DTA.

Electron microscopy and electron diffraction studies were performed on an HU-125 transmission electron microscope with an accelerating voltage of 100 kV. Samples were supported onto Formvar films, *i.e.*, supports reinforced by a sputtered carbon film. Samples were supported by ultrasonic dispersion of a dry compound in the absence of solvents to exclude artifacts. A sputtered film of thallium chloride was used as the standard.

Results and Discussion

Kinetics of thermal conversion. Pyrolysis of complex 1 in the mode of thermal analysis (Fig. 1) demonstrated that three groups of endo effects are observed in the DTA curve in the range of 20—480 °C: (1) at 130 and 160 °C, (2) at 215 and 245 °C, and (3) at ~400 °C. The first group of endo effects is associated with a two-stage dehydration of crystal hydrate of 1 and is accompanied by 15.2% weight loss (the calculated value is 17.23 wt.%). The second group is accompanied by an insignificant weight loss (~6.3%) and, apparently, results from polymerization of dehydrated monomers. The third group occurs due to thermolysis of the polymer that formed and is characterized by a substantial weight loss (~36.7%).

Studies of the kinetics of gas evolution on thermolysis of 1 under isothermal conditions at T_{exp} = 340—370 °C demonstrated that the rate of gas evolution $w(\eta)$ decreases monotonically in the course of conversion (Fig. 2, *a*) and is adequately approximated by the equation of the rate of the first-order reaction (Fig. 2, *b*):

$$w(\eta) = k(1 - \eta), \qquad (1)$$

where $k/s^{-1} = 1.1 \cdot 10^6 \exp\{-30000/(RT)\}$; $\eta = (\alpha^{\Sigma}_t - \alpha^{\Sigma}_0)/(\alpha^{\Sigma}_f - \alpha^{\Sigma}_0)$ is the degree of gas evolution; and α^{Σ}_0, α^{Σ}_t, and α^{Σ}_f are the numbers of moles of gaseous products evolved per mole of the compound under study after heating of the sample (t_0), at the moment $\tau = t - t_0$, and at the end of gas evolution (hereinafter, the
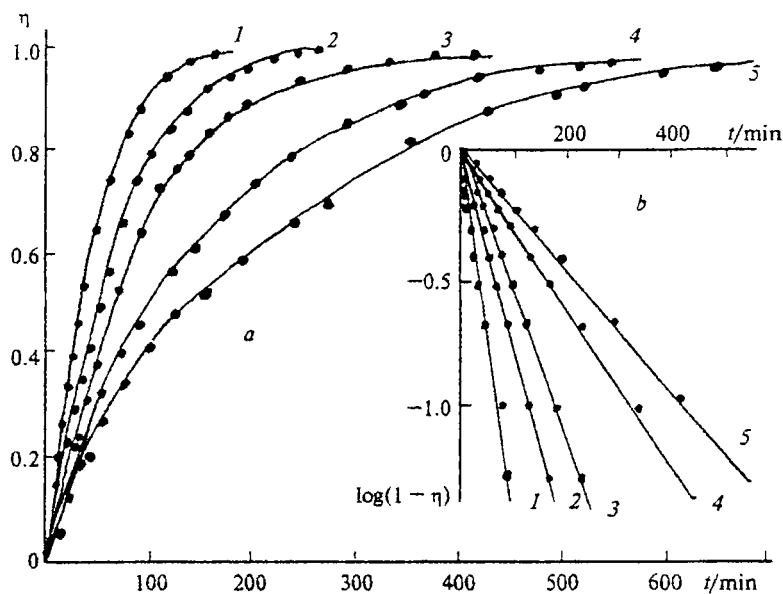

Fig. 2. Thermolysis of Co(OCOCH=CHCOO)·2H₂O in a self-generated atmosphere: *a*, the kinetics of gas evolution $\eta(t)$; *b*, semilogarithmic anamorphism [log(1 − η), *t*]; at $T/°C$ = 380 (*1*), 370 (*2*), 360 (*3*), 350 (*4*), and 340 (*5*).

activation energy is given in cal mol^{-1}). The tempera-
ture dependence of the rate constant of gas evolution
upon thermolysis of 1 differs substantially from the
corresponding temperature dependence of the rate con-
stant of gas evolution upon thermolysis of cobalt acry-
late Co(CH$_2$=CHCOO)$_2 \cdot$ 2H$_2$O, which was determined
in the same temperature range[3] (k/s^{-1} = 3.0 $\cdot$ 10^{14}
exp{$-57000/(RT)$}).

**Products of conversion of 1. Gaseous and condensed
products.** The total amount of gases evolved at the end of
conversion at T_r (Fig. 3, curve *1*) is smaller than the
maximum possible value (>2.0 mol). As T_{exp} increased,
the value of $\alpha^\Sigma_{f,T_r}(T_{exp})$ = 1.3 $\cdot$ 10^2 exp{$-5600/(RT)$}
increased and became equal to $\alpha^\Sigma_{f,T_r}(T_{exp})$ = 1.35
(340 °C)—1.80(370 °C).

The major gaseous product of conversion of complex
1 is CO$_2$, whose presence was confirmed by IR spectros-
copy and mass spectrometry. The yield of CO$_2$ at the
end of conversion (see Fig. 3, curve *2*) increased as T_{exp}
increased, $\alpha^{CO_2}_{f,T_r}(T_{exp})$ = 2.1 $\cdot$ 10^2 exp{$-6400/(RT)$}.
The yields of CO (according to mass spectrometry and

IR spectroscopy) and H$_2$ (mass spectrometry) (see
Fig. 3, curve *3*) are almost two orders of magnitude
lower than the yield of CO$_2$. According to the data of
mass spectrometry, products of conversion contain a
vapor of H$_2$O and a substantially smaller amount of a
vapor of maleic acid along with CO$_2$, H$_2$, and CO.
Condensation of H$_2$O and HOCOCH=CHOCOH on
"cold" (T_r) walls of the reaction vessel was observed even
at the early stages of conversion. The presence of
HOCOCH=CHOCOH was confirmed by a comparison
of the IR absorption spectrum of the condensate with
the reference absorption spectrum of maleic acid.

In the course of conversion, the yield of CO$_2$ in-
creased monotonically in parallel with the total amount
of gases evolved (Fig. 4, curves *1* and *2*). The yield of
maleic acid peaked at low degrees of gas evolution (see
Fig. 4, curve *3*), after which it remained virtually un-
changed and correlated with the loss of weight by the
sample (curve *5*).

Solid products of conversion. The degree of the loss of
weight by the sample at the end of gas evolution in-
creased as T_{exp} increased (see Fig. 3, curve *9*), but it
remained smaller than the values expected upon pyroly-
sis of complex 1 to Co or CoO. Solid products of
thermolysis are X-ray amorphous. According to the data
of electron diffraction study, the major metal-containing
product of conversion is well crystallized CoO with an
admixture of poorly crystallized Co$_3$O$_4$ or Co.

The change in the topography of the solid phase in
the course of conversion was monitored by optical mi-
croscopy. It was demonstrated that the initial powder of
1 consists of transparent particles, which rotate the
plane of polarized light in skew polarizers and occur
both as crystalline flattened prisms (in some cases, they
are well-faceted) with average size ~50×15×5 μm^3 (frac-
tion 1) and as shapeless glassy particles with size 5—70
μm, which exhibit no pronounced optical activity (frac-
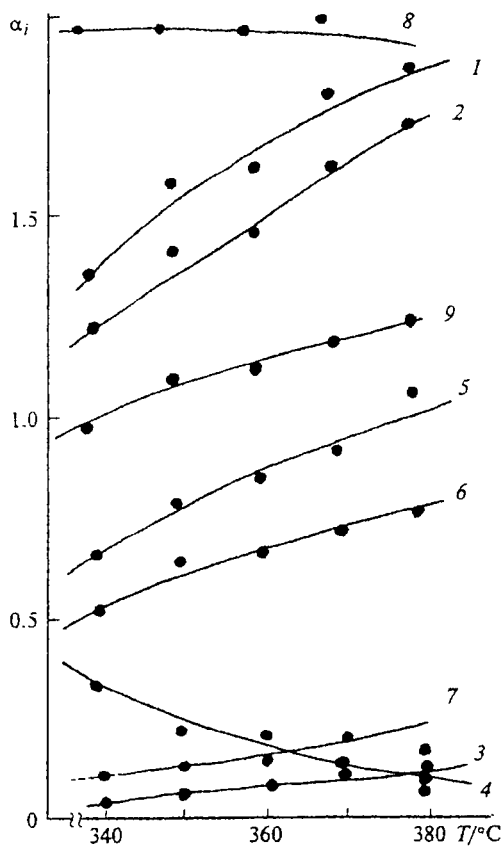tion 2). This is associated with the conditions of crystal-

Fig. 3. Dependence of the yields of the products at T_r at the
end of conversion of Co(OCOCH=CHCOO) $\cdot$ 2H$_2$O on T_{exp};
(m_0/V) $\cdot$ 10^3 = 2.04 g cm^{-3}: *1*, α_f^Σ; *2*, $\alpha_f^{CO_2}$; *3*, $\alpha_f^{H_2}$ and α_f^{CO};
4, $\alpha_f^{(=CHCOO)_2}$; *5*, 10$\alpha_f^{(=CHCOOH)_2}$ ≈ 10$\alpha_f^{(=C-)_2}$; *6*, $\alpha_f^{(=CH-)_2}$;
7, α_f^{CoO}; *8*, $\alpha_f^{H_2O}$; and *9*, ($\Delta m/\pi_0$) $\cdot$ 10^{-2}.
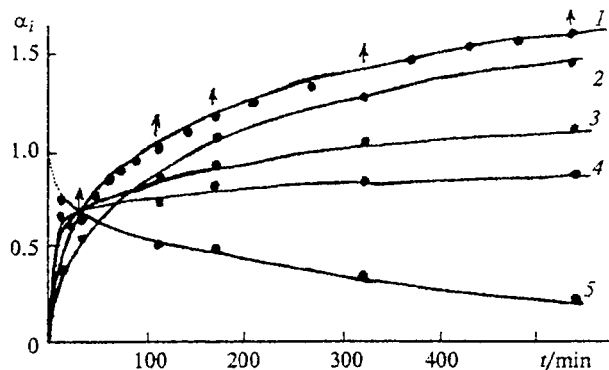
Fig. 4. Kinetics of accumulation of the products of thermolysis
of Co(OCOCH=CHCOO)$_2 \cdot$ 2H$_2$O at 350 °C: *1*, α_f^Σ; *2*, $\alpha_f^{CO_2}$;
3, 10$\alpha_f^{(=CHCOOH)_2}$ ≈ 10$\alpha_f^{(=C-)_2}$; *4*, $\alpha_f^{(=CHCOO)_2}$; and
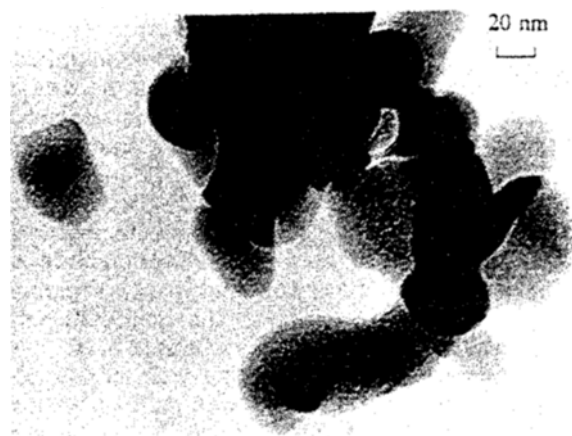*5*, ($\Delta m/\pi_0$) $\cdot$ 10^{-2}.

Fig. 5. Electron micrograph of initial particles of fraction 2.

lization of the sample in the course of synthesis and characterizes the morphological composition of cobalt maleate. Fraction 1 is a well crystallized compound, and fraction 2 is an amorphous compound. Some large crystals have macrodefects as spalls and cracks. The estimated weight ratio of fractions 1 and 2 was 1 : 1.

Optical studies of the changes in the topography of particles of fraction 1 demonstrated that even at low degrees of gas evolution, particles lost their ability to rotate the plane of polarization of transmitted light. This indicates that the sample became amorphous and is, apparently, associated with high rates of dehydration and polymerization, which occurred before the major gas evolution. In the course of conversion, a dark film was formed on particles, which points to the fact that

surface reactions occurred, a dislocation decorated network appeared, and the reactions were localized on growth defects. All the aforesaid are evidence for the heterogeneous character of conversion of crystals of fraction 1.

Reaction centers and a dark film are observed on shapeless blocks (fraction 2), and a dislocation network is absent. At the end of conversion of complex 1, a powder of the product consists of nontransparent particles, which retain the shape of the initial particles. The specific surface of the samples of 1 under study remained virtually unchanged upon thermolysis and was 30.0 ± 2.0 m^2 g^{-1}.

On the whole, from the topochemical standpoint, thermolysis of 1 is a heterogeneous process.

Only amorphous particles (fraction 2) were studied by electron microscopy. In the case of these initial samples, a uniform network of the increased electron density with the unit cell dimensions of ~2.0 nm is observed (Fig. 5). The morphology (Fig. 6, *a*) and microdiffraction of the final products of thermolysis were studied by electron microscopy. It was demonstrated that the samples contain both individual clusters (primarily, CoO), which are characterized by increased electron density, and aggregates formed by 3—10 clusters. The clusters are distributed over the matrix with the lower electron density. They are approximately spherical; the average size is ~4.0 nm (see Fig. 6, *b*). Simultaneously, rather large aggregates occur as cubic crystals of dimension 10.0—20.0 nm.

Therefore, a compound, which consists of nano-sized particles stabilized in the matrix of metal-containing particles (their sizes vary within narrow limits), was formed in the course of thermal conversion of complex 1.
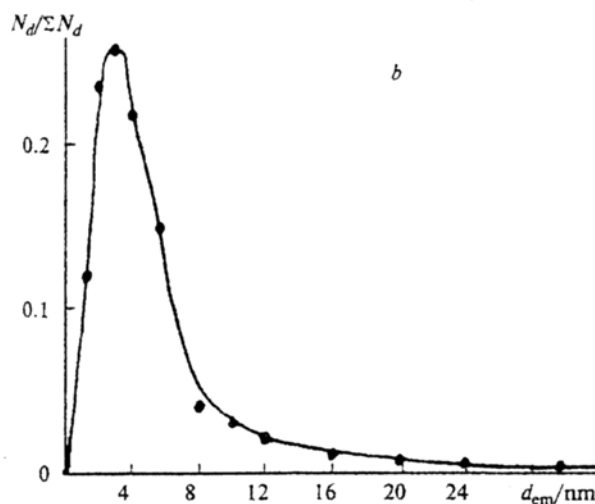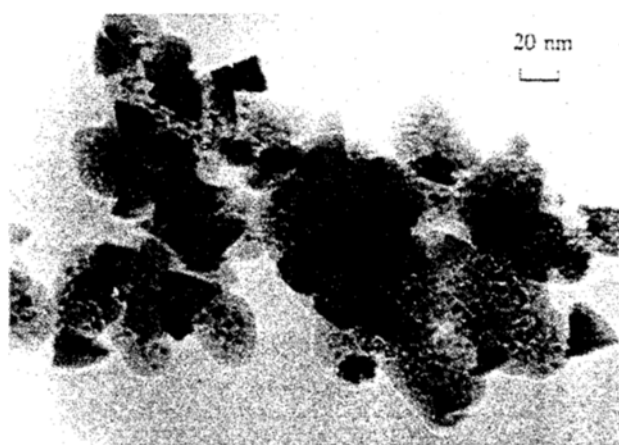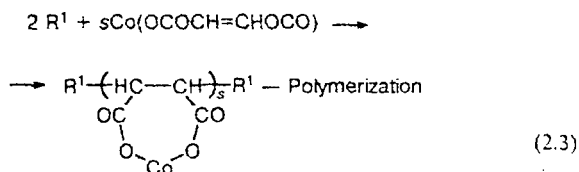

Fig. 6. *a*, Electron micrograph of particles of the product of thermolysis of 1 (T_{exp} = 350 °C, t = 9 h). *b*, Distribution of electron-dense particles in the product of thermolysis of 1 (based on the results of electron microscopy); N_d is the number of particles with the size d (ΣN_d = 390).

Possible pathways of pyrolysis of 1. Thermal conversions of **1**, like crystal hydrates of transition metal acrylates,[2-5] proceed in three stages, namely, dehydration (<160 °C), (co)polymerization of dehydrated monomers (200—250 °C), and decarboxylation of carboxylate groups of the metallopolymer that formed (>300 °C). The third process is accompanied by evolution of the major amount of gases and the weight loss of the sample upon thermolysis.

From the crystal-chemical standpoint, the structure of **1** is similar to the structure of cobalt(ii) maleate trihydrate studied previously,[1,10] which occurs as the coordination three-dimensional polymer $[Co(OCOCH=CHOCO) \cdot 2H_2O]_n \cdot nH_2O$. The major structural unit of the polymer is a coordination polyhedron about Co^{II}. Four O atoms of the tetradentate maleate ligand and two O atoms of two coordinated water molecules occupy the vertices of a slightly distorted octahedron. The metal ion is located in the center of the polyhedron. The third H_2O molecule (water of crystallization) is more weakly held (in thermal respect) in the structure and is involved in a network of hydrogen bonds through which an infinite hydrogen-bonded chain of alternating coordination and crystallization H_2O molecules can be formed. The formation of a seven-membered chelate ring, which involves a metal ion bonded to two O atoms of both carboxylate groups, is an interesting characteristic feature of the structure of cobalt(ii) maleate trihydrate. Apparently, this is also true for complex **1**.
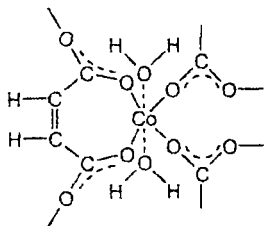
The remaining O atoms of the maleate ligand are coordinated to two adjacent Co^{+2} atoms to form a three-dimensional framework. Apparently, dehydration of the crystal hydrate causes no fundamental changes in the structure because water molecules are not involved in formation of the framework, unlike a number of crystal hydrates of transition metal carboxylates.[11] It is very significant that the Co—O bonds in these particles differ in length (vary within 0.2071—0.2114 nm).[1] This range can be extended as a result of dehydration due to a change in the dentation of the ligand. Therefore, it is highly probable that an increase in the thermal vibrations of the lattice of the dehydrated monomer of **1** (the temperature increases) leads to the cleavage of the weakest Co—O bonds and formation of a maleic mono- or biradical, which, in turn, like acrylates of transition metals,[3,5,6] can initiate polymerization of dehydrated monomers in the solid phase:

$[Co(OCOCH=CHCOO)]_n \longrightarrow$

$\longrightarrow [Co(OCOCH=CHCOO)]_{n-x} + x(\cdot OCOCH=CHOCO\cdot),$ (2.1)

$(\cdot OCOCH=CHOCO\cdot) + 2\ RH \longrightarrow$

$\longrightarrow (HOCOCH=CHOCOH) + R^1 \quad - \text{Initiation},$ (2.2)

$2\ R^1 + sCo(OCOCH=CHOCO) \longrightarrow$

(2.3)
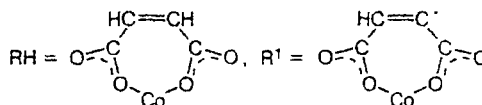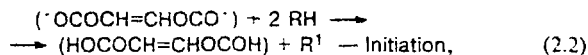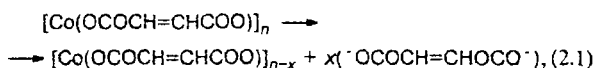
When heated, the resulting cross-linked polymer can undergo decarboxylation

(2.4)
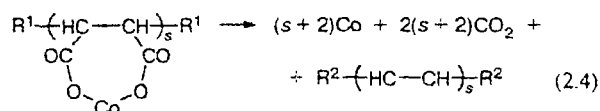
where $R^2 = HC{\equiv}C-$.

The $R^2(CHCH)_sR^2$ polymer formed as a result of decarboxylation can undergo additional thermopolymerization to give, for example, a cross-linked structure with a system of conjugated multiple bonds:

$HC{\equiv}C-(-CHCH-)_s-C{\equiv}CH \longrightarrow$

$\longrightarrow -HC{=}C-(-CHCH-)_s-C{=}CH-$ (2.5)
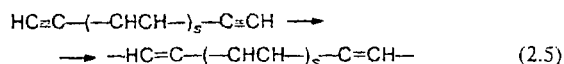
Therefore, the composition of the solid product that formed in the course of conversion can be written in general form as portions of C—H—O fragments

$CoO_z(=CHCOO)_{2p-x}(\equiv CCOO)_{2q-y}(=CH-)_x(\equiv C-)_y,$ (2.6)
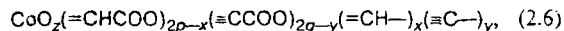
where $p + q = 1$. The formation of oxides of Co may be associated with oxidation reactions:

$zCo + \lambda_1 CO_2 = zCoO + (\lambda_1 - z)CO_2 + zCO,$ (3.1)

$zCo + \lambda_2 H_2O = zCoO + (\lambda_2 - z)H_2O + zH_2.$ (3.2)
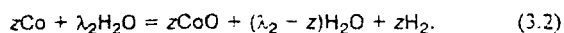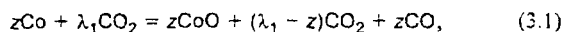
Using equations of the material balance, analogous to those considered previously in Refs. 3, 5, and 6, and the quantitative data on the yields of CO_2, H_2, and CO, the composition of the products of thermolysis of **1** both in the course and at the end of conversion can be calculated. Analysis of the experimental data and the results of calculations demonstrated that in the T_{exp} range under study, $\alpha^{(\equiv CCOO)_2} \approx 0$, *i.e.*, $q \approx y$, $\alpha^{(=CHCOOH)_2}$

$\approx \alpha^{(\ni C-)_2}$, and $\alpha^{(=CHCOO)_2} + \alpha^{(=CH-)_2} \approx 1 - 2\alpha^{(=CHCOOH)_2}$. In the course of conversion (see Fig. 4) at a constant temperature T_{exp}, the number of $(=CHCOO)_2$ fragments, $\alpha^{(=CHCOO)_2}$, decreased, and $\alpha^{(=CH-)_2}$ increased, whereas the value of $\alpha^{(\ni C-)_2}$ remained virtually unchanged almost from the beginning of gas evolution. At the end of conversion, the yields α^{CO_2}, $\alpha^{(=CHCOOH)_2} \approx \alpha^{(\ni C-)_2}$, $\alpha^{(=CH-)_2}$, and α^{FeO} increased, and the yield $\alpha^{(=CHCOO)_2}$ decreased (but remained higher than zero) as T_{exp} increased, which is indicative of a possible difference in the thermal stability of the intrachain and terminal carboxylated groups. The ratio $\gamma = (\alpha^{(=CHCOO)_2} + \alpha^{(=CH-)_2})/\alpha^{(\ni C-)_2}$ slightly decreased from 12.9 (340 °C) to 9.2 (380 °C) as the temperature increased. The value of 2γ can characterize the effective chain length of the polymer formed. Therefore, the effective chain length decreases as the temperature increases.

At the end of thermolysis, the portion of the oxide phase of Co slightly increased as the temperature increased, but it was no more than 15.0 mol.% of the total metal content of the initial compound. An increase in the portion of the oxide phase is associated with an increase in the rate of oxidation according to reactions (3.1) and (3.2) and is accompanied by an increase in the yields of CO and H_2. It can be suggested that the specific density of the decarboxylated polymer was[12] $\rho_p \approx 1.3-1.4$ g cm^{-3}, $\rho_{Co} \approx 8.9$ g cm^{-3}, and $\rho_{CoO} \approx 6.47$ g cm^{-3}, and the metal-containing phase content of the product of pyrolysis of 1 was ~69.0—74.3 wt.% (26.0—38.0 vol.%).

Therefore, studies of thermolysis of 1 allow conclusions that from the phenomenological standpoint, thermal conversion of 1 is analogous to pyrolysis of acrylates of transition metals. The process involves three temperature-separated successive macrostages, namely, dehydration of the initial crystal hydrate, solid-phase radical polymerization of dehydrated monomers, and decarboxylation of metal-containing carboxylate groups of the polymer that formed. At the end of thermolysis, a new compound formed. It consists of nano-sized particles of the metal-containing phase distributed over the decar-

boxylated polymeric matrix, which stabilizes these particles. Both intrachain and terminal metal-containing carboxylate groups of the polymer that formed in the course of thermolysis of 1 exhibit different thermal stability with respect to decarboxylation. The terminal groups are least stable. The causes of different stability of intrachain metal-carboxylate groups remain unclear and call for further investigation.

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