# Thermal decomposition of transition metal carboxylates
## 3. Composition of decomposition products and channels of transformation of anhydrous copper(II) formate

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Thermal decomposition of anhydrous $Cu(HCOO)_2$ (**1**) affords $H_2$, CO, $CO_2$, $H_2O$, HCuOOH, CuHCOO, Cu, and the polymeric product, which contains $-CH_2O$, $-C(O)OH-$, and $-RCH-O-$ groups. Decomposition of **1** proceeds in stages with formation of copper(I) formate as an intermediate. Possible pathways of decomposition of **1**, including isomeric forms of the $HCO_2^{\bullet}$ radical as intermediates, were analyzed.

**Key words:** copper formate; thermal decomposition; reaction mechanism.

Anhydrous salt **1** is best suited to study the mechanism of thermal decomposition of carboxylates of transition metals, which are, generally, crystal hydrates $M(HCOO)_n \cdot H_2O$, because the crystal structure of **1** is known and decomposition of **1** is not complicated by dehydration. Presently, there is no consensus on the mechanism of chemical processes occurring upon decomposition of compound **1**. Previously, it was suggested[1,2] that thermal decomposition of **1** proceeds in stages with the formation of copper(I) formate (**2**) as an intermediate. However, based on the results of mass-spectral study of decomposition of compound **1** under conditions which exclude the possibility of secondary reactions, the authors of Ref. 3 believed that decomposition of **1** proceeds according to the following scheme: $Cu(HCOO)_2 \rightarrow Cu + CO_2 + HCOOH$ followed by decomposition of formic acid to $H_2$ and $CO_2$. The possibility of the $Cu^{II} \rightarrow Cu^{I} \rightarrow Cu^{0}$ conversion was discussed also for other copper carboxylates, namely, for acetate,[4] acrylate,[5] malonate, and fumarate,[6] taking into account the low standard redox potential of the $Cu^{II}/Cu^{I}$ couple ($E^0 = +0.158$ V[7]).

Previously,[8,9] we studied the thermal decomposition of the crystalline powder of **1** under a self-generated atmosphere; it was demonstrated that the conversion is a complex process from the viewpoint of both kinetics and topography. Acceleration of decomposition of **1** is associated with accumulation of internal microstrains in the decomposed crystals. The nuclei of copper metal (the final product of conversion of **1**, which, as kinetic IR-spectral studies demonstrated,[9] forms as a result of decomposition of intermediate **2**) may be the source of these microstrains. However, up to now, the qualitative composition, the quantitative ratios of decomposition products, and their dependence on the characteristics of decomposition of **1** are not known with certainty (see Refs. 2, 3, 10—16).

The aim of this work is to study the composition of the products of decomposition of compound **1** at the end of decomposition and its change in the course of conversion and to analyze of the possible pathways of chemical conversions upon thermal decomposition of **1**.

## Experimental

Salt **1** was prepared by the reaction of $Cu(OH)_2 \cdot CuCO_3$ (analytically pure grade) with an excess of formic acid (90 %)[2] followed by recrystallization from formic acid. Found: Cu, 40.8 %. Calculated: Cu, 41.4 %.

Thermal decomposition of preevacuated compound **1** in a self-generated atmosphere was studied in the static nonisothermal system at 120—180 °C and $(m_0/V) \cdot 10^3 = 0.675$—$2.20$ g cm$^{-3}$ ($m_0$ is the initial weight of the sample; $V$ is the volume of the reaction vessel). The part of the reaction vessel with a tube filled with the substance studied, which was heated to the temperature of the experiment ($T_{exp}$), did not exceed 0.05 V. Before the experiment, the sample was evacuated for 30 min at room temperature. The kinetics of decomposition was studied by the accumulation of gaseous products of decomposition of compound **1** using a membrane null-manometer. After the experiment, the loss of weight by the sample, the total amount of gases evolved at room temperature, and the amount of gaseous products condensed at 77 K were determined.

The products of thermal decomposition of salt **1** and the kinetics of accumulation of these products were studied by mass spectrometry with the use of a modernized ion source based on an MI 1201V mass-spectrometer.[17] The heated tube filled with compound **1** was placed in the immediate vicinity of the ionization region; in this case, the Knudsen mode of inleakage occurs. The pressure in the ionization chamber was $10^{-4}$ Pa, $U_i = 70$ V. The kinetic experiment was carried out according to the following scheme: the tube filled with the

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compound studied was placed in the system, the system was evacuated, the mass spectrum of the background was measured, then the tube was heated, and the mass spectrum was scanned with a scan step of 6.6 min in the range $m/z$ = 18—46 until gas evolution was stopped. Because of the fact that the volatility of compound **1** is very small and the molecular peak of **1** is absent in the mass spectra of the background and pyrolysis products, the mass spectrum observed is the spectrum of the products of thermal decomposition. The values of peak intensities obtained for $m/z$ = 18 $[H_2O]^+$, 28 $[CO]^+$, 44 $[CO_2]^+$, and 46 $[HCOOH]^+$ were summarized.

IR spectroscopic study of the gaseous and condensed products of decomposition of **1** were carried out on a Specord 75 IR and UR-10 instruments in the frequency range 400—4000 cm$^{-1}$.

## Results and Discussion

**Qualitative composition of the products of decomposition of 1.** The IR absorption spectra of gaseous products of decomposition of **1** condensed at 77 K show a system of bands in the region 3600—3700, 2320—2340, and 625—675 cm$^{-1}$ typical of absorption of $CO_2$[18] and absorption bands (ν/cm$^{-1}$) at 3100 m, 3025 m, 2940 s, 2865 w, 1800 s, 1750 v.s, 1370 m, 1220 m, 1115 s, 995 s, 930 w, 640 m, 620 w attributable to the HCOOH vapor. The mass-spectral study of the gaseous products of decomposition of **1** at the end of conversion revealed the presence of $H_2$ ($m/z$ = 2), $H_2O$ (18), CO (28), $CO_2$ (44), and HCOOH (46). Therefore, gaseous products of decomposition of **1** are identical to those formed upon decomposition of $Fe(HCOO)_3$[19] and dehydrated $Fe(HCOO)_2 \cdot 2H_2O$.[20]

In the course of thermal decomposition of **1**, condensation of the liquid on "cold" (room temperature) walls of the reaction vessel was observed even at the early stages of decomposition because of the fact that the process was studied in a nonisothermal system. The IR spectrum of this condensate is similar to the absorption spectrum of liquid HCOOH. A comparison[8] of the loss of weight by the sample with the corresponding gas evolution at low depths of conversion is also indicative of the occurrence of condensation.

Kinetic IR spectroscopic studies of conversions in the solid phase upon the thermal decomposition of **1** in the COO$^-$ stretching and bending vibration region (see Ref. 9) point to the fact that in the course of conversion, the HCOO$^-$ groups typical of **1** disappear and intermediate **2** forms and then disappear. After termination of gas evolution, the IR spectrum of the solid product of decomposition of **1** shows a weak absorption in the region of stretching vibrations of —COO$^-$, —CH$_2$—O—, and —RCH—O— groups; this absorption is similar to that found previously for the products of thermal decomposition of $Fe(HCOO)_2$[20,21] and $Fe(HCOO)_3$,[19] which may be associated with the formation of the polymeric product of composition $(CH_2O)_r(CH(COOH)O)_s$, where $r \gg s$. Apparently, the differences between the loss of weight by the sample after decomposition of **1** (53.2—55.3 wt. %) and the value that would be expected upon decomposition of **1** to metallic copper (58.8 %) is determined by the partial oxidation of copper to CuO as well as by the formation of the polymeric product.

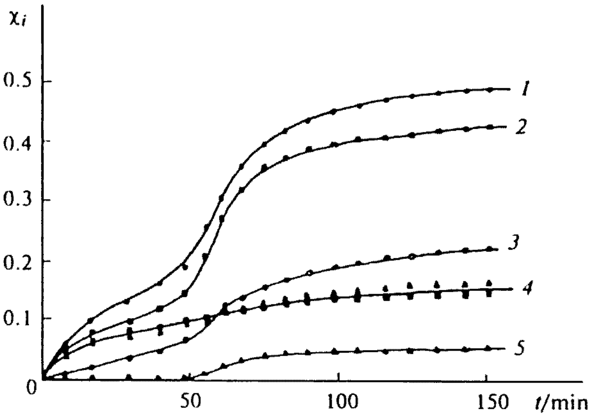


**Fig. 1.** Time dependences of the yields of the volatile products ($\chi$) of decomposition of **1** based on the data of mass-spectral analysis at $T_{exp}$ = 160 °C: *1*, $0.5\chi_\Sigma$; *2*, $\chi_{CO_2}$; *3*, $\chi_{HCOOH}$; *4*, $\chi_{CO}$, $\chi_{H_2O}$; *5*, $\chi_{H_2}$.

**Peculiarities of evolution of the products in the process of decomposition.** Mass-spectral study of volatile products, which was carried out in the course of thermal decomposition of **1** in the mode of high-vacuum pyrolysis under conditions, which excludes the possibility of occurrance of secondary reactions, makes it possible to follow the kinetics of appearance and accumulation of these products (Fig. 1). Based on the experimental data obtained, it may be concluded that conversion has a complex character and the following characteristic features may be pointed out:

— at early stages of decomposition, the rate of accumulation of volatile products ($w = d\chi_i/dt$) drops, reaching the minimum value, after which it increases to the maximum value and then decreases to zero at the end of decomposition (here, $\chi_i = (I_i)_t/(I_\Sigma)_f$, $(I_i)_t$ is the total intensity of the major mass peak of the $i$-th compound at the $t$ moment; $(I_\Sigma)_f$ is the total intensity of all major mass peaks of compounds observed at the end of conversion; $\chi_i \sim \alpha_i$, where $\alpha_i$ is the number of moles of the $i$-th compound yielded per mole of the initial compound);

— $CO_2(\chi_{CO_2})$ forms in the highest yield; the kinetics of its accumulation qualitatively follows the $\chi_\Sigma(t)$ curve;

— at early stages of conversion (up to $\chi_\Sigma$ = 0.30—0.34), $H_2O$, CO, and HCOOH are evolved, $\chi_{CO_2} > \chi_{H_2O} \approx \chi_{CO} > \chi_{HCOOH}$. Evolution of $H_2O$ and CO is virtually completed at this stage of decomposition. After $w_{min}(\chi_\Sigma)$, the rate of accumulation of these products is small. At deeper stages of conversion and at the end of decomposition, $\chi_{CO_2} > \chi_{HCOOH} > \chi_{H_2O} \approx \chi_{CO}$;

— after reaching $w_{\min}(\chi_\Sigma)$, the rate of evolution of $CO_2$ and HCOOH increases and $H_2$ appears; the amount of the latter was calculated taking into account the material balance according to the following equation: $I_{H_2} = 0.5(I_{CO_2} + I_{CO} - I_{HCOOH}) - I_{H_2O}$;

— at the initial depths of conversion of **1**, the following condition is fulfilled: $\chi_{CO} + \chi_{HCOOH} = \chi_{H_2O} + \chi_{HCOOH} \approx \chi_{CO_2}$.

Apparently, the above-mentioned characteristic features of the $\chi_i(t)$ curves are associated with the successive conversion $Cu(HCOO)_2 \rightarrow CuHCOO \rightarrow Cu$ in the course of which HCOO groups decompose, channels of this decomposition being different at different stages.

Inspite of some qualitative similarity in kinetic curves of accumulation of volatile products of decomposition of **1** in the conditions of high-vacuum pyrolysis ($m_0 \simeq 1$ mg, where $m$ is the weight loss in the sample) and of gas evolution upon thermal decomposition of the polycrystalline powder of **1** in a self-generated atmosphere[8] ($m_0$ = 60—150 mg) at close $T_{exp}$ ~160 °C (*cf.* Figs. 1 and 2), these curves account for different conversion mechanisms. At the initial stages of decomposition, $w_{\min}$ does not depend on $T_{exp}$, which is, apparently, indicative of the differences in kinetics of decomposition of the fine-crystalline and macrocrystalline fractions of the powder of **1**.[8,9] Because of this, the depth of conversion of **1**, which is determined from gas evolution (see Fig. 2, curve *1*) or from the weight loss (curve *3*), may not be associated with the true mechanism of thermal decomposition of **1**, namely, with the disappearance of HCOO groups in the process of successive conversion of $Cu(HCOO)_2$.

Figure 2 shows that at early stages of gas evolution, the ratio $(\alpha_{H_2} + \alpha_{CO})/\alpha_{CO_2}$ is small (~0.1), and this ratio gradually increases to 0.49 in the course of conversion (here, $\alpha_{CO_2} = \alpha^{\Sigma}{}_{>} - \alpha^{v}{}_{HCOOH+H_2O}$, $\alpha_{H_2} + \alpha_{CO} = \alpha^{\Sigma}{}_{<}$; $\alpha^{\Sigma}{}_{>}$ and $\alpha^{\Sigma}{}_{<}$ are the numbers of moles of gaseous products at $T_c$, which are condensed and not condensed at 77 K, respectively; $\alpha^{v}{}_{HCOOH+H_2O}$ is the number of moles of HCOOH and $H_2O$ in a saturated vapor at $T_c$). However, in the experiment on high-vacuum pyrolysis, this ratio is 0.7—0.9 at the initial stages of evolution of volatile products (see Fig. 1); as the depth of conversion increases, this ratio decreases (to 0.45 at the end of decomposition), and this value is close to the corresponding data on gas evolution. Therefore, only at the end of decomposition can the yields of the products in experiments on gas evolution characterize the proportion of channels of conversion of HCOO upon decomposition of **1**.

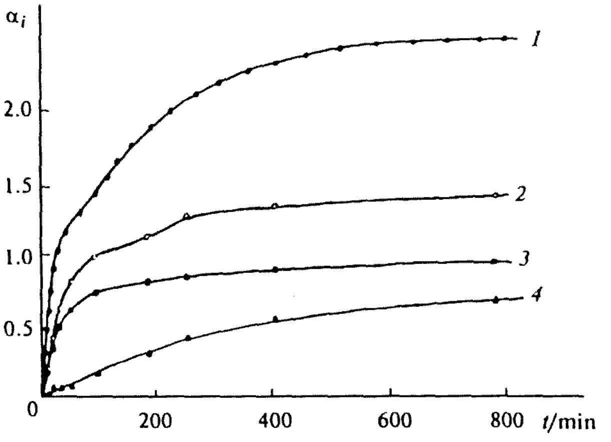


**Fig. 2.** Time dependences of the yields of the gaseous products of decomposition of polycrystalline powders of **1** at $T_{exp}$ = 160 °C: *1*, $\alpha_\Sigma$; *2*, $\alpha_{CO_2}$; *3*, $(\Delta m/\varkappa_0)\cdot 10^{-2}$ ($\varkappa_0$ is the number of moles of **1** in the sample before decomposition); *4*, $\alpha_{CO} + \alpha_{H_2}$.

**Calculations of the composition of the products of conversion of 1.** The products of thermal decomposition of **1** ($H_2$, $CO_2$, CO, HCOOH, CuHCOO, Cu, and, probably, CuO and the polymeric product) form as a result of successive conversion of **1**

$$Cu(HCOO)_2 \rightarrow CuHCOO + P_1 \rightarrow CuO_x + P_2,$$

where $P_1$ and $P_2$ are the products of decomposition; $CuO_x$ is the general formula for copper and its oxides ($0 \le x \le 1$). For $Cu(HCOO)_2$, CuHCOO, and $CuO_x$, we may write the balance equation

$$\lambda + \omega + \theta = 1, \qquad (1)$$

where $\lambda = \alpha_{Cu(HCOO)_2}$, $\omega = \alpha_{CuHCOO}$, $\theta = \alpha_{CuO_x}$ (at $t = 0$ $\lambda = \alpha^0{}_{Cu(HCOO)_2} = 1$). The depth of conversion with respect to HCOO groups with the use of Eq. (1) is as follows:

$$\eta_{HCOO} = 1 - \lambda - 0.5\omega = 0.5\omega + \theta = 0.5(1 - \lambda + \theta). \quad (2)$$

At the beginning of conversion, $\lambda = 1$, $\omega = \theta = \eta_{HCOO} = 0$; at the end of conversion, $\lambda = \omega = 0$, $\theta = \eta_{HCOO} = 1$.

The composition of conversion products may be described by the system of equations of material balance (1) and (1a)—(1f).

$$\alpha_{CO_2} + \alpha_{CO} + \alpha_{HCOOH} + 2\lambda + \omega + \alpha_v = 2\eta, \qquad (1a)$$

$$\alpha_{H_2} + \alpha_{H_2O} + \alpha_{HCOOH} + \lambda + 0.5\omega + \alpha_v = \eta, \qquad (1b)$$

$$2\alpha_{CO_2} + \alpha_{CO} + \alpha_{H_2O} + 2\alpha_{HCOOH} + 4\lambda + 2\omega + {} + \alpha_v + x\theta = 4\eta, \qquad (1c)$$

$$\alpha_{CO} + \alpha_{H_2} = p, \qquad (1d)$$

$$\alpha_{CO_2} = n, \qquad (1e)$$

$$1.875\alpha_v + x\theta = q - 5.875(1 - \eta). \qquad (1f)$$

Here, $h = \eta_{HCOO}$, $\alpha_v$ is the number of moles of the polymeric product per mole of the initial compound as in the known work,[8] let us consider, for simplicity of calculations, the polymeric product as $(CH_2O)_r$ assuming that the portion of $CH_2O$ groups in the polymeric product formed is substantially higher than the portion of CH(COOH)O groups), $q = 1/16[(m_{res}(t)/\pi_0) - 63.55]$, where $m_{res}(t)$ is the weight of the sample at the moment $t$; $\pi_0$ is the number of moles of **1** in the initial sample. The values of $n$, $p$, and $q$ were determined experimentally (Table 1): $p = \alpha^{\Sigma}_{<}$, $n = \alpha^{\Sigma}_{>} - \alpha^{v}_{HCOOH+H_2O}$.

Based on the data of mass-spectral study of accumulation of volatile products of thermal decomposition of **1** upon high-vacuum pyrolysis, we assumed that $\alpha_{H_2O} \approx \alpha_{CO}$ both at the end of decomposition and in the course of conversion throughout the range of experimental parameters $T_{exp}$ and $m_0/V$; then, the composition of the products at the end of conversion can be calculated ($\eta = 0 = 1$, $\alpha_v \approx x0 = x$, $q = 2.875x$). Therefore, we obtain the following equations for the yields of the decomposition products at the end of conversion:

$$\alpha_v = x = 8q/23, \quad (1g)$$

$$\alpha_{HCOOH} = 1 - p - 8q/23, \quad (1h)$$

$$\alpha_{CO} = \alpha_{H_2O} = 1 + p - n, \quad (1i)$$

$$\alpha_{H_2} = n - 1. \quad (1j)$$

The results of these calculations, which are presented in Fig. 3, demonstrated that at constant $T_{exp}$, an increase in the $m_0/V$ ratio results in an increase in the yields of $CO_2$, $H_2$, HCOOH, the polymeric product, and CuO and in a decrease in the yields of $H_2O$, CO, and Cu (see Fig. 3, *a*). In this case, $\alpha_{CO_2} > \alpha_{H_2} > \alpha_{HCOOH} > \alpha_v$, and $\alpha_{CO_2} > \alpha_{H_2O} + \alpha_{CO}$. An increase in $m_0/V$ at constant $T_{exp}$ exerts only a slight effect on the proportion of channels of conversion of **1**, which results in formation of HCOOH, $H_2$, and the polymeric product: the $\alpha_{HCOOH}/\alpha_{H_2}$ and $\alpha_{HCOOH}/\alpha_v$ ratios are 0.48—0.63 and 3.0—5.0, respectively, with increasing $(m_0/V) \cdot 10^3$ (from 2.21 to 0.667 g $cm^{-3}$). The value $(m_0/V)$ substantially affects the ratio of routes of formation of HCOOH and $H_2O$ + CO. Thus, as the $m_0/V$ ratio increases, the $\alpha_{HCOOH}/\alpha_{H_2O}$ ratio is 0.52, 0.98, and 5.20 at $(m_0 \cdot 10^3)/V$ = 0.667, 1.30, and 2.21 g $cm^{-3}$, respectively, and, therefore, the portion of channels of formation of $H_2O$ and CO in the overall balance of conversion of **1** decreases.

**Table 1.** Dependence of $n$, $p$, and $q$ on $T_{exp}$ at the end of conversion of **1** ($m_0/V$ = 1.31(±0.01) · $10^{-3}$ g $cm^{-3}$)

| $T_{exp}$/°C | $n$ | $p$ | $q$ |
|---|---|---|---|
| 120 | 1.13 | 0.42 | 0.50 |
| 125 | 1.25 | 0.50 | 0.30 |
| 130 | 1.28 | 0.53 | 0.31 |
| 135 | 1.25 | 0.61 | 0.16 |
| 140 | 1.42 | 0.71 | 0.21 |
| | 1.44 | | 0.17 |
| | 1.46 | | 0.14 |
| 150 | 1.49 | 0.68 | 0.105 |
| 160 | 1.43 | 0.72 | 0.11 |
| 170 | 1.54 | 0.72 | 0.075 |
| 180 | 1.64 | 0.75 | 0.06 |
| | 1.69 | 0.74 | 0.05 |

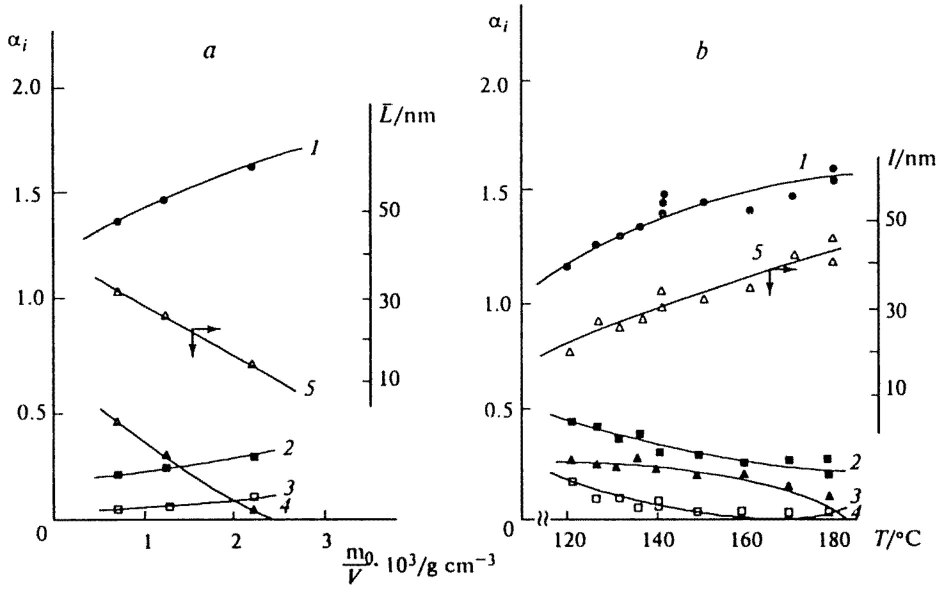


Fig. 3. Yield of the products of decomposition at the end of conversion of **1** at constant $T_{exp}$ = 140 °C (*a*) and $m_0/V$ = 1.31(±0.01) · $10^{-3}$ (*b*): *1*, $\alpha_{CO_2}$, $\alpha_{H_2}$ + 1; *2*, $\alpha_{HCOOH}$; *3*, $\alpha_v = x$; *4*, $\alpha_{H_2O} \simeq \alpha_{CO}$; *5*, $\bar{L}$ ($\bar{L}$/nm is the average size of the particles of the solid product calculated from $S_{sp}$ under the assumption that the particles of copper metal have a spherical shape).

With constant $m_0/V$ ratio, an increase in $T_{\rm exp}$ (see Fig. 3, *b*) results in a decrease in the yields of HCOOH, $H_2O$, CO, the polymeric product, and CuO and in an increase in the yields of $H_2$, $CO_2$, and Cu. The yield of $CO_2$ is the highest among all yields of the products of decomposition of **1**: $\alpha_{CO_2} > \alpha_{HCOOH} > \alpha_{H_2O} \approx \alpha_{CO} > \alpha_v = x$, and $\alpha_{CO_2} > \alpha_{H_2}$. Note that the yields of $H_2$ and $CO_2$ at the end of decomposition of **1** are close to those reported previously for the same $T_{\rm exp}$ range (see Ref. 22). An increase in $T_{\rm exp}$ assists in a decrease in the contribution of reactions accompanied by formation of HCOOH, $H_2O$, CO, the polymeric product, and CuO as compared to formation of $H_2$. Simultaneously with an increase in $T_{\rm exp}$, a decrease (as compared to the channels of formation of HCOOH) in the contribution of the routes of formation of the polymeric product and CuO and a decrease in the portion of the channels of formation of $H_2O$ and CO are observed at $T_{\rm exp}$ = 160 °C (Fig. 4).

**Possible routes of thermal decomposition of 1.** The data we obtained previously[8,9] and which are presented in this work make it possible to consider the thermal decomposition of **1** as a two-stage process similar to decomposition of $Cu^{II}$ acetate (see Refs. 4, 23) and $Fe^{III}$ formate (see Ref. 19); this process is determined by successive reduction $Cu^{II} \rightarrow Cu^{I} \rightarrow Cu^{0}$. The yield of the H—C—O-containing products upon decomposition of **1** is associated with the conversion of formate groups, which are contained in **1** and **2**, through different channels; this process is complicated by the change in the relative contribution of these channels to the overall balance of decomposition of HCOO groups with increasing depth of decomposition. This is evidenced by changes in the quantitative ratio of the products in the course of decomposition in the experiment on high-vacuum pyrolysis of **1**.

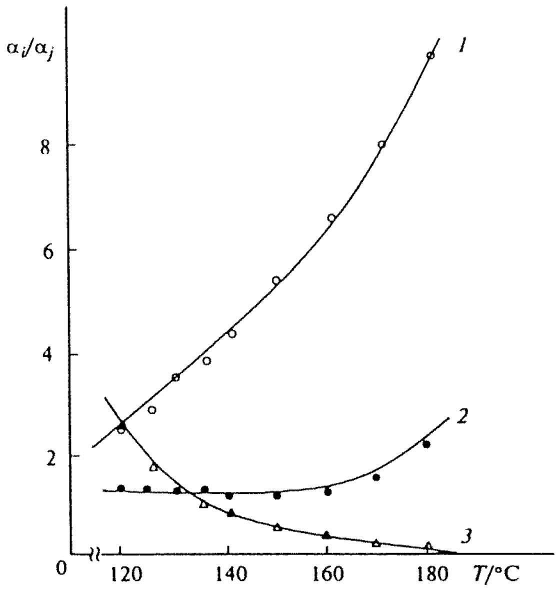
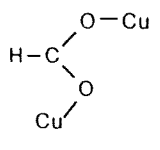


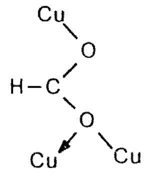
**Fig. 4.** The ratio of the channels of decomposition of **1** with the formation of $H_2$, HCOOH, $H_2O$, and CO, the dependences of $\alpha_v$ and $x$ on $T_{\rm exp}$: *1*, $\alpha_{HCOOH}/\alpha_v$; *2*, $\alpha_{HCOOH}/\alpha_{CO}$; *3*, $\alpha_{HCOOH}/\alpha_{H_2}$.

The difference in the routes of conversion of HCOO groups upon decomposition of **1** and **2** may be one possible cause of the change in the contribution of the channels of conversion of these groups to the overall balance of the products of decomposition of **1**; this difference is determined by characteristic features of the crystal structures of **1** and **2**.

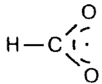
According to X-ray structural data,[24] the crystals of **1** have a framework-net structure[25] formed from Cu atoms and HCOO groups of two types, which are contained in the crystal in equal amounts (bidentate groups, which are present in the structure of **1** in an *anti-syn* conformation (*a*-2-*s*) with substantially different C—O bond lengths, and tridentate groups, which are incorporated into the structure of **1** in an *anti-syn*(*anti*) conformation (*a*-3-*sa*) with nearly equal C—O bond lengths.



*a*-2-*s*



*a*-3-*sa*

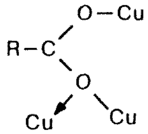
In the crystal structure of **1**, the COO fragment of the bidentate (*a*-2-*s*) HCOO group corresponds to the asymmetrical H—O—C=O structure,[28] whereas this fragment in the tridentate (*a*-3-*sa*) HCOO group corresponds to the symmetrical structure of the  $H{-}C(O)(O)^{\bullet}$ radical.[26,27] The lengths of the Cu—O bonds formed by the (*a*-2-*s*) and (*a*-3-*sa*) HCOO groups are also different; in the case of the (*a*-3-*sa*) HCOO group, the Cu—O bonds are shorter. Correspondingly, these bonds also differ in strength. Therefore, rupture of the least strong Cu—O bonds with the formation of the $HCO_2^{\bullet}$ radical is the most probable process. If it is assumed that the structure of the $HCO_2^{\bullet}$ radical formed is similar to the structure of the COO fragment of the formate group opened in the crystal-chemical structure, the appearance of asymmetrical as-$HCO_2^{\bullet}$ radicals upon decomposition of **1** would be expected. Estimations demonstrated that the reaction

$$Cu(HCOO)_2(s) \rightarrow CuHCOO(s) + \text{as-}HCO_2^{\bullet}(gas)$$

is endothermal with the thermal effect of 32.5 kcal mol$^{-1}$. From here on, we assume for thermal calculations $\Delta_fH°$[as-$HCO_2^{\bullet}$(gas)] = −36.0 kcal mol$^{-1}$ (*cf.* Refs. 26, 27: −150.5 kJ mol$^{-1}$), $\Delta_fH°$[s-$HCO_2^{\bullet}$(gas)] = −52.6 kcal mol$^{-1}$ (*cf.* Ref. 29: −219.5 kJ mol$^{-1}$), $\Delta_fH°$[Cu(HCOO$_2$(s)] = −180.0 kcal mol$^{-1}$ (*cf.* Ref. 13: −752.4 kJ mol$^{-1}$), $\Delta_fH°$[CuHCOO(s)] = −95.0

kcal mol$^{-1}$ (−397.1 kJ mol$^{-1}$)*, $\Delta_f H°[CO_2(gas)]$ = −94.1 kcal mol$^{-1}$ (*cf.* Ref. 27: −393.3 kJ mol$^{-1}$), $\Delta_f H°[H(gas)]$ = 52.0 kcal mol$^{-1}$ (*cf.* Ref. 27: 217.4 kJ mol$^{-1}$). The thermal effect of this reaction is close to the value of the effective activation energy of the initial rate of gas evolution ($E_{a,eff}$ = 33.0 kcal mol$^{-1}$)[8] and the rate of disappearance of HCOO groups ($E_{a,eff}$ = 27.8 kcal mol$^{-1}$)[9].

The crystal structure of **2** was not studied. However, it may be believed[25] that structural units of compound **2** are similar to the structure of the binuclear copper(I) acetate, $Cu_2(CH_3COO)_2$,[32,33] which is a ribbon structure with a square Cu—CuO$_3$ coordination occurring through tridentate (*s*-3-*sa*) RCOO groups.



In the structure of $Cu_2(CH_3COO)_2$, as well as in the structure of **1**, the C—O bond lengths in the tridentate group have close values, whereas, the Cu—O bonds differ in length. Therefore, apparently, decomposition of **2** does not afford s-HCO$_2^{\cdot}$.

The HCO$_2^{\cdot}$ formed may be converted through different channels depending on their structure and concentration in the reaction zone. At low concentrations of HCO$_2^{\cdot}$ in the reaction zone, these groups may disappear in different ways.

Isomerization and decomposition[29,34–36]

$$\text{s-HCO}_2^{\cdot} \rightleftharpoons \text{as-HCO}_2^{\cdot} + 16.5\ \text{kcal mol}^{-1}, \qquad (2.1)$$

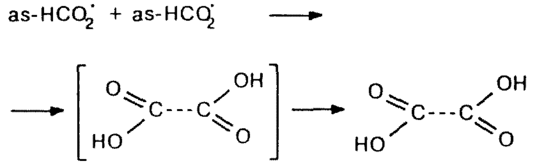
$$\text{s-HCO}_2^{\cdot}\text{(gas)} \longrightarrow \text{H}^{\cdot}\text{(gas)} + \text{CO}_2\text{(gas)} + 6.0\ \text{kcal mol}^{-1}, \qquad (2.2a)$$

$$\text{as-HCO}_2^{\cdot}\text{(gas)} \longrightarrow \text{H}^{\cdot}\text{(gas)} + \text{CO}_2\text{(gas)} - 10.5\ \text{kcal mol}^{-1}\ (-43.9\ \text{kJ mol}^{-1}). \qquad (2.2b)$$

Based on the results of quantum-chemical calculations, the value of $E_{a,2.1}$ of forward reaction (2.1) is 36—38 kcal mol$^{-1}$ (150.5—158.8 kJ mol$^{-1}$). Taking into account the thermal effect of back reaction (2.1), $\bar{E}_{a,2.1}$ = 51—53 kcal mol$^{-1}$ (171.4—179.7 kJ mol$^{-1}$).[29,34] For reactions (2.2a) and (2.2b), $E_{a,2.2a}$ = 16—18 kcal mol$^{-1}$ (66.9—75.2 kJ mol$^{-1}$) and $E_{a,2.2b}$ = 38—40 kcal mol$^{-1}$ (*cf.* Ref. 35: 158.8—167.2 kJ mol$^{-1}$).[35] Assuming that the pre-exponential factors of the rate constants of forward and back reactions (2.1) and of reactions (2.2a) and (2.2b) are close, the $k_{2.1}/\bar{k}_{2.1}$ and $k_{2.2b}/\bar{k}_{2.2a}$ ratios are $6.3 \cdot 10^9$—$7.6 \cdot 10^8$ and $9.3 \cdot 10^{-13}$—$3.6 \cdot 10^{-11}$, respectively, in the studied range of $T_{exp}$ = 120—180 °C. Therefore, the probability that reaction (2.2a) and forward reaction (2.1) proceed is substantially higher than that of reaction (2.2b) and back reaction (2.1).

Reactions with the matrix (with **1** or **2**).

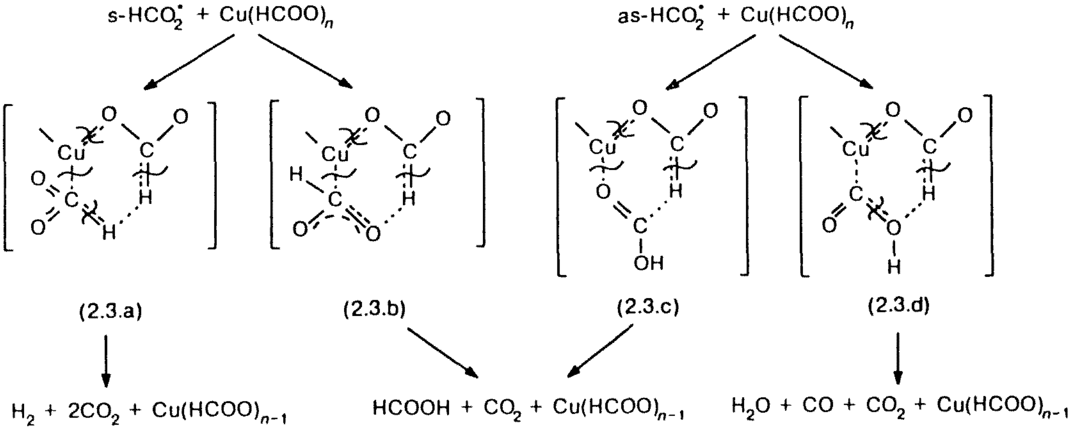
At high concentrations of HCO$_2^{\cdot}$ radicals, recombination processes may occur along with reactions (2.1—2.3d); these recombination processes also afford the above-mentioned products. However, in the case of salt **1**, unlike the thermal decomposition of Fe(HCOO)$_3$,[19] the contribution of recombination reactions to the overall balance of conversions is, apparently, insignificant. The absence of oxalic acid in the products of decomposition of **1** indicates that reactions (2.4) and (2.5) in the conversion zone virtually do not occur.



(2.4)

$$\text{as-HCO}_2^{\cdot} + \text{CO}_2 \longrightarrow \text{HO(O)CC(O)O}^{\cdot} \longrightarrow \text{H}_2\text{C}_2\text{O}_4 + \text{CO}_2 \qquad (2.5)$$

Low concentrations of HCO$_2^{\cdot}$ radicals in the decomposition zone and high rates of diffusion of CO$_2$, which is dissolved in the matrix, from the conversion



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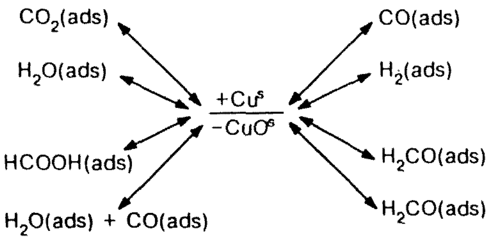
* The estimate was based on a comparison of the known data on $1/n\Delta_f H°[CuX_n(solid)]$ and $\Delta_f H°[X^-(solution)]$[27,30,31], where X$^-$ is the anion.

zone (reaction 2.5) may be the most probable causes of low rates of reactions (2.4) and (2.5).

Hydrogen atoms formed according to reactions (2.2a) and (2.2b) may react rapidly with the matrix

$$H^{\cdot} + Cu(HCOO)_n \rightarrow H_2 + CO_2 + Cu(HCOO)_{n-1} \quad (2.6)$$

<u>Surface reactions.</u> When copper metal appears in the course of decomposition of **1**, $H_2O$, CO, $CO_2$, and HCOOH formed are adsorbed on the surface of copper and may react with the surface copper atoms ($Cu^s$) as well as with each other

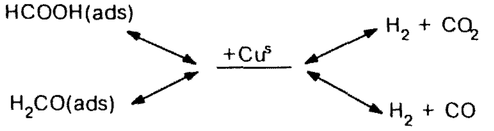


(2.7a)

(2.7b)

(2.7c)

(2.7d)



(2.7e)

(2.7f)

Adsorbed HCOOH and $H_2CO$, which appear according to reactions (2.7c) and (2.7d), react with each other to form the polymeric product:[20]

$$\begin{aligned} &HCOOH(ads) + H_2CO(ads) \xrightarrow[-H_2]{Cu^s} \\ &\longrightarrow [HCOC(O)OH](ads) \xrightarrow[rapidly]{+H_2CO} \\ &\longrightarrow [-O-C(COOH)H-(O-CH_2)_x-]_m \end{aligned} \quad (2.7g)$$

For forward reaction (2.7e), according to the data on decomposition of the dispersed powder HCOOH,[37] $E_a$ is 27—29 kcal $mol^{-1}$; the pre-exponent factor is $10^{13}$—$10^{13.5}$ $s^{-1}$. Under the conditions of our experiment, the rate of reaction (2.7e) $w_{2.7e}$ = 0.5—1.6 $s^{-1}$ and (0.48—1.5)$\cdot 10^{-2}$ $s^{-1}$ at 180 °C and 120 °C, respectively, if the catalytic activity of copper metal formed is comparable to that of the dispersed copper powder.[37] In this case, for reaction (2.7g) to proceed, it is necessary that the rate of this reaction be higher than 1.6 $s^{-1}$ and $1.5\cdot 10^{-2}$ $s^{-1}$ at 180 °C and 120 °C, respectively.

Reaction (2.7d) may be the most probable source of formation of $H_2CO$. This is evidenced by a decrease in the yields $\alpha_{H_2O}$ and $\alpha_{CO}$ at the end of decomposition at constant $T_{exp}$ and by an increase in the $m_0/V$ ratio against the background of an increase in $\alpha_{HCOOH}$ and $\alpha_{CO_2}$, which is accompanied by an increase in $\alpha_v$ (see Fig. 3, *a*). Note that an increase in dispersity of the solid product of conversion of **1** correlates with an increase in the yield $\alpha_v$, as was observed in the case of thermal decomposition of $Fe^{II}$ formate (see Ref. 20) and $Fe^{III}$ formate (see Ref. 19). Apparently, the contribution of reactions (2.7a) and (2.7b) to surface reactions (2.7a—2.7g) is insignificant because $\alpha_v \approx \alpha_{CuO}$. On the whole, the contribution of surface reactions, which afford CuO and the polymeric product, is small. This is evidenced by the low yields $\alpha_{CuO}$ and $\alpha_v$ at the end of decomposition.

Therefore, reactions (2.1—2.7g) provide a qualitative explanation for the formation of products of thermal decomposition of **1**. In the framework of the scheme of chemical conversions considered, it may be assumed that the concentration of $HCO_2^{\cdot}$ radicals formed is low, and recombination processes do not proceed; the s-$HCO_2^{\cdot}$ radical is used mainly according to reactions (2.1), (2.3a), (2.3b), (2.2a), and (2.6); the as-$HCO_2^{\cdot}$ radical is used to a large degree according to reactions (2.3c) and (2.3d); mainly, reactions (2.7g—2.7d) proceed on the surface.

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