Thermal decomposition of transition metal carboxylates

1. Decomposition of anhydrous copper(II) formate. Morphology and regularities of gas evolution

A. S. Rozenberg and E. I. Aleksandrova*

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588

Thermal solid-phase decomposition of anhydrous copper(II) formate has been studied at 120—180 °C. The rate of gas evolution during the decomposition depends on the depth of conversion and can be presented as the sum of first-order reaction rates and the rate of the autocatalytic process (a second-order reaction). The evolution of the solid phase during thermolysis has been observed by optical microscopy. The decomposition of copper formate is a complex topochemical process, a combination of homogeneous and heterogeneous transformations and dispersion of large crystals.

Key words: copper(II) formate, thermal solid-phase decomposition, kinetics; gas evolution; morphology; specific surface.

Transition metal carboxylates, especially formates and oxalates, attract attention of researchers as sources of nanoparticles of metals and (or) their oxides.[1] In recent years, thermal decomposition of metal formates has been used for preparing high-temperature superconducting ceramics with improved parameters.[2,3] However, regularities of the formation of ultradispersed particles and their stabilization upon thermolysis of solid states have virtually not been studied until presently.[4—8] These studies would allow one to obtain detailed information about both kinetic regularities and the mechanism of solid-phase transformations, as well as their relationships with the evolution of the solid state morphology, composition of gaseous products, surface size, size distribution of highly dispersed particles formed, and their physicochemical parameters. This is necessary for the development of scientific approaches to control the processes of preparation and stabilization of nanoparticles in the solid phase.

Thermal decomposition of anhydrous copper(II) formate, $Cu(HCOO)_2$ (**1**), was described in several works. In particular, it has been shown that the rate of thermal decomposition of compound **1** depends substantially on the method of its synthesis.[9—11] At the same time, presently available kinetic data obtained under isothermal conditions[9—11] and by thermal analysis[12—14] are very contradictory. The dependence of both qualitative and quantitative composition of gaseous products of the transformation of formate **1** on the duration and temperature of decomposition, especially at early stages of the process, seems even more uncertain.[10—19] Therefore, the mechanism of decomposition of compound **1** as well as that of other 3d-metal formates is yet unclear.[13,15,16,18]

In this work, we consider the results of studying the kinetic regularities of the thermal decomposition of compound **1** in a self-generated atmosphere, morphologic changes in the solid phase upon thermolysis, and the relationships between the dispersity of solid-phase products of the transformation and kinetic parameters of the decomposition.

Results and Discussion

Topochemical peculiarities of decomposition of anhydrous copper formate (1). Observation by optical microscopy (OM) shows that initial sample **1** is a powder with a specific surface (S_{sp}^0) equal to 10.5 $m^2 g^{-1}$ and consists of lamellar crystals occurring as both individual particles and agglomerates with low mechanical strength. The mean size of the individual crystals is $(1.0—2.0)\times(10.0—15.0)\times(30.0—50.0)$ μm^3; they are transparent, blue in transmitted light, and have smoothed ("fused") edges and microrelief of the facet surface, which testifies to desolvation. Comparison of the results of the OM studies with the S_{sp}^0 values of samples **1** shows that the mean size of the particles calculated under the assumption of their spherical shape from the S_{sp}^0 values for $\rho_{Cu(HCOO)_2} = 2.58$ g cm^{-3} (see Ref. 20) is ~0.2 μm, *i.e.*, the particles are smaller in fact than was expected from the data of OM observations. This allows one to draw the conclusion that the crystals **1** studied have a sufficiently high porosity. The agglomerates reach

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 72—76, January, 1996.

100—300 μm in diameter. The large crystals (>15×80 μm^2 in size) have fractures, chips, and intrinsic heterogeneities. The crystals change their color in transmitted polarized light.

The OM observations of the decomposition of compound **1** were carried out at T_{exp} = 160 °C (where T_{exp} is the temperature of the experiment) at various stages of transformation corresponding to the following losses of mass by the sample: Δm (wt. %) = 9.0 (0.164), 17.2 (0.313), 32.9 (0.59), 37.8 (0.69), 49.5 (0.905), and 54.8 (1.0) (the depth of conversion is given in parentheses, $\eta_{\Delta m} = \Delta m_t/\Delta m_\infty$, where Δm_t and Δm_∞ are the losses of mass at the *t* moment and at the end of transformation, respectively). It is noteworthy that an increase in $\eta_{\Delta m}$ also results in an increase in $\Delta S_{sp}(\eta_{\Delta m}) = S_{sp}(\eta_{\Delta m}) - S_{sp}{}^0$. For example, ΔS_{sp} = 7.3, 7.1, 8.2, 9.4, 10.2, and 13.5 $m^2\ g^{-1}$ for Δm presented above, respectively.

The results of the OM observations make it possible to distinguish the following main processes occurring in the thermal transformation of crystals **1**:

— the intensity of the color (from blue to brown) of the crystal increases as $\eta_{\Delta m}$ increases, and large crystals are colored more intensely, which testifies to the homogeneous character of the transformation in the bulk crystal;

— the heterogeneous process occurs simultaneously and is manifested most distinctly in the regions of macrodefects (fractures, chips, *etc.*); it develops against the background of the homogeneous process and results in the formation of optically nontransparent golden-brown forms, whose shape is close to a sphere (apparently, this is copper metal);

— the reactivities of crystals **1** differs: both completely decomposed and unchanged initial particles are present along with partially decomposed crystals in the samples studied at early stages of transformation;

— large crystals disperse at $\eta_{\Delta m} \gtrsim 0.3$: the striped structure is manifested, followed by cracking of crystals along the longest facet; the dispersion results in a decrease in the mean size of particles to ~10 μm and is accompanied by an increase in S_{sp} at the depths of conversion mentioned (see above).

At the end of transformation, the decomposition products are optically nontransparent. They have the characteristic copper glance in transmitted light. The specific surface at $\eta_{\Delta m}$ = 1.0 is more than twice as high as $S_{sp}{}^0$.

It should be mentioned that the copper mirror appears at T_{exp} > 160 °C on the surface of the reaction tube in the immediate vicinity of the sample studied.

Kinetic peculiarities of gas evolution upon decomposition of compound 1. The morphologic changes in the solid phase upon thermolysis of crystals **1** are accompanied by gas evolution. The gas evolution kinetics during decomposition of the powder of formate **1** in a self-generated atmosphere at T_{exp} = 120—180 °C has a complex character. At a fixed m_0/V ratio (where m_0 and V are the initial mass of the substance studied and the volume of the reaction vessel, respectively), three regions of change in the transformation rate, $w = d\eta/dt$, can be distinguished, depending on the depth of gas evolution $\eta_{\Delta\alpha}$ ($\eta_{\Delta\alpha} = \alpha_t^\Sigma/\alpha_\infty^\Sigma$, where α_t^Σ and α_∞^Σ are the number of moles of gaseous products yielded per mol of initial substance at moment *t* and at the end of transformation, respectively). These regions are manifested most distinctly at low temperatures (Fig. 1). At the initial stages of gas evolution ($\eta_{\Delta\alpha} \lesssim 0.2$), the rate $w(\eta_{\Delta\alpha})$ drops linearly to the minimum value w_{min} (region 1). The $w(\eta_{\Delta\alpha})$ value increases from w_{min} to w_{max} as $\eta_{\Delta\alpha}$ increases ($0.2 \lesssim \eta_{\Delta\alpha} \lesssim 0.5$) (region 2). Then, after reaching w_{max}, further increase in $\eta_{\Delta\alpha}$ results in decrease in $w(\eta_{\Delta\alpha})$ down to $w(1.0) = 0$ (region 3). The w_{min} and w_{max} values increase as T_{exp} increases, and $\Delta w = w_{max} - w_{min}$ decreases, while $\eta_{\Delta\alpha}(w_{min})$ and $\eta_{\Delta\alpha}(w_{max})$ remain almost unchanged. At $T_{exp} \gtrsim 150$ °C, $w(\eta_{\Delta\alpha})$ drops in the whole range of $\eta_{\Delta\alpha}$ values.

In region 1, the $w(\eta_{\Delta\alpha})$ value changes according to a first-order law. At $m_0/V = 1.3(\pm 0.1) \cdot 10^{-3}$ g cm^{-3}

$$w(\eta) = k_1(\eta_{1\infty} - \eta), \qquad (1)$$

where k_1 and $\eta_{1\infty}$ are constants,

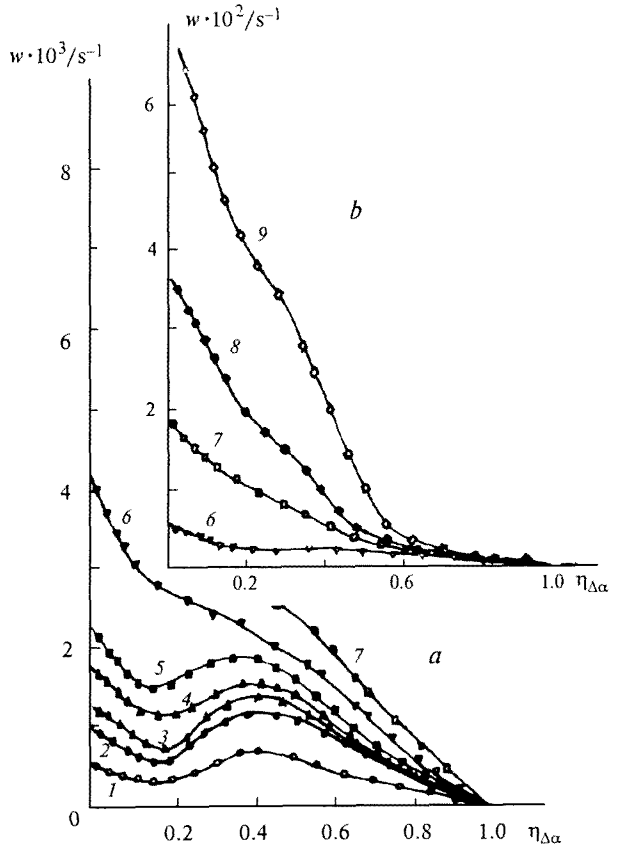

Fig. 1. Dependence $w(\eta_{\Delta\alpha})$ at various T_{exp}/°C: *1*, 120; *2*, 125; *3*, 130; *4*, 135; *5*, 140; *6*, 150; *7*, 160; *8*, 170; *9*, 180 (m_0/V = $(1.31\pm0.01)\cdot10^{-3}$ g cm^{-3}); T_{exp} = 120—150 °C (*a*) and 150—180 °C (*b*).

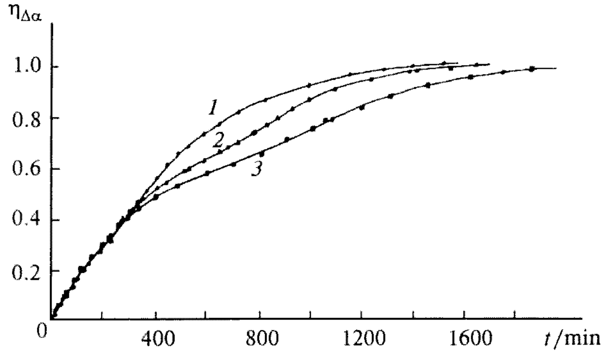

Fig. 2. Dependence $\eta_{\Delta\alpha}(t)$ at T_{exp} = 140 °C and various m_0/V: *1*, $2.25 \cdot 10^{-3}$ g cm^{-3}; *2*, $1.31 \cdot 10^{-3}$ g cm^{-3}; *3*, $0.675 \cdot 10^{-3}$ g cm^{-3}.

$k_1 = 1.3 \cdot 10^{11} \exp[-(33000 \pm 1500)/(RT)]$ s^{-1}, and $\eta_{1\infty}$ = 0.42(±0.03) and is independent of T_{exp}.

In regions 2 and 3, the $w(\eta_{\Delta\alpha})$ value is described satisfactorily by the equation

$$d\omega/dt = k_2(1 - \omega)^2(\omega + \xi_0), \qquad (2)$$

where $\omega = \{\eta - \eta_{1\infty}[1 - \exp(-k_1 t)]\}/(1 - \eta_{1\infty})$; k_2 and ξ_0 are constants, $k_2 = 3.5 \cdot 10^2 \exp[-(12000 \pm 1000)/(RT)]$ s^{-1}, and $\xi_0 = 1.2 \cdot 10^3 \exp[-(8500 \pm 1000)/(RT)]$. Therefore, $w(\omega = 0) = k_2\xi_0 = 4.2 \cdot 10^5 \exp[-20500/(RT)]$ s^{-1}.

At the constant decomposition temperature, the change in the m_0/V ratio within $(0.675-2.25) \cdot 10^{-3}$ g cm^{-3} (Fig. 2) exerts almost no effect on k_1 and $\eta_{1\infty}$ values (T_{exp} = 140 °C: $k_1 = 1.05(\pm 0.06) \cdot 10^{-4}$ s^{-1}, $\eta_{1\infty} = 0.42(\pm 0.02)$). An increase in m_0/V results in an increase in k_2 and a decrease in ξ_0: $k_2 = 2.32 \cdot 10^{-4}$ s^{-1} ($\xi_0 = 5.75 \cdot 10^{-2}$), $1.67 \cdot 10^{-4}$ s^{-1} ($6.5 \cdot 10^{-2}$), and $0.95 \cdot 10^{-4}$ s^{-1} ($10.5 \cdot 10^{-2}$) for $(m_0/V) \cdot 10^3$ = 2.2, 1.3, and 0.675 g cm^{-3}, respectively. Thus, an increase in the m_0/V ratio favors the acceleration of the process in region 2 and indicates the effect of gaseous decomposition products on the rate of decomposition of compound **1**.

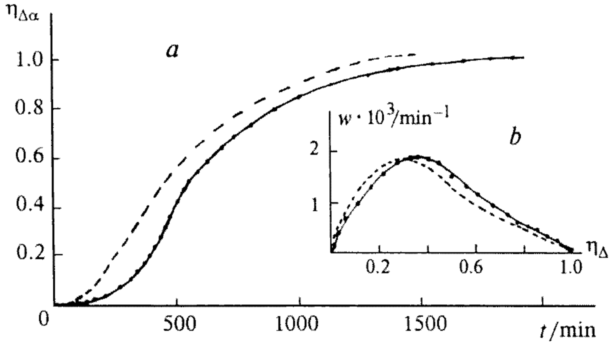

Fig. 3. Dependences $\eta_{\Delta\alpha}(t)$ (*a*) and $w(\eta_{\Delta\alpha})$ (*b*) for a uniform polycrystalline powder of compound **1** with $S_{sp}{}^0$ = 0.8 m^2 g^{-1} at T_{exp} = 140 °C and $m_0/V = 1.31 \cdot 10^{-3}$ g cm^{-3}. The dotted line shows the dependence $w(\omega)$ for a powder of compound **1** with $S_{sp}{}^0$ = 10.5 m^2 g^{-1} for regions 2 and 3.

It should be mentioned that Eq. (2) describes the dependence of the transformation rate on the depth of gas evolution for the thermal decomposition of the uniform-in-size large-crystalline sample with $S_{sp}{}^0$ = 0.8 m^2 g^{-1} (Fig. 3). Comparison under similar conditions (T_{exp} = 140 °C, $m_0/V = 1.31 \cdot 10^{-3}$ g cm^{-3}) of the decomposition rate of this sample with the corresponding dependence $w(\omega)$ obtained for regions 2 and 3 of the thermolysis of the studied polycrystalline powder with $S_{sp}{}^0$ = 10.5 m^2 g^{-1} shows that the k_2 values are close ($2.01 \cdot 10^{-4}$ and $1.67 \cdot 10^{-4}$ s^{-1}, respectively), while the ξ_0 values for the large-crystalline powder are lower ($4.1 \cdot 10^{-3}$ and $6.5 \cdot 10^{-2}$, respectively), and, hence, large-crystalline samples are more thermally stable (see Fig. 3).

The analysis of the results of OM observations and formal kinetic regularities of gas evolution shows that after reaching w_{min} the transformation rate $w(\eta_{\Delta\alpha})$ increases simultaneously with the dispersion of large crystals of **1** ($\eta_{\Delta m} \gtrsim 0.3$ corresponds to $\eta_{\Delta\alpha} \gtrsim 0.2$). It is likely that one of the reasons for increasing $w(\eta_{\Delta\alpha})$ can be the process of accumulation of intrinsic local strains in the decomposing crystal, which finally results in its dispersion. However, this assumption should be specially studied.

For the initial rate of gas evolution during the decomposition of compound **1**, $w_0 = k_1\eta_{1\infty}$, the effective activation energy ($E_{a,eff}$) is 33.0 kcal mol^{-1} (138.0 kJ mol^{-1}) and close to that observed previously for the decomposition of anhydrous copper formate: $E_{a,eff}$ = 28.4±2.4 kcal mol^{-1} (119.0±10.0 kJ mol^{-1})[11] or 29.5 kcal mol^{-1} (123.0 kJ mol^{-1}).[9] For the initial decomposition rate of compound **1** in regions 2 and 3, $w(\omega = 0) = k_2\xi_0$, the $E_{a,eff}$ value is 20.5 kcal mol^{-1} (86 kJ mol^{-1}) and is comparable with that obtained previously for the decomposition of dehydrated copper formate: $E_{a,eff}$ = 21.3 kcal mol^{-1} (89.0 kJ mol^{-1}).[10] It is of interest to note in this connection that the heat effect (Q) of the decomposition of compound **1** to form two HO(O)C$^\cdot$ radicals

$$Cu(HCOO)_2(s) \rightarrow Cu(s) + 2\ HO(O)C^\cdot - Q$$

is 74.0 kcal mol^{-1} (320.0 kJ mol^{-1}), taking into account that $\Delta_f H°[Cu(HCOO)_2(s)]$ = −179.0 kcal mol^{-1} (−750.0 kJ mol^{-1})[20] and $\Delta_f H°[HO(O)C^\cdot(g)]$ = −52.5 kcal mol^{-1} (−219.5 kJ mol^{-1}),[21] or, calculating per HO(O)C$^\cdot$ radical formed, it is 37.0 kcal mol^{-1} (160.0 kJ mol^{-1}). This value is close to the $E_{a,eff}$ value presented above for the decomposition of compound **1** in region 1.

Overall gas evolution and loss of mass by the sample upon decomposition of compound 1. The decomposition of samples **1** under static nonisothermal conditions in a self-generated atmosphere results in the evolution of 1.79—2.72 mol of gaseous products ($\alpha_f{}^\Sigma$) at the end of the transformation. This amount is lower than the maximum possible gas evolution ($\alpha_f^\Sigma = 3.0$) expected for the reaction

$$\mathrm{Cu(HCOO)_2(s) = Cu(s) + H_2 + 2\ CO_2(g)}.$$

At the fixed T_{exp}, an increase in the m_0/V ratio results in a decrease in α_f^Σ. For example, for T_{exp} = 140 °C = const, the following values of α_f^Σ are found: 2.61 ($m_0/V = 0.675 \cdot 10^{-3}$ g cm^{-3}), 2.41 ($1.31 \cdot 10^{-3}$ g cm^{-3}), 2.33 ($2.20 \cdot 10^{-3}$ g cm^{-3}). An increase in T_{exp} at the fixed $m_0/V = 1.31 \cdot 10^{-3}$ g cm^{-3} favors an increase in α_f^Σ (Table 1): $\alpha_f^\Sigma = 0.465 \cdot 10^2 \exp[-2500/(RT)]$. The ratio of condensing ($\alpha_>^\Sigma$) and noncondensing ($\alpha_<^\Sigma$) at 77 K gaseous decomposition products ($\alpha_f^\Sigma = \alpha_>^\Sigma + \alpha_<^\Sigma$) at the end of transformation depends on T_{exp} and m_0/V. However, $\alpha_>^\Sigma > \alpha_<^\Sigma$ in the whole region studied. An increase in T_{exp} at a fixed m_0/V ratio results in an increase in $\alpha_>^\Sigma$ and $\alpha_<^\Sigma$, while an increase in m_0/V at T_{exp} = 140 °C = const decreases these values: $\alpha_>^\Sigma$ and $\alpha_<^\Sigma$ are 1.85 and 0.76 ($m_0/V = 0.675 \cdot 10^{-3}$ g cm^{-3}), 1.75 and 0.71 ($1.31 \cdot 10^{-3}$ g cm^{-3}), 1.70 and 0.63 ($2.2 \cdot 10^{-3}$ g cm^{-3}), respectively.

The loss of mass by the samples of compound **1** at the end of transformation also depends on T_{exp} (see Table 1) and m_0/V. At T_{exp} = 140 °C = const, a decrease in m_0/V results in the increase in $\Delta m/m_0$ from 0.532 to 0.553. At the same time, the $\Delta m/m_0$ at the end of decomposition of compound **1** are somewhat lower than the loss of mass expected for the decomposition of copper formate **1** to copper metal (0.588).

In the course of transformation, the ratio between the gas evolution and the loss of mass by the sample changes. For example, at 160 °C at the beginning of thermolysis (before $\eta_{\Delta\alpha} \approx 0.5$), $\eta_{\Delta m}$ increases linearly as $\eta_{\Delta\alpha}$ increases (Fig. 4):

$$\eta_{\Delta m}\Delta m_\infty/\pi_0 = \Delta m/\pi_0 = 145\eta_{\Delta\alpha},$$

where π_0 is the number of moles of compound **1** in the sample studied before decomposition. At $\eta_{\Delta\alpha} \lesssim 0.5$, the ratio $\eta_{\Delta m}/\eta_{\Delta\alpha} = 1.73 > 1$, which allows one to suppose that the products formed are condensed at room temperature. In fact, at the beginning of decomposition of formate **1**, the liquid phase is formed on "cool" parts of the reaction vessel, which is retained up to the end of transformation and disappears upon evacuation.

Table 1. Effect of T_{exp} at m_0/V = const on the level of gas evolution and loss of mass of the sample of compound **1** at the end of transformation

T_{exp}/°C	α_f^Σ	$\alpha_>^\Sigma$	$\alpha_<^\Sigma$	$\Delta m/m_0$ (%)
120	1.79	1.37	0.42	49.5
125	1.97	1.47	0.50	52.0
130	2.03	1.50	0.53	51.9
135	2.19	1.57	0.61	53.7
140	2.33	1.64	0.61	53.1
	2.35	1.66	0.71	54.2
	2.41	1.74		54.4
150	2.44	1.76	0.68	55.5
160	2.43	1.71	0.72	54.8
170	2.54	1.82	0.72	55.7
180	2.67	1.92	0.74	55.3
	2.71	1.97	0.75	56.2

At $\eta_{\Delta\alpha} > 0.5$ and its further increase, the rate of the change in $\eta_{\Delta m}$ becomes lower than the rate of the change in $\eta_{\Delta\alpha}$.

The specific surface changes rather distinctively in the course of transformation (see Fig. 4). It increases as $\eta_{\Delta\alpha}$ increases, but in the range of $0.2 < \eta_{\Delta\alpha} < 0.5$ the rate of increase in S_{sp} decreases and then at $\eta_{\Delta\alpha} = 0.5$ again increases, which, according to the data of the OM observations, could be caused by dispersion. An increase in S_{sp} at the early stages of decomposition of compound **1** without visible (by OM) change in the habitus of crystals can probably be associated with the development of heterogeneous transformation in the regions of macrodefects. At the end of decomposition of formate **1**, the level of the S_{sp}^f values is two-three times higher than S_{sp}^0 and depends on T_{exp} and m_0/V. For example, at $m_0/V = 1.31 \cdot 10^{-3}$ g cm^{-3}, an increase in T_{exp} results in a decrease in S_{sp}^f from 39.8 m^2 g^{-1} (120 °C) to 16.9 m^2 g^{-1} (180 °C). A decrease in m_0/V at 140 °C results in an increase in S_{sp}^f: 21.0, 26.0, and 41.0 m^2 g^{-1} at $(m_0/V) \cdot 10^3$ = 0.67, 1.31, and 2.20 g cm^{-3}, respectively.

Assuming that the copper metal is the main solid product of the transformation of compound **1** and its particles are spherical, their average size (16—35 nm) was determined on the basis of the data on S_{sp}.

Thus, the decomposition of the polycrystalline powder of anhydrous copper(II) formate at 120—180 °C in a self-generated atmosphere is a complex process from the viewpoint of both the gas evolution kinetics and the morphology of the solid phase, which is affected by T_{exp} and the m_0/V ratio. It is supposed that the increase in the rate of decomposition is associated with the accumulation of intrinsic strains in decomposing crystals of **1**,

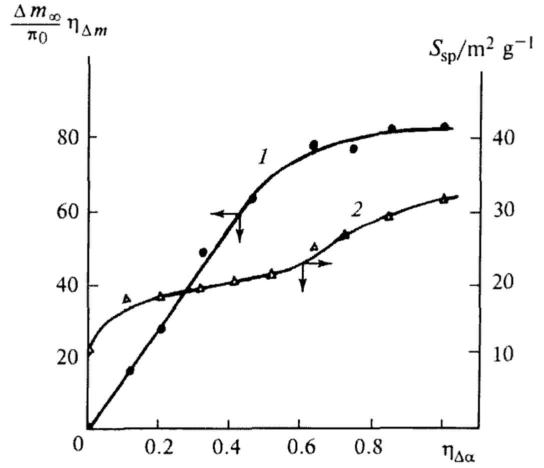

Fig. 4. Dependences of $\eta_{\Delta m}\Delta m_\infty/\pi_0$ (*1*) and S_{sp} (*2*) on $\eta_{\Delta\alpha}$ during thermolysis of compound **1**. T_{exp} = 160 °C, m_0/V = $1.31 \cdot 10^{-3}$ g cm^{-3}.

resulting in their cracking and dispersion in the process of transformation. This hypothesis should be additionally studied by spectroscopy and will be considered in detail elsewhere. The established change in the yield of gaseous and condensed products of decomposition of compound **1** at the end of transformation, depending on the conditions of decomposition (T_{exp}, m_0/V), makes it possible to draw a conclusion that formate **1** can decompose *via* various routes, however, this should be studied additionally.

Experimental

Anhydrous copper(II) formate (**1**) was prepared by the reaction of $Cu(OH)_2 \cdot CuCO_3$ (analytically pure grade) with an excess of formic acid (90 %)[11] followed by recrystallization from formic acid. Found (%): Cu, 40.8. Calculated (%): Cu, 41.4.

Thermal decomposition of compound **1** in a self-generated atmosphere was studied under the static nonisothermal conditions at 120 to 180 °C and $(m_0/V) \cdot 10^3 = 0.675$ to 2.2 g cm^{-3}. The heated part of a reaction vessel with a tube filled with the substance studied did not exceed 0.05 V. Before the experiment, the sample studied was evacuated for 30 min at ~20 °C and $p \approx 10$ Pa.

The kinetics of transformation was studied by the accumulation of gaseous products of decomposition of compound **1** by a membrane null-manometer. After the experiment, the amount of gases evolved at ~20 °C, the amount of gaseous products condensed at 77 K, and the loss of mass of the sample were determined. The specific surface of the solid decomposition products and the initial sample were determined by low-temperature nitrogen adsorption (the BET method[22]).

Optical microscopic observations were performed in transmitted and reflected light on an MBI-15 instrument.

References

1. I. D. Morokhov, L. I. Trusov, and S. P. Chizhik, *Ul'tradispersnye metallicheskie sredy* [*Ultradispersed Metallic Media*], Atomizdat, Moscow, 1977 (in Russian).
2. S. M. Portnova, Yu. I. Krasikov, N. G. Kuznetsov, and I. V. Bakalaeva, *Zh. Neorg. Khim.*, 1990, **35**, 237 [*J. Inorg. Chem. USSR*, 1990, **35** (Engl. Transl.)].
3. T. N. Andrianova, A. I. Khol'kin, A. I. Pol'skikh, and A. V. Chereshkevich, *Zh. Prikl. Khim.*, 1992, **65**, 2429 [*J. Appl. Chem. USSR*, 1992, **65** (Engl. Transl.)].
4. *Fiziko-khimiya ul'tradispersnykh sistem, Dokl. II Vsesoyuz. konf.* [*Physical Chemistry of Ultradispersed Systems, Proc. II All-Union Conf.*], Riga, 1989, 265 (in Russian).
5. D. Dollimore and D. Nicholson, *J. Chem. Soc.*, 1962, 960.
6. D. Dollimore and J. Dollimore, *J. Chem. Soc. A*, 1966, 278.
7. A. Kwiatkowski, *Pr. Inst. Masz. Mat.*, 1972, **14**, No. 1, 5.
8. Yu. I. Khinchenko, V. P. Vasilenko, *et al.*, *Poroshk. Metall.* [*Powder Metallurgy*], 1977, 743 (in Russian).
9. V. P. Kornienko, M. N. Selikhova, and Yu. S. Krasnoperova, *Uch. Zap. Khar'k. Un-ta. Tr. Khim. Fak. i NII Prikl. Khimii* [*Manual of Chem. Dept. and Research Institute of Applied Chemistry of Khar'kov Univ.*], 1957, 82 (in Russian).
10. B. V. Erofeev and L. S. Kravchuk, *Kinet. Katal.*, 1969, **10**, 533 [*Kinet. Catal.*, 1969, **10** (Engl. Transl.)].
11. A. K. Galwey, D. M. Jamirson, and M. C. Brown, *J. Phys. Chem.*, 1974, **78**, 2664.
12. M. Adhikary, M. K. Majumdar, and A. K. Pati, *Fortil. Technol.*, 1976, **13**, 285.
13. I. V. Arkhangel'skii, L. N. Komissarova, and V. R. Felikman, *Koord. Khim.*, 1977, 385 [*Sov. J. Coord. Chem.*, 1977 (Engl. Transl.)].
14. I. V. Fedorova, V. A. Shurov, A. A. Fedorov, and M. S. Gaisinovich, *Zh. Prikl. Khim.*, 1992, **65**, 736 [*J. Appl. Chem. USSR*, 1992, **65** (Engl. Transl.)].
15. G. Diega-Mariadasson and G. Pannetier, *Bull. Soc. Chim. Fr.*, 1971, 3166.
16. V. V. Aleksandrov, V. V. Boldyrev, V. A. Bocharnikov, and V. G. Morozov, *Tez. dokl. Soveshch. po kinetike i mekhanizmu khimicheskikh reaktsii v tverdom tele* [*Abstrs. of Conf. on Kinetics and Mechanism of Chemical Solid State Reactions*], Novosibirsk, 1977, **1**, 133 (in Russian).
17. V. A. Vecher, S. V. Dalidvich, and E. A. Gusev, *Thermochim. Acta*, 1985, 383.
18. A. Gorski and A. Krašnicka, *J. Therm. Anal.*, 1987, 1243.
19. G. Barclay and C. H. Kennard, *J. Chem. Soc.*, 1961, 3289.
20. *Termicheskie konstanty veshchestv* [*Thermal Constants of Substances*], Ed. V. P. Glushko, issues IV, VI, part 1, Izd. AN SSSR, Moscow, 1972 (in Russian).
21. B. Ruscie, M. Schwarz, and J. Berkewitz, *J. Phys. Chem.*, 1989, 6780.
22. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area, and Porosity*, Academic Press, London—New York, 1982.

Received March 21, 1995;
in revised form June 28, 1995