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Obtaining Bismuth (III) Formates through the Interaction of Oxonitrate with Formic Acid Solutions

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Abstract

The paper studied an opportunity of obtaining bismuth formates from solid basic bismuth nitrate by its interaction with formic acid solutions of different concentrations at process temperatures of (22±1) and (55±2) °C. Interaction products of bismuth oxohydroxonitrate having the composition $Bi_6O_4(OH)_4(NO_3)_6 \cdot H_2O$ with formic acid solutions were studied by X-ray phase analysis (XPA), thermogravimetry (TG), electron microscopy, IR spectroscopy, and chemical analysis. It was found that solubility isotherms had two branches driven by the formation of bismuth formates with the composition BiOCOOH and $Bi(COOH)_3$ and proceeded via a maximum at bismuth concentrations in solutions of 31 and 23 g/L at 22 and 55 °C, respectively. An opportunity to obtain bismuth oxide formate was demonstrated through treatment of bismuth (III) formate with water at the mass ratio of water to bismuth formate of 10. Bismuth oxide formate is spherical particles with a size of about 6 μm comprising of smaller crystals, and middle-sized bismuth is needles crystallised as druses with a size of about 100 μm. It was demonstrated that thermal decomposition of basic bismuth formate in air allowed obtaining tetragonal (β) bismuth oxide. It was found that thermal decomposition of a mixture of bismuth oxide formate and oxohydroxynitrate (~50 %) proceeded in several steps, began at 200 °C and completed at 560 °C with the formation of monoclinic (α) bismuth oxide. It was demonstrated that thermal decomposition of a mixture of bismuth oxonitrate/oxoformiate was a promising synthesis method of basic bismuth oxonitrate with the composition $Bi_5O_6(NO_3)_2OH$ or $Bi_5O_7NO_3$.

Key words: bismuth, bismuth oxides, bismuth formates, bismuth oxonitrate, solid-solution system, thermal decomposition

INTRODUCTION

Bismuth carboxylates are used in the synthesis of bismuth-containing oxide materials, such as photocatalysts, gas sensors, in ion conductors, *etc.* In this regard, the development of simple and reliable synthesis methods of these compounds becomes important. Paper [1] noted that known synthesis methods of bismuth formate based on the interaction of bismuth oxide, bismuth carbonate and bismuth metal with formic acid do not ensure significant yields of bismuth formate due to its extremely low solubility in formic acid. The authors of [1] propose carrying out its synthesis by the reaction of bismuth acetate with a 100-fold excess of formic acid. Herewith, one should note that synthesis of initial bismuth acetate is related to the use of such an inaccessible reagent, as acetic anhydride. Indeed, bismuth formate is usually synthesised by dilution of bismuth oxide in formic acid and boiling the solution followed by crystallization of bismuth formate from the resulting solution when its cooling [2–4]. Herewith, the yield of bismuth into the final product is insignificant due to the low solubility of bismuth oxide in formic acid. However, paper [5] demonstrated the possibility in principle of obtaining bismuth formate by the reaction of the solid-solution system resulting from treatment of 2 g of bismuth oxide with 30 mL of a formic acid solution by boiling for 10 min.

Resulting from our studies, it was found that the curve of solubility of bismuth oxide in an aqueous solution of formic acid consisted of two branches due to the formation in the system of formates of the composition $Bi(COOH)_3$ and BiOCOOH, and this process could be used for their preparation. However, one should note that bismuth oxide is obtained by catalytic treatment of bismuth-containing nitric acid solutions of the production of its compounds at 670 °C. This step is related to the release of toxic nitrogen oxides into the atmosphere. In this regard, the study of an opportunity to obtain bismuth formates resulting from the interaction of bismuth oxohydroxonitrate with formic acid solutions is of practical interest.

The purpose of the present work is obtaining bismuth formates by the interaction of bismuth oxohydroxynitrate with formic acid solutions of different concentrations at process temperatures of (22±1) and (55±2) °C.

EXPERIMENTAL

Chemically pure or exceptionally pure ("ch. ch." or "os. ch.") mineral acids, salts and alkalis were used in the work. Initial $Bi_6O_4(OH)_4(NO_3)_6 \cdot H_2O$ was obtained from a solution of bismuth nitrate (420 g/L) during its dilution with water with a 1 : 20 ratio (pH ~ 0.8) at the process temperature of no less than 50 °C. The interaction of bismuth oxonitrate with formic acid solutions was carried out in teflon or glass vessels equipped with stirrers, thermostating of which was carried out in WB-2 water baths. The ratio of the amounts of the initial reagents was 10 g $Bi_6O_4(OH)_4(NO_3)_6 \cdot H_2O$ to 100 ml of solutions of different HCOOH concentrations. The mixture was stirred at (22±1) and (55±2) °C for 3 h. The precipitate was filtered and air dried.

X-ray phase analysis (XPA) of precipitation products was carried out using Bruker D8 Advance diffractometer using CuK_α-irradiation, the rotation speed of a meter is 0.5 deg/min. Initial structural data (lattice parameters and atomic coordinates) are taken from the database of inorganic crystal structures, ICSD (FIZ Karlsruhe, Germany). Infrared absorption spectra were recorded using Infralum FT 801 Fourier-spectrometer in the medium frequency range of 500–4000 cm^{-1} and Bruker Vector 22 in the medium frequency range of 400-4000 cm^{-1}. Samples were prepared as calcined KBr pellets. Thermal analysis (TA) of samples was carried out in STA 449 F1 Jupiter synchronous thermoanalytical complex (Netzsch, Germany) in the dynamic mode at heating in the atmosphere of O_2/Ar (80/20 %). Analysis of gaseous products formed during heat treatment was carried out using QMS 403D quadrupole mass spectrometer (Netzsch, Germany). Electron microscope images of products were obtained using Hitachi TM 1000 scanning electron microscope. Trace amounts of bismuth in solutions were defined photocolorimetrically using sodium iodide [6]. The concentration of the free acid in bismuth-containing solutions was defined by acid-base titration after preliminary masking of bismuth with a chelating agent (III) [7].

RESULTS AND DISCUSSION

Research findings on the interaction of solid bismuth (III) oxohydroxonitrate with formic acid solutions of different concentrations at (22±1) and (55±2) °C demonstrate (Fig. 1) that solubility curves comprise two branches. In the rising part of the curve with increasing the concentration of formic acid is between 1.1 and 3.74 mol/L at process temperature of 22 °C, bismuth concentration in solutions increases from 6.8 to 25.83 g/L, and at process temperature of 55 °C with an increase in

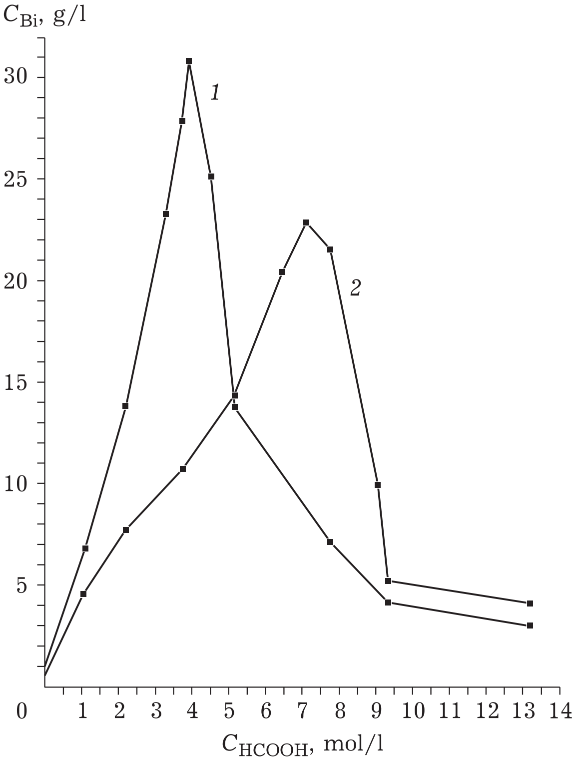

Fig. 1. Concentration of bismuth in a solution C_{Bi} versus the initial concentration of formic acid (C_{HCOOH}) at temperatures of 22 (*1*) and 55 °C (*2*).

the acid concentration from 1.04 to 6.47 mol/L, bismuth concentration in solutions increases from 4.53 to 20.40 g/L. With further increase in the concentration of formic acid, the maximum bismuth concentration in solutions is 30.80 g/L at the process temperature of 22 °C and 22.85 g/L at 55 °C.

The X-Ray diffraction patterns of powders (Fig. 2) obtained in the rising section of the dependence C_{Bi}-CHCOOH with molar ratios of formic acid to bismuth (n) of 3.3–11.3, and a temperature of 22 °C contain reflexes of the initial basic bismuth nitrate ($[Bi_6O_4(OH)_4(NO_3)_6] \cdot H_2O$) and bismuth oxide formate (BiOCOOH). In the decreasing section of the dependence, the bismuth (III) formate ($Bi(HCOO)_3$) was obtained. In the peak region, the precipitate is a mixture of the initial basic bismuth nitrate and bismuth oxide formate. At 55 °C, the curve also has two branches, In the upstream section of the branch, the precipitate is the bismuth oxide formate, and in descending one – bismuth (III) formate.

By XPA data, the intensity of diffraction maxima (see Fig. 2, curve *1*) typical for basic bismuth nitrate ($[Bi_6O_4(OH)_4(NO_3)_6] \cdot H_2O$) decreases with increasing the concentration of formic acid in a solution. Reflexes (see Fig. 2, curve *2*) corresponding to bismuth oxide formate (BiOCOOH) (JCPDS 35-939) appear in X-ray diffraction patterns with increasing acid concentration to 3.74 mol/L, and the precipitate is a mixture of bismuth oxide formate and bismuth (III) formate with n = 13.7 (see Fig. 2, curve *3*). X-ray diffraction patterns of products obtained in the descending section of C_{Bi}–CHCOOH dependence at $n = 15.7$ and higher have diffraction maxima related to bismuth (III) formate (($Bi(HCOO)_3$) (JCPDS 35-936) (see. fig. 2, curve *4*). At 55 °C, the solubility curve has no explicit maximum, the formation of bismuth oxide formate (BiOCOOH) occurs with the acid/bismuth ratio = 3.2–21.6. By XPA data, at $n = 21.6$, the curve passes through a maximum, and the reaction product is bismuth oxide formate (BiOCOOH). With further increasing acid concentration, one could observe x-ray reflexes of bismuth (III) formate in a molar ratio of formic acid to bismuth of 28.3 and above. One should note that bismuth oxonitrate individual compound can be obtained as an individual compound resulting from water processing of medium formate of bismuth at a mass ratio equal of 10 (see Fig. 2, curve 5), or water treatment of a mixture of bismuth oxoformate and bismuth (III) formate.

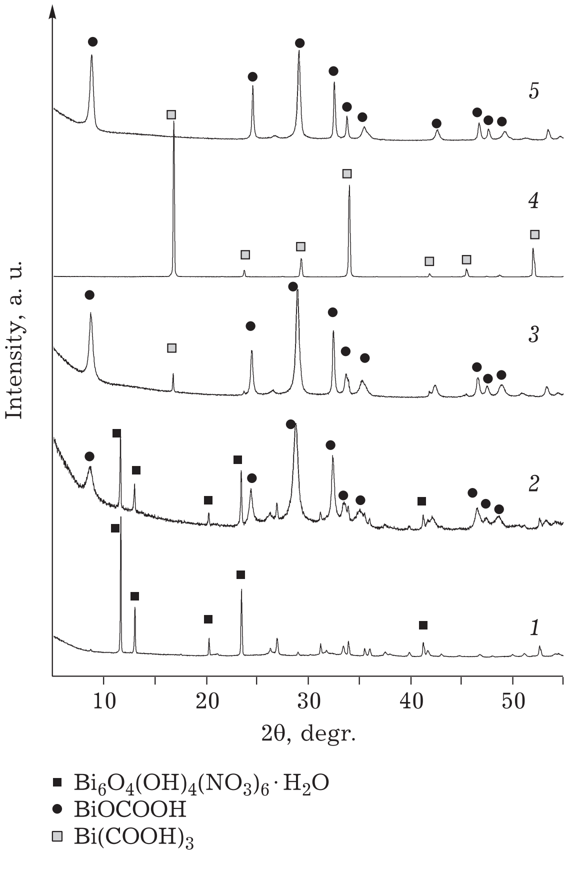

Fig. 2. Diffraction patterns of the initial basic bismuth nitrate (*1*), a mixture of basic bismuth nitrate and bismuth oxide formate (*2*), a mixture of bismuth oxide formate and bismuth (III) formate, (*3*) and bismuth (III) formate (*4*), washed with water (*5*).

Infrared absorption spectra of samples obtained under the interaction of bismuth (III) oxohydroxonitrate and a formic acid solution at 22 °C and a molar ratio of formate ions to bismuth of 3.3 (Fig. 3) for 3 h indicate the beginning of the transition of bismuth (III) oxohydroxonitrate into basic bismuth formate. The spectrum of $[Bi_6O_4(OH)_4](NO_3)_3 \cdot H_2O$ (see Fig. 3, curve *1*) contain bands typical for the nitrate ion with a symmetry not higher than C_{2v} in 1400–700 cm^{-1} region [8, 9]: usually inactive in the IR spectra of the free nitrate ion (D_{3h}), a fully symmetrical valence vibration $\nu_1(A_1)$ appears as a band of medium intensity at 1040 cm^{-1}, a band of medium intensity at 811 cm^{-1} refers to the non-planar deformation vibration $\nu_2(A_2)$, and a weak band with a maximum at 723 and a shoulder at 705 cm^{-1} – to the flat deformation vibration $\nu_4(E)$. A very intense band with two maxima in the 1420–1290 cm^{-1} range corresponds to the antisymmetric valence vibration $\nu_3(E)$ of nitrate groups that take part in hydrogen bonding. Wide diffuse absorption bands in the 3600–3300 cm^{-1} range should be referred to stretching vibrations of crystallization water molecules and OH^- groups that take part in strong hydrogen bonding. A wide band of a small intensity at 1631 cm^{-1} corresponds to deformation vibrations of crystallization water molecules. An intense band with maxima at 565 cm^{-1} may be referred to fan vibrations of water molecules [9]. Vibration bands of initial $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$ in the 1420–1290 cm^{-1} range, at 1040, 811 and 723 cm^{-1}, and also stretching, deformation, and oscillating vibrations of water remain in spectra of a sample obtained resulting from an exchange reaction of bismuth oxohydroxonitrate and a formic acid solution at 22 °C for 3 h (see Fig. 3, curve *2*), and absorption bands relating to the formate ion appear [10]. In spectra of a sample obtained resulting from an exchange reaction of bismuth oxohydroxonitrate and a formic acid solution for 3 h at 55 °C, bands typical for $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$ were not detected, and IR spectra analysis indicate the formation of bismuth oxide formate (see Fig. 3, curve 3). Vibration bands of carboxylate groups appear in its spectra: asymmetric ν_4 as the wide band with a maximum at 1540 cm^{-1} and "shoulders" at 1580 and 1480 cm^{-1} and symmetric stretching vibrations ν_2 at 1335 and 1280 cm^{-1} and symmetric flat deformation vibrations ν_3 at 760 cm^{-1} [10]. There are no bands of stretching vibrations of the carbonyl group that are present in spectra of the initial formic acid in the 1725–1700 cm^{-1} range, which indicates proton substitution in the carboxylic group of the carboxylic acid for the Bi-containing cation [11, 12]. Bands of stretching ν_1, flat ν_5 and non-flat ν_6 deformation vibrations of the C–H bond at 2832, 1384 и 1090 cm^{-1}, respectively, also appear [10]. The relatively wide band of medium intensity at 550 cm^{-1} belongs to stretching vibrations of the Bi–O bond [4].

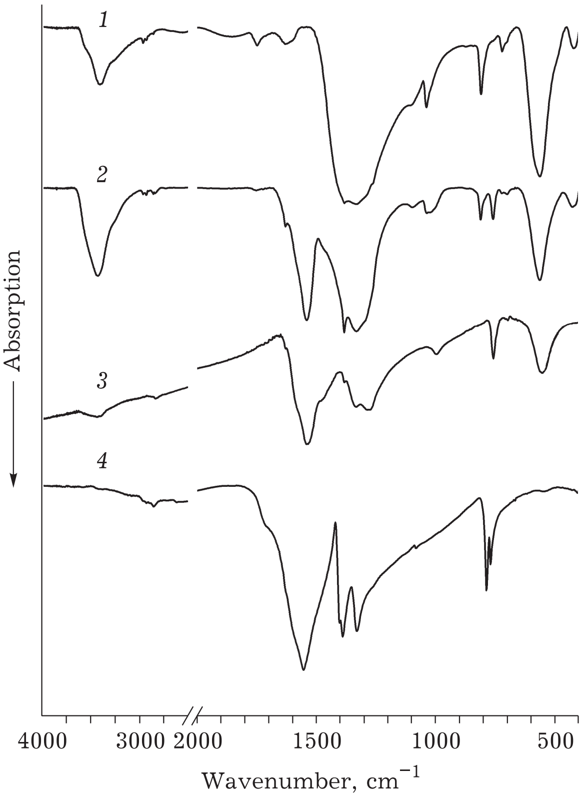

Fig. 3. Infrared absorption spectra of the initial basic bismuth nitrate (*1*), a mixture of the initial basic bismuth nitrate and bismuth oxide formate (*2*), bismuth oxide formate (*3*) and bismuth(III) formate.

Infrared spectra of samples of bismuth (III) formate obtained at $n = 15.7$ and a temperature of 22 °C also contain vibration bands typical for formate ions [10]. Strong bands of stretching asymmetric ν_4 (and 1555 cm^{-1}) and symmetric ν_2 vibrations of carboxylate groups appear at 1332 cm^{-1}. Asymmetric stretching vibrations of carboxylate groups in medium formate light scattering (LS) spectra appear as three bands, which indicates the presence of unequal bonds of the bismuth cation with the carboxylate ligand and proves the structure of this compounds, the former containing three independent formate groups coupled with the bismuth cation via the oxygen atom with bonds of different length [2]. Two bands of symmetric flat deformation vibrations ν_3 at 788 and 771 cm^{-1} also indicate the presence of different carboxylate groups [10]. The difference $\Delta\nu(COO^-) = \nu_4 - \nu_2$ from the IR spectrum of bismuth (III) formate is 247 cm^{-1} [13]. Thus, one may conclude about the bidentate bridging coordination of formate groups in the compound under study [14], as confirmed by the structural data [2]. The bands of stretching ν_1 and ν_6 non-planar deformation vibrations of the C–H bond appear as weak bands at 2853 and 1084 cm^{-1}; a strong band with two maxima at 1403 cm^{-1} and 1391 and corresponds to flat deformation vibrations ν_5 of the C–H bond.

Thermal analysis of the bismuth oxide formate sample obtained resulting from the interaction of basic bismuth nitrate with a formic acid solution in atmospheric Ar-O_2 (20/80 %) indicate the progression of the decomposition reaction in two steps (Fig. 4*a*). The first step consists in the release of water and carbon dioxide during decomposition of bismuth oxide formate in the minimal rate region at a temperature of 220 °C. Only carbon dioxide is released in the second step in the minimum rate region at 330 °C. The step-wise mass loss in the temperature region of 200–340 °C is observed in a TG curve, which indicates the formation of intermediate basic bismuth carbonate that is decomposed with the formation of a β-Bi_2O_3 tetragonal modification. There is product mass increase in the TG curve at 220 °C, which is apparently due to the partial formation of metal

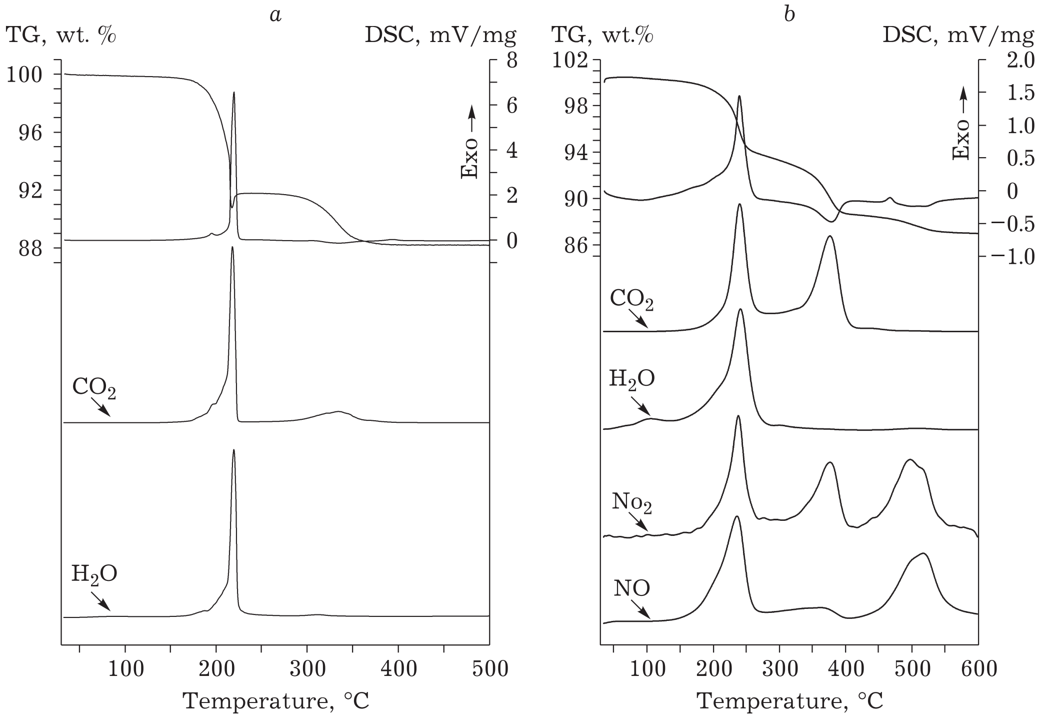

Fig. 4. TG/DSC curves of heating the bismuth oxide formate sample (*a*) and a mixture (50/50 %) of basic bismuth nitrate and bismuth oxide formate (*b*) in the temperature range of 60–600 °C in an atmosphere of O_2/Ar (20/80 %). Recorded mass, *m*/*e*: H_2O^+ 18 CO_2^+ 44, NO^+. 30, and NO_2^+ 46.

bismuth and its oxidation with increasing temperature. The exo-effect at 370–410 °C is driven by a phase transition of tetragonal bismuth oxide into monoclinic α-Bi_2O_3. Hence, the thermal decomposition process of bismuth oxide formate can be used to produce β-Bi_2O_3.

Figure 4, *b* presents the TA curves of a product obtained resulting from incomplete (~50 %) substitution of base bismuth nitrate with bismuth oxide formate. It can be seen that the decomposition process of this mixture proceeds in several steps and is accompanied by the release of water, carbon dioxide and nitrogen oxides. As indicated by X-ray data, the thermal decomposition process is related to the formation of $Bi_5O_6(NO_3)_2OH$ [15] and $Bi_5O_7NO_3$ [16] as intermediates and is completed at 560 °C by the formation of α-Bi_2O_3. Thus, more detailed studies of the thermal decomposition process of base bismuth nitrate and bismuth oxide formate allow selecting preparation conditions for these basic bismuth nitrates as individual compounds.

Electron microscope images indicate that a mixture of the initial compound and bismuth oxide formate as spherically shaped particles of approximately 2 μm in size comprising crystal flakes of 0.1 μm in thickness (see Fig. 5, *b*) is formed during treatment of the initial basic bismuth nitrate monohydrate (Fig. 5, *a*) that is short prismatic crystals of 2–10 μm in size diluted with formic acid solutions (1.1–3.74 mol/L). A mixture of bismuth oxide formate and bismuth (III) formate obtained at 22 °C is spherically shaped aggregates of 3–5 μm in size comprising smaller crystal flakes with the 0.1 μm thickness, and at 55 °C, this is irregularly shaped aggregates that are packed by crystal flakes with a thickness of about 0.1–0.3 μm. Bismuth oxide formate obtained at 55 °C represents 5–7 μm spherical particles comprising irregular shape smaller crystals (see Fig. 5, *c*). Bismuth (III) formate particles obtained at 22 °C are elongated prismatic crystals with a length of 80 μm, and needles with a length of about 50-70 μm crystallized as druses with a size of 80–120 μm are obtained at 55 °C (see Fig. 5 *d*).

CONCLUSION

Thus, a solubility curve has two branches during the interaction of basic bismuth nitrate with formic acid solutions. Bismuth oxide formate (BiOCOOH) is formed in the rising section of the dependence C_{Bi}–C_{HCOOH}, and bismuth (III) formate ($Bi(HCOO)_3$) – in descending. Bismuth oxide formate has been obtained in 92.6 % yield during treatment of basic bismuth nitrate with a 2.2 M

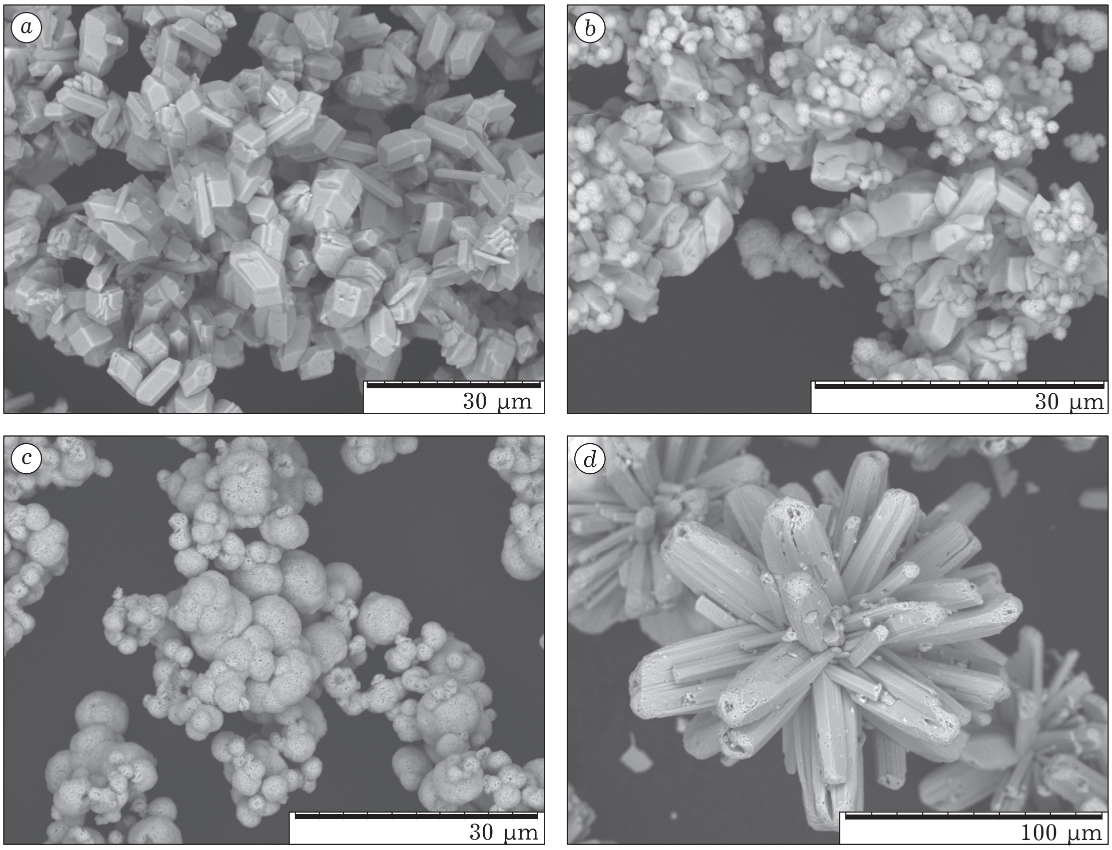

Fig. 5. Photomicrographs of the initial basic bismuth nitrate (*a*), a mixture of basic bismuth nitrate and bismuth oxide formate (*b*), bismuth oxide formate (*c*), bismuth (III) formate (*d*). Temperature, °C *a*, *b* – 22; *c*, *d* – 55.

formic acid solution at 55 °C and a mass ratio of the acid to bismuth of 10, and bismuth (III) formate – in 90.2 %. at 22 °C and acid concentration ≥7.77 mol/L.

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