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Synthesis of High-Purity Bismuth (III) Oxogallate through the Interaction of Oxohydroxobismuth (III) Nitrate Trihydrate with the Solution of Gallic Acid

O. A. LOGUTENKO[1], V. I. EVSEENKO[1], YU. M. YUKHIN[1] and V. A. LOGVINENKO[2]

[1]*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)

E-mail: OLogutenko@solid.nsc.ru

[2]*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)

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Abstract

The interaction of oxohydroxobismuth (III) nitrate trihydrate with the solutions of gallic acid was studied by means of X-ray phase analysis, thermogravimetry, IR spectroscopy and chemical analysis. The effect of temperature of pH of the medium on the rate of the exchange of nitrate ions for gallate ions was studied. The conditions of the formation of bismuth oxogallate trihydrate having the composition $C_6H_2(OH)_3COOBiO \cdot 3H_2O$ were investigated. The reasonability of the synthesis of high-purity bismuth oxogallate through the interaction of oxohydroxobismuth (III) nitrate trihydrate with the solution of gallic acid was demonstrated.

Keywords: bismuth (III) oxogallate, synthesis, IR spectra, thermal analysis

INTRODUCTION

Hydroxybismuth (III) gallate is widely used as a medicinal agent (Dermatol) [1, 2]; it is promising for use as a light-sensitive component of photolayers [3], as well as in the synthesis of bismuth-containing oxide materials. The composition of this compound is usually represented by hydroxogallate $C_6H_2(OH)_3COOBi(OH)_2$ [1, 4–6]. This composition was also given in the pharmacopeia of RF [7]. However, according to the pharmacopoeia of the USA, bismuth (III) hydroxy gallate has the composition $C_6H_2(OH)BiO_2(OH)COOH$ [8], that is, the substitution of two hydrogen ions in the molecule of gallic acid takes place at the phenol hydroxyl groups. The composition of this compound was represented in [9] as $C_6H_2(OH)_3COOBi(OH)_2 \cdot H_2O$.

The synthesis of bismuth (III) hydroxy gallate is usually carried out by adding the solution of bismuth nitrate to the solution of gallic acid heated to 60 °C [4], or the reverse order of reagent addition is used [5], followed by washing the precipitate with water at a temperature of 30–40 °C and drying at 40–50 °C. The method of obtaining bismuth hydroxy gallate by dissolving crystalline bismuth nitrate in diluted acetic acid ($\rho = 1.041$ g/cm^3) and deposition from the solution of bismuth hydroxide by adding ammonia is known. Then the precipitate is separated by filtering, washed, mixed with water; gallic acid is added to the resulting mixture. The synthesis of bismuth hydroxy gallate is carried out under heating with water bath, and then the product is filtered and dried at 60–70 °C [6]. The possibility to synthesize bismuth (III) hydroxy gallate by treating solid bismuth hydroxy carbonate with a small excess of gallic acid in the presence of water until paste is formed was demonstrated; the paste is placed into boiling water and mixed. The product is filtered, washed with water and dried at 30–35 °C [10]. A common disadvantage of the listed synthesis methods is almost complete impossibility to obtain the product of high purity because of the low degree of bismuth purification from accompanying metals.

Bismuth-containing nitrate solutions are usually used to synthesize bismuth compounds. These solutions are prepared by dissolving metal bismuth of Vi 1 grade (major impurities being lead and silver) in the solutions of nitric acid with the concentration 7–9 mol/L. The process is accompanied by the evolution of toxic nitrogen oxides into the gas phase according to reaction [11]

$$Bi + 6HNO_3 = Bi(NO_3)_3 + 3NO_2 + 3H_2O \quad (1)$$

It was shown previously [12] that it is reasonable to obtain bismuth nitrate solutions from the metal by means of preliminary oxidation of metal bismuth adding technical bismuth oxide into the bismuth melt at a temperature of (350±50) °C. As a result, fine crystalline powder with particle size ≤3 mm is formed; therefore, the reaction surface of metal bismuth increases, which allows, at the process temperature increased to (600±50) °C, efficient oxidation of bismuth with atmospheric oxygen according to reaction

$$2Bi_{met} + 3/2O_2 = Bi_2O_3 \quad (2)$$

Preliminary transformation of metal bismuth into its oxide may allow one to decrease the consumption of nitric acid by a factor of 2 and to eliminate the evolution of nitrogen oxides into the atmosphere at the stage of obtaining the solutions of bismuth nitrate, because now the dissolution of the oxide proceeds as follows:

$$Bi_2O_3 + 6HNO_3 = 2Bi(NO_3)_3 + 3H_2O \quad (3)$$

Bismuth deposition from nitrate solutions inevitably brings bout the problem of purification of these compounds from the accompanying metals that may precipitate together with bismuth [11, 13]. We demonstrated previously [14] that efficient purification of bismuth from such major accompanying metals as lead and silver cannot be achieved through the deposition of bismuth hydroxy gallate from nitrate solutions by adding the solution of gallic acid (at a ratio of gallate ions to bismuth in solution 1 : 1, process temperature 60 °C), followed by single washing of the precipitate with nitric acid solution with pH 1 and double washing with distilled water; the concentration of accompanying metals in the final product is 0.20 and 0.015 %, respectively. In this connection, in our opinion, in order to synthesize bismuth hydroxy gallate of high purity, it is reasonable to carry out preliminary purification of bismuth from accompanying metals by bismuth deposition from nitrate solutions in the form of oxohydroxobismuth (III) nitrate trihydrate. The high degree of bismuth purification from accompanying metals during the hydrolysis of nitrate solutions allows a broad use of oxohydroxobismuth (III) nitrate trihydrate for the synthesis of bismuth compounds of high purity according to the solid-to-solution reaction [13].

In the present work, we studied the interaction of oxohydroxobismuth (III) nitrate trihydrate with the aqueous solutions of gallic acid for the purpose of obtaining high-purity bismuth (III) oxogallate.

EXPERIMENTAL

Synthesis of bismuth hydroxy gallate was carried out using metal bismuth of Vi 1 grade, which usually serves as the initial raw material for the synthesis of bismuth (III) compounds of the reagent grade purity. Metal bismuth had the following composition (mass concentration), %: bismuth >97.8, lead 1.2, zinc $2 \cdot 10^{-3}$, iron $3 \cdot 10^{-3}$, antimony $1 \cdot 10^{-3}$, copper $5 \cdot 10^{-3}$, silver 0.06, arsenic $1 \cdot 10^{-4}$, tellurium $1 \cdot 10^{-4}$. Metal oxidation was performed in a reactor made of stainless steel equipped with a screw for melt mixing. The single load of metal bismuth into the oxidation reactor was 150–160 kg; the resulting technical-grade oxide was dissolved in nitric acid of the “ch.” reagent grade with the concentration of 6 mol/L [12].

Oxohydroxobismuth (III) nitrate trihydrate having the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ (with bismuth and nitrate ion content equal to 72.28 and 17.38 %, respectively) was obtained by adding ammonium carbonate solution (2.5 mol/L) to the nitric acid solution of bismuth (380 g/L Bi, 110 g/L HNO_3) until pH about 0.9 was achieved. The precipitate was separated by filtering, washed with distilled water and dried in the air. Weighed 50 g (0.0286 mol) portions of oxohydroxobismuth nitrate trihydrate were treated with 500 mL of the solution of gallic acid prepared by dissolving the acid in distilled water at a temperature of 70 °C. The initial molar ratio of gallate ions to bismuth was 1 : 1. The precipitates were separated by filtering with the help of vacuum, washed with distilled water and dried in the air. Enlarged tests of the synthesis method of bismuth (III) oxogallate were carried out as follows. Into 30 L of deionised water, we added consecutively: 2.05 L of nitric acid ($\rho = 1.3$ g/cm^3), 3.05 kg of bismuth hydroxy nitrate; the reaction mixture was stirred for 15 min. Then 2.0 kg of gallic acid were added gradually to the mixture; stirring for 4 h was carried out. The molar ratio of gallic acid to bismuth was 1.07; the concentration of the free acid was 0.75 mol/L. The mother solution in the amount of 31.8 L with bismuth content of 0.16 g/L was separated from the precipitate by decantation, the precipitate was put onto the nutsche filter, washed with 30 L of deionised water and dried at a temperature of 80 °C.

X-ray phase analysis of the products was carried out with the help of a DRON-3 diffractometer using the CuK_α radiation, the rotation speed of the counter 2 deg/min, $I = 1000$. The curves of differential thermal analysis (DTA) and thermogravimetry, or mass changes (TG) of the samples under investigation were recorded with a MOM derivatograph (Hungary) in the air with the heating rate of 10 °C/min. Studies of the water content of the samples were carried out with a Netzsch derivatograph (Germany) in the atmosphere of helium. The IR absorption spectra (400–4000 cm^{-1}) were recorded with a Specord 75-IR spectrophotometer. The samples were prepared in the form of tablets with calcined KBr. Macroamounts of bismuth (III) in the liquid and solid phases were determined by titrating with the solution of complexon III using xylenol orange as the indicator; micro-amounts were determined by means of photocolorimetry in the presence of potassium iodide or by means of atomic absorption. The products of interaction were preliminarily dissolved in nitric acid (1 : 1). Iodometric titration was used for the quantitative determination of gallate ions [15]. The concentration of nitrate ions was determined photometrically using sodium salicylate [16] after the transfer of nitrate ions into solution as a result of preliminary treatment of the precipitates with sodium hydroxide solution with the concentration 2 mol/L at a temperature of 70–90 °C. The specific surface of the obtained samples was measured suing the chromatographic method of thermal desorption of argon.

RESULTS AND DISCUSSION

Investigation results showed (Fig. 1) that it is necessary to stir the mixture for not less than 25 h at the process temperature of 70 °C for the synthesis of bismuth hydroxy gallate according to the exchange reaction between solid oxohydroxobismuth (III) nitrate trihydrate and the solution of gallic acid. With an increase in the process temperature to 90 °C, the necessary stirring time decreases to 10 h. In this situation, the ratio of galalte ions to bismuth in the precipitate is 1.0, and the ratio of nitrate ions to bismuth does not exceed 0.02, while the concentrations of the acid and bismuth in solution are 0.36 and 0.012 g/L, respectively. However, an increase in the concentration of hydrogen ions in solution to 0.6 mol/L (see Fig. 1, curves *1* and *4*) allows one to substantially accelerate the interaction between oxohydroxobismuth (III) nitrate trihydrate and gallic acid, and to carry out a complete exchange of nitrate ions for gallate ions at a temperature of 70 °C within 3 h.

In this connection, we studied the interaction of oxohydroxobismuth (III) nitrate trihydrate with the solutions of gallic acid at 70 °C depending on pH of the medium. One can see (Fig. 2, curve *2*) that the molar ratio of gallate ions to bismuth in the precipitate increases with an increase in acidity. With the equilibrium concentration of nitric acid in solution, which

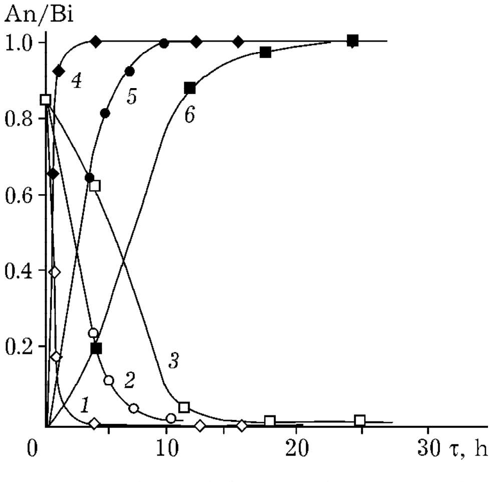

Fig. 1. Dependence of the ratio of nitrate ions (*1–3*), gallate ions (*4–6*) to bismuth in the precipitate on stirring time. Temperature, °C: 90 (*2*, *5*), 70 (*1*, *3*, *4*, *6*); concentration of hydrogen ions, mol/L: 0.36 (*2*, *3*, *5*, *6*), 0.6 (*1*, *4*).

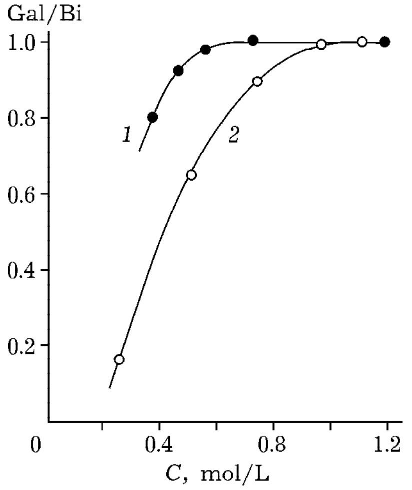

Fig. 2. Dependence of the ratio of gallate ions to bismuth in the precipitate on the concentration of nitric acid in solution. Process temperature 20 (*1*) and 70 °C (*2*); stirring time 1 h.

is approximately 1 mol/L, the moalr ratio reaches 1 : 1 within 1 h, which is the evidence of almost complete substitution of nitrate ions for gallate ions and the formation of bismuth (III) oxogallate according to reaction

$$[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O + 6HGal = 6BiOGal + 5HNO_3 + 5H_2O \qquad (4)$$

We also studied the possibility to synthesize bismuth hydroxy gallate at usual temperature by means of gradual addition of bismuth hydroxy nitrate and the crystals of gallic acid to the solution of nitric acid during mixing. One can see (see Fig. 2, curve *1*) that at the process temperature of 20 °C, mixing time 1 h and hydrogen ion concentration in the system ≥0.5 mol/L, complete substitution of nitrate ions for galalte ions occurs. So, the rate of the exchange of nitrate ions for gallate ions in the reaction between oxohydroxobismuth (III) nitrate trihydrate and gallic acid is essentially dependent on the acidity of the reaction medium, which is due to an increase in the solubility of oxohydroxobismuth (III) nitrate trihydrate with an increase in the concentration of hydrogen ions in solution.

Oxohydroxobismuth (III) nitrate trihydrate having the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ (with monoclinic crystal structure, space group $P2_1/c$) is composed of nitrate ions, water molecules and polycations in which two $[Bi_6O_5(OH)_3]^{5+}$ groups are connected with each other through the symmetry centre by two bridge oxygen atoms [17]. According to the results of X-ray studies (Fig. 3), with an increase in stirring time and consequent decrease in the ratio of nitrate ions to bismuth in the precipitate from 0.84 to ≤0.02 the intensity of the diffraction maxima d/n characteristic of the compound $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$, equal to 13.60, 7.50, 6.73, 3.55, 3.29, and 2.12 Å, decreases sharply. The position of these maxima remains almost unchanged, but the maxima 11.37, 4.52, 3.98, 3.30 and 2.90 Å corresponding to bismuth (III) oxogallate appear in the diffraction patterns. At the process temperature of 70 °C and the concentration of hydrogen ions in solution 0.6 mol/L, the molar ratio of gallate ions to bis-

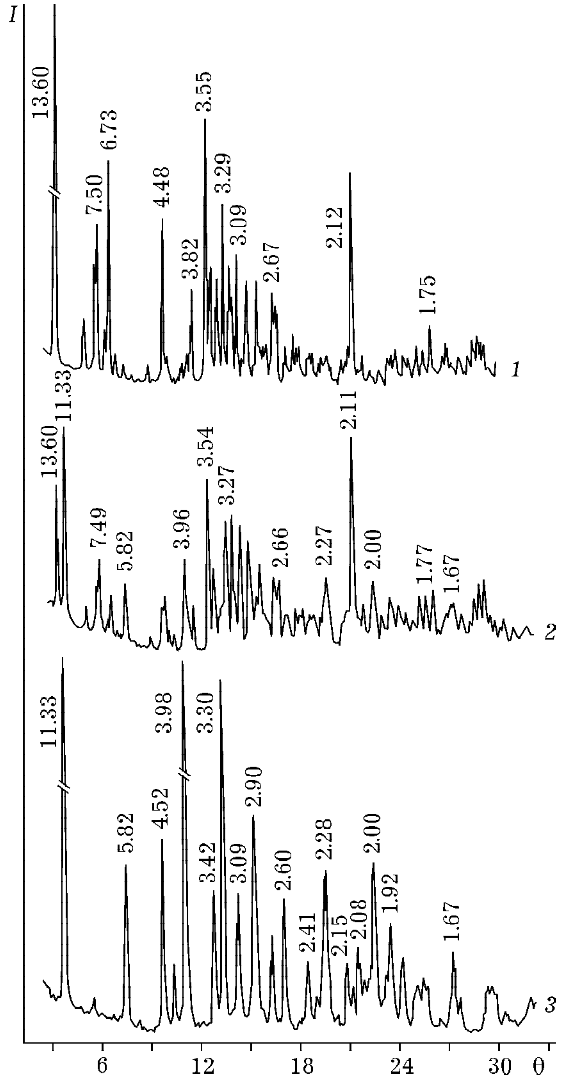

Fig. 3. Diffraction patterns of the samples of oxohydroxobismuth (III) nitrate trihydrate (*1*) and the products obtained as a result of its treatment with the solutions of gallic acid at a temperature of 70 °C for 0.5 (*2*) and 3 h (*3*). *I* is signal intensity, θ is Bragg angle.

muth in the precipitate is euqal to 0.6 : 1 after stirring the mixture for 0.5 h. With an increase in stirring time to 3 h, almost complete substitution of nitrate ions by galalte ions and the formation of bismuth (III) oxogallate are observed (see Fig. 3, curve *3*); in this compound, the molar ratio of gallate ions to bismuth is 1 : 1.

The analysis of the data of IR absorption spectra of the samples (Fig. 4) also provides evidence of the gradual transition from the initial oxohydroxobismuth (III) nitrate trihydrate to bismuth oxogallate with an increase in stirring time. The spectrum of the compound $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ (see Fig. 4, curve *1*) within the spectral range 1400–700 cm^{-1} contains the bands characteristic of nitrate ions with the symmetry not higher than C_{2v} [18]: ν_1 (1040 and 1030 cm^{-1}), forbidden in the IR spectrum of the free NO_3^- ion (D_{3h}), ν_2 (810 cm^{-1}), ν_4 (725 cm^{-1}) and a very intense band with several maxima within the range 1420–1290 cm^{-1} corresponding to the stretching antisymmetrical vibration ν_3 of the free nitrate ion. A broad diffuse absorption band below 3600 cm^{-1} should be attributed to the stretching vibrations of crystal water and OH^- groups participating in strong hydrogen bonds. The band at 1620 cm^{-1} corresponds to the deformation vibrations of the molecules of crystal water. An intense band with the maxima at 600 and 565 cm^{-1} may be attributed to the radial (fan) vibrations of water molecules [19]. The spectrum of the sample obtained at the process temperature of 70 °C, stirring time 30 min and hydrogen ion concentration 0.6 mol/L (see Fig. 4, curve *2*), in addition to a decrease in the intensities of bands corresponding to nitrate ions, exhibits the appearance of absorption bands that may be related to gallate ions.

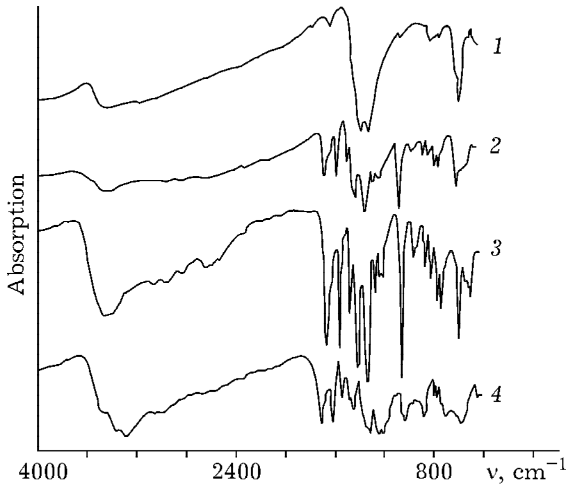

Fig. 4. IR absorption spectra of oxohydroxobismuth (III) nitrate trihydrate samples and the products obtained as a result of its treatment with the solutions of gallic acid at a temperature of 70 °C for 0.5 (*2*) and 3 h (*3*), and gallic acid monohydrate (*4*).

In the IR spectrum of gallic acid monohydrate (see Fig. 4, curve *4*), a broad intense band with the maxima at 3360 and 3280 cm^{-1} and a shoulder at ~3460 cm^{-1} corresponds to the stretching vibrations of crystal water, *meta*- and *para*-phenol groups and the carboxylic group of the acid. Deformation vibrations of phenol groups are characterized by the band at 1375 cm^{-1}. The stretching vibrations of the C=O bond of carboxylic group (ν (C=O)) correspond to the band with the maximum at 1710 cm^{-1}. Weak bands with eth maxima at 3060, 1105 and 970 cm^{-1} are related to the corresponding stretching and out-of-plane deformation vibrations of the C–H aromatic ring [20, 21].

The IR spectrum of bismuth (III) oxogallate (see Fig. 4, curve *3*) does not contain bands characteristic of oxohydroxobismuth (III) nitrate trihydrate. A comparison between the IR spectra of gallic acid monohydrate and bismuth (III) oxogallate (see Fig. 4, curves *3* and *4*) provides evidence in favour of the substitution of protons in carboxylic groups by bismuth cations. For instance, in the spectrum of bismuth (III) hydroxy gallate, the character of absorption in the region of 3600–2000 cm^{-1} changes substantially; only one maximum (3470 cm^{-1}) remains. Instead of the band ν (C=O) 1710 cm^{-1}, an intense asymmetric band ν_{as} of the deprotonated carboxylic group appears; its maximum is at 1620 cm^{-1}. The high value of ν_{as} of carboxylate ions may be due to the high degree of covalence of the oxygen-bismuth band [22]. The appearance of the absorption band at ~940 cm^{-1} in the IR spectrum of bismuth oxogallate in the region of pendular vibrations of crystal water [19] may be the evidence of the presence of H_2O molecules coordinated to bismuth cation in this compound. The band with the maximum at 495 cm^{-1} may be related to the valent bond Bi–O [23].

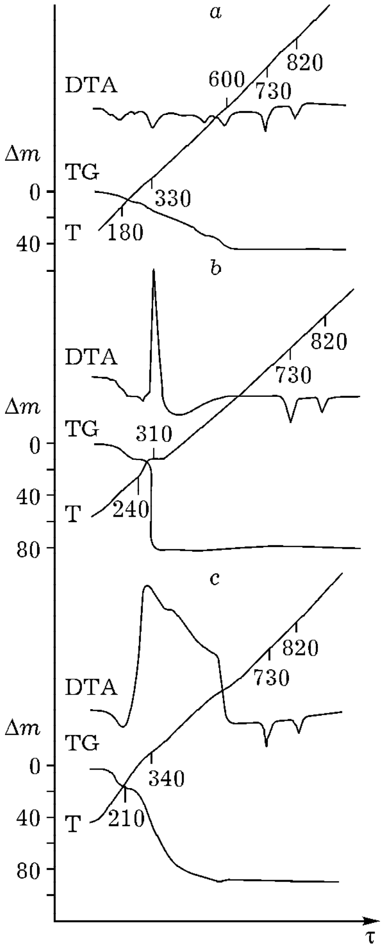

Fig. 5. Derivatograms of oxohydroxobismuth (III) nitrate trihydrate (*a*) and the products obtained as a result of its treatment with the solutions of gallic acid at a temperature of 70 °C for 0.5 (*b*) and 3 h (*c*).

The data of DTA, TG and DTG of the samples of oxohydroxobismuth (III) nitrate trihydrate in the air (Fig. 5, *a*) provide the evidence of the consecutive detachment of three water molecules (endo-effects at 125, 180 and 220 °C). Then, starting from the removal of one water molecule from the inner sphere of the complex (endo-effect at 270 °C), dehydroxylation process starts. The next five endo-effects at 330, 375, 440, 520 and 600 °C are connected with the completion of this process and the destruction of five nitrate ions [13]. The endo-effect at 730 °C is a polymorphous transformation of α-Bi_2O_3 into the high temperature modification δ-Bi_2O_3, while the subsequent endo-effect at 824 °C corresponds to melting of bismuth oxide [24].

The character of the derivatogram of bismuth hydroxy gallate (see Fig. 5, *c*) is likely to be due to the following processes: removal of three water molecules (the endothermal effect at 210 °C), destruction of gallate ions with a sharp exo-effect at 340 °C and the formation of bismuth oxide. It should be noted that bismuth oxide may be synthesized through thermal decomposition of oxohydroxobismuth (III) nitrate trihydrate at 600 °C. Attention should be paid to a sharp decomposition of its mixture with bismuth (III) oxogallate at much lower temperatures (see Fig. 5, *b*), which may be used in the synthesis of fine crystal bismuth oxide because the process may be carried out at low temperatures and thus agglomeration of the product may be avoided. It also follows from the data of thermal analysis (Fig. 6) that the initial mass loss in the compound starts at a temperature of ~60 °C and finishes at ~190 °C. Mass losses are 12.0–12.5 % and are due to the removal of three water molecules from the compound. It is necessary to stress that this process is reversible. The X-ray studies provide evidence that the composition of the sample of bismuth (III) oxogallate kept for 1 day in the air corresponds to the composition of the initial compound.

Our investigations and the data obtained previously on the hydrolytic purification of bismuth from the accompanying metals during deposition from nitric acid solutions allowed us to propose a scheme of the synthesis of bismuth (III) oxogallate trihydrate.

It is reasonable to carry out the synthesis of bismuth (III) oxogallate trihydrate by the interaction of oxohydroxobismuth (III) nitrate trihydrate with the solutions of gallic acid at a

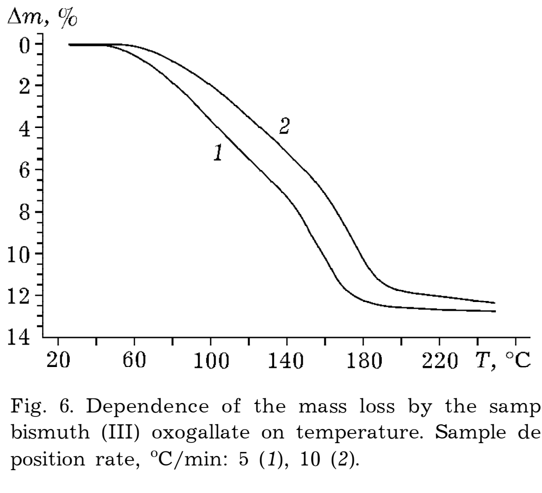

Fig. 6. Dependence of the mass loss by the sample of bismuth (III) oxogallate on temperature. Sample decomposition rate, °C/min: 5 (*1*), 10 (*2*).

molar ratio of gallate ions to bismuth equal to 1.0–1.1, the concentration of the free nitric acid in solution 0.5–1.0 mol/L, and process temperature 20–70 °C. When carrying out enlarged tests, 4.09 kg of bismuth hydroxy gallate was obtained; its composition was as follows (mass concentration, %): bismuth 50.8, lead $1.8 \cdot 10^{-4}$, copper $5 \cdot 10^{-6}$, silver $6 \cdot 10^{-6}$, iron $3.6 \cdot 10^{-4}$, zinc $4.3 \cdot 10^{-5}$, cadmium $3.1 \cdot 10^{-5}$. The degree of bismuth recovery into the product for processing bismuth hydroxy nitrate was 99.9 %, specific surface of the resulting product was 10.4 m^2/g.

CONCLUSION

Thus, it is reasonable to carry out the synthesis of high-purity bismuth (III) oxogallate trihydrate from metal bismuth according to the following route: 1) preliminary oxidation of metal bismuth with atmospheric oxygen; 2) purification of bismuth from accompanying metals by means of its precipitation from nitrate solutions in the form of oxohydroxobismuth (III) nitrate trihydrate, and 3) its transformation into bismuth (III) oxogallate trihydrate by treating with the aqueous solution of gallic acid.

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