Ecologically Safe Method of Obtaining Bismuth (III) Tribenzoate

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Abstract

Precipitation of bismuth (III) benzoates from hydrochloric and nitric solutions depending on the concentration of benzoate ions, process temperature and the concentration of hydrogen ions in solution was studied by means of X-ray phase analysis, IR and Raman spectroscopy, thermogravimetry and chemical analysis. It was established that, depending on synthesis conditions, precipitating compounds can be bismuth oxide benzoate $BiOC_7H_5O_2$ or bismuth tribenzoate $Bi(C_7H_5O_2)_3$. The reasonability to obtain medical bismuth tribenzoate from metal bismuth after its preliminary oxidation with atmospheric oxygen was demonstrated. The formed bismuth oxide is dissolved in nitric acid (1 : 1), and bismuth (III) benzoate is precipitated by adding the bismuth-containing solution to the solution of sodium benzoate at the molar ratio of benzoate ions to bismuth equal to 3.0–3.2, and process temperature (70±10) °C.

Key words: bismuth (III) oxide benzoate, bismuth (III) tribenzoate, synthesis, IR and Raman spectra, thermal analysis

INTRODUCTION

Benzoic acid C_6H_5COOH is present in many plants either in the free form or in the form of esters [1, 2]. Natural benzoic acid and its derivatives play an important part in the interaction of plants with the environment; its biosynthesis includes numerous stages participated by aromatic acids and amines [2]. Benzoic acid possesses antiseptic, antifungal [3, 4] and preservative [5–7] action, it is used in the production of dyes and remedies.

Neutral benzoate, similarly too many other bismuth (III) salts, exhibits anti-infectious, analgesic action on the lymphatic tissue and mucous membranes [8, 9]; it is also promising for obtaining fine powders of metal bismuth and its oxides.

Different compositions of the compounds of bismuth with benzoic acid are described in literature. For instance, a white substance with the assigned composition $(C_7H_5O_2)_6Bi_4O_3$ was obtained after boiling a mixture of bismuth oxide Bi_2O_3 and benzoic acid (9.4 g each of the reagents) with water added [10]. With the help of this method, bismuth tribenzoate and basic benzoate were synthesized; the authors [11] described their compositions as $(C_7H_5OO)_3Bi$ and $C_7H_5OOBi(OH)_2$, respectively. To obtain bismuth tribenzoate, two methods were proposed in [12]. The first one is based on the interaction of bismuth-containing nitrate solution with sodium benzoate, the second one is based on the interaction of bismuth hydroxide with benzoic acid; bismuth hydroxide was obtained preliminarily through the interaction of bismuth nitrate with water. However, the composition of the synthesized compound is not reported in [12]. It is stressed that the treatment of neutral bismuth benzoate with alcohol leads to the removal of the excess benzoic acid with the formation of bismuth sub-benzoate [12].

The authors of [13] proposed a method to obtain neutral bismuth salts. The method is

based on the interaction of bismuth triacetate with the corresponding organic acid, and toluene is used as the solvent. Acetic acid formed as a result of the reaction is removed by distillation. The reaction may be represented in the following form:

$$Bi(OCOCH_3)_3 + 3RCO_2H = Bi(OCOR)_3 + 3CH_3CO_2H$$
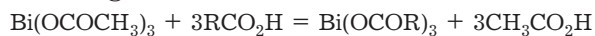
According to these studies, the yield of bismuth tribenzoate is 95 %, its melting point is 293−295 °C. A more detailed description of the synthesis of bismuth tribenzoate from triacetate was described in [9].

The structural studies of bismuth tribenzoate obtained as a result of the exchange reaction between bismuth triacetate and benzoic acid were carried out by the authors of [14]. In [15], the data of powder diffraction patterns of bismuth benzoate having the composition $C_{21}H_{15}BiO_6$ are reported.

So, in the listed methods of the synthesis of bismuth tribenzoate the initial compounds are bismuth oxide, hydroxide or triacetate. The schemes of their synthesis are rather complicated. In addition, the synthesis of bismuth tribenzoate through the interaction of bismuth-containing nitrate solution with sodium benzoate is connected with the dissolution of metal bismuth in nitric acid, which is accompanied by the evolution of nitrogen oxides.

The main industrial method of obtaining bismuth compounds, both with organic and with inorganic anions, is hydrolytic precipitation. To study the compositions of precipitated bismuth compounds, it is reasonable to use perchlorate solutions in which bismuth does not form complexes with perchlorate ions [16]. When diluted with water, unlike for the solutions of bismuth salts in other mineral acids (sulphuric, nitric, and hydrochloric), no formation of the precipitates of mixed bismuth hydroxocomp-lexes containing the anions of mineral acids occurs.

We carried out the investigation of the effect of benzoate ion concentration, process temperature and the concentration of hydrogen ions in solution on the degree of bismuth precipitation from perchlorate and nitrate solutions and the composition of the formed compounds, determined the conditions for the deposition of bismuth (III) tribenzoate. An ecologically sound and practically promising method to obtain bismuth (III) tribenzoate directly from nitrate so-

lutions from the production of bismuth compounds was proposed.

Experimental

Mineral acids, salts and alkalis of "kh. ch." or "os. ch." reagent grade were used in the work. Initial solutions of bismuth perchlorate (900 g/L) and nitrate (420 g/L) were prepared by dissolving bismuth oxide of "os. ch. 13-3" reagent grade in perchloric or nitric acid with the concentration 6 mol/L.

Hydrolytic precipitation of bismuth from solutions was performed in fluoroplastic vessels equipped with mixers; thermostating was carried out with WB-2 water bath. Bismuth benzoates were precipitated from perchloric and nitric solutions by adding the corresponding bismuth-containing solution to the aqueous solution of sodium benzoate or benzoic acid. The volume ratio of the initial and final solutions was 1 : 10, this ratio was corrected by adding distilled water. The mixture was stirred for 1 h. The precipitate was separated by filtering, washed with distilled water, and dried in the air.

X-ray phase analysis (XPA) of the precipitated products was carried out on a DRON-3 diffractometer with CuK_α radiation; a frequency of rotation of the counter was 0.5 deg/min. The curves of differential thermal analysis (DTA) and mass changes (TG) of the samples under investigation were recorded using a MOM derivatograph (Hungary) at the heating rate of 10 °C/min. The IR absorption spectra were recorded with a Specord IR-75 spectrophotometer (400−4000 cm^{-1}). The samples were prepared as tablets in calcined KBr. Raman spectra were recorded on a Bruker FT Raman spectrometer RFS 100/S using a Nd:YAG laser (maximal power: 5 W, laser wavelength 1.064 μm). Electron microscope images of the products were determined using a JEM-2000FXII electron microscope operating at 200 kV. Measurement of solution pH was measured with an OP-264 pH-meter (Hungary). The concentration of free acid in nitric bismuth-containing solutions was determined by means of acid-base titration after preliminary masking of bismuth with the solution of complexon III [17].

Determination of the macro amounts of bismuth was performed by means of titration

with the solution of complexon III, with xylenol orange as the indicator. Microamounts were determined by means of photocolorimetry using sodium iodide [18] and by means of atomic absorption on a Saturn-2M spectrophotometer (LSP-1 hollow-cathode lamp for bismuth, $\lambda = 223.1$ nm, current 30 mA). Precipitated products were transformed into solution by treating with the solution of HNO_3 (1 : 1). Determination of the anions of benzoic acid in the solid reaction products was carried out after their transfer into solution by the preliminary treatment of precipitates with the solution of NaOH 2 mol/L at 70−90 °C. The concentration of benzoate ions in precipitates was determined using photocolorimetry [19]. The concentration of nitrate ions was determined by means of photometry with sodium salicylate [20].

Fig. 1. Dependence of the degree of bismuth (III) precipitation (R) on the molar ratio of benzoate ions to bismuth (n) in perchloric (*1−3*) and nitric (*4−6*) solutions on addition of sodium benzoate (*2−4, 6*) and benzoic acid (*1, 5*). Temperature, °C: 25 (*2, 4*), 70 (*1, 3, 5, 6*).

RESULTS AND DISCUSSION

Investigation of the precipitation of bismuth benzoates from perchloric solutions at a temperature of 25 and 75 °C by adding the solution of sodium benzoate (Fig. 1, curves *2* and *3*) or benzoic acid at 70 °C (curve *1*) showed that the degree of bismuth precipitation depends on the introduced amount of benzoate ions and on process temperature. With an increase in the concentration of benzoate ions and process temperature, the degree of bismuth precipitation (R) increases. With the molar ratio of benzoate ions to bismuth in solution $n = 1.0$ (see Fig. 1), the degree of bismuth precipitation increases to 82.7, 99.9 and 99.9 %, respectively.

Bismuth precipitation from perchloric solutions with the solution of benzoic acid at 70 °C and n varied within the range 0.25 to 4.0 leads to the formation of bismuth tribenzoate precipitates having the composition $Bi(C_7H_5O_2)_3$. For $n = 3.0$, bismuth content of the precipitate is 36.4 % (calculated: 36.5 %), benzoate ions 63.6 % (63.5 %), n in the precipitate is equal to 3.0, the equilibrium pH of solution is 1.1. The diffraction patterns of bismuth tribenzoate contain diffraction maxima with d/n values, Å: 2.71, 2.81, 3.08, 3.25, 3.45, 3.67, 3.96, 4.87, 5.63, 9.71; diffraction maxima related to free benzoic acid with d/n, Å: 2.57, 2.96, 3.21, 3.44, 3.73, 4.19, 4.64, 5.15, 5.45, 10.9 are absent.
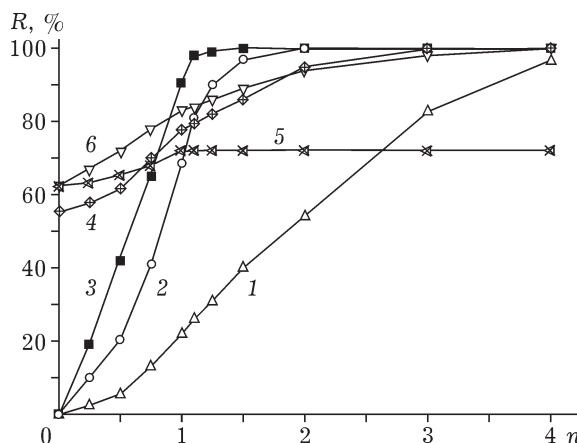
According to the data of chemical analysis of the products of bismuth precipitation from perchlorate solutions with the solution of sodium benzoate at 70 °C and n variation from 0.25 to 4.0 (pH of solution changes correspondingly from 1.3 to 5.2, respectively), the precipitates are composed of bismuth oxide benzoate $BiOC_7H_5O_2$. The precipitates have the following composition, %: bismuth 60.6 (calculated: 60.4), benzoate ions 35.5 (35 %), $n = 1.0$. According to XPA data, the compound is X-ray amorphous. The data of chemical and X-ray phase analyses, IR and Raman spectroscopy provide evidence that the precipitates obtained at 25 °C and different n are also composed of bismuth oxide benzoate.

Adding the nitric solution of bismuth to the solution of benzoic acid heated to 70 °C, with an increase in the molar ratio of benzoate ions to bismuth in the system, the degree of bismuth precipitation increases (see Fig. 1, curve 5). Starting from $n = 1.0$ the degree of bismuth precipitation does not exceed 72.0 %, the acidity of solution is 0.41 mol/L, and it remains almost unchanged with further increase in n. The products of precipitation at $n = 1.0$, according to XPA data, is a mixture of benzoic acid and $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$; it is characterized by diffraction maxima with d/n, Å: 1.73, 2.18, 2.63, 3.29, 3.78, 6.73, 7.55; at $n = 3.0$ the product of precipitation is a mixture of

$Bi(C_7H_5O_2)_3$, $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$ and benzoic acid.

Adding the nitric solution of bismuth to the solution of sodium benzoate at a temperature of 25 and 70 °C with an increase in the molar ratio of benzoate ions to bismuth the degree of bismuth precipitation increases (see Fig. 1, curves *4* and *6*). At 25 °C and $n = 1.0$ the degree of bismuth precipitation is 77.8 %, and the acidity of solution is 0.22 mol/L. Under these conditions, the precipitation product is (according to XPA data) a mixture of benzoic acid and $[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4H_2O$ with diffraction maxima d/n, Å: 1.69, 2.22, 2.39, 2.78, 3.31, 4.11, 4.66, 8.45. An increase in n to 3.0 is accompanied by an increase in the degree of bismuth precipitation to 99.8 % and a decrease in solution acidity to 0.034 mol/L. According to XPA data, the product of decomposition is a mixture of benzoic acid, $Bi(C_7H_5O_2)_3$ and $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ with diffraction maxima d/n, Å: 1.75, 2.12, 2.67, 3.09, 3.29, 3.55, 4.48, 6.73, 7.60, 13.60.

An increase in process temperature to 70 °C leads to an increase in bismuth precipitation degree; for $n = 1.0$ the degree of bismuth precipitation is 83.1 %, the acidity of solution is 0.43 mol/L, and the product is a mixture of $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$ and benzoic acid. For $n = 3.0$, the degree of bismuth precipitation is 98.1 %, the acidity of solution 0.15 mol/L, and the product of precipitation (according to XPA data) is bismuth tribenzoate having the composition $Bi(C_7H_5O_2)_3$, however, the concentration of nitrate ions in the precipitate is 4.70 %. Single washing of the precipitate with water at 70 °C, according to XPA data, has no effect on its composition; the content of nitrate ions in the precipitate decreases to 1.45 %. Washing with the solution of benzoic acid (0.1 mol/L) at 70 °C, followed by washing with distilled water, allows us to purify the precipitate from nitrate ions and decrease their content from 4.70 to 0.067 %. Multiple washing with water at a temperature of 70 °C cause changes in the composition of the precipitate and lead to the formation of bismuth oxide benzoate $BiOC_7H_5O_2$, which is confirmed by the data of IR and Raman spectroscopy, chemical and X-ray phase analyses. Investigation confirmed that bismuth oxide benzoate having the composition $BiOC_7H_5O_2$ can be obtained after washing bismuth tribenzoate $Bi(C_7H_5O_2)_3$ with alcohol at a temperature of 25 °C [12].

The features of the structure of bismuth oxide benzoate (I) and bismuth tribenzoate (II) were revealed through the analysis of IR and Raman absorption spectra. The assignment of characteristic bands in the spectra (Table 1) was made according to literature data for benzoic acid [21–24] and benzoates of other metals [23–26]. In the IR spectra of bismuth benzoates, there are characteristic bands of the stretching vibrations of carbon-carbon bonds of the aromatic ring (1600–1450 cm^{-1}), in-plane (1090–1310 cm^{-1}) and out-of-plane (750–1000 cm^{-1}) bending vibrations of C–H in the cycle. Due to the conjugation of the substituent with the ring [27] usually weak characteristic band in the region 1600–1560 cm^{-1} manifests itself as a band of medium intensity at 1592 cm^{-1} (I, II).

In the IR spectra of the compounds under investigation, instead of the band of stretching vibrations of the carbonyl group $\nu(C{=}O)$ at 1690 cm^{-1}, the bands of stretching vibrations of carboxylate groups appear: asymmetric $\nu_{as}(COO^-)$ at 1530, 1513 cm^{-1} (I) and 1550, 1538, 1525 cm^{-1} (II), and symmetrical $\nu_s(COO^-)$ at 1389 cm^{-1} (I) and 1385, 1356 cm^{-1} (II). This is an evidence of the substitution of protons in the carboxylic group of the acid for Bi-containing cation. The dependence between $\Delta\nu(COO^-) = \nu_{as}(COO^-) - \nu_s(COO^-)$ and the type of coordination of carboxylate group with metal ions is well known [27–29]. In the case of bismuth benzoate, $\Delta\nu(COO^-)$ points to the bidentate coordination of the benzoate ligand in bismuth oxide benzoate, while in the case of bismuth tribenzoate its value is likely to point to the bidentate and bidentate bridging coordination of the ligand [30].

The substitution of protons in the carboxylic group of benzoic acid for Bi-containing cation is also confirmed by the disappearance of the band of scissor vibration $\nu(OH)_{COOH}$ at 1424 cm^{-1} and a weak broad band in the region 2500–3000 cm^{-1} related to the stretching vibrations of $\nu(OH)_{COOH}$, the appearance of a weak band of scissor vibration $\delta_s(COO^-)$ at 855 cm^{-1} (I) and a band of medium intensity at 862 cm^{-1} (II). A band at 452 cm^{-1} appears in the IR spectrum of bismuth tribenzoate; it

TABLE 1

Important vibrational frequencies (cm^{-1}) in the spectra of benzoic acid, bismuth (III) oxide benzoate and tribenzoate, and their assignment

Benzoic acid C_6H_5COOH		Bismuth oxide benzoate $BiOC_7H_5O_2$		Bismuth tribenzoate $Bi(C_7H_5O_2)_3$		Band assignment
IR	RS	IR	RS	IR	RS	
2924−2850 w.	2913−2840 w.	−	−	−	−	$\nu(CH) + \nu(OH)$
2674−2559 w.		−	−	−	−	$\nu(OH)_{COOH}$
1688 s.	1634 s.	−	−	−	−	$\nu(C=O)$
−	−	1530 shoulder	1544 shoulder	1550 shoulder	1553 m.	$\nu_{as}(COO^-)$
		1513 s. sh.	1514 w.	1538 s.sh.	1539 s.	
				1525 shoulder		
1582 m. sh.	1587 m.	1592 m. sh.	1600 s.	1592 m. sh.	1601 s. sh.	$\nu(rings)$
1424 s.	1426 w.	−	−	−	−	$\delta(OH)_{COOH}$
−	−	1389 s. sh.	1406 s.	1385 shoulder	1375 m.	$\nu_s(COO^-)$
				1356 s. sh.	1352 s.	
1292 s.	1289 s.	−	−	−	−	$\nu(C-OH)$
1127 m.	1131 m.	1122 w.	1138 w.	1131 m.	1133 m.	$\nu(C-COO)$
934 s. br.	938 v. s.	−	−	−	−	$\delta_\gamma(OH)_{COOH}$
−	−	855 shoulder	834 m.	862 s. sh.	864 v. s.	$\delta_s(COO^-)$
−	−	820 shoulder	815 shoulder	818 w.	820 m.	$\delta_\omega(COO^-) + \delta_\gamma(CH)$
708 s. sh.	709 v. s.					$\delta(O-C=O)$[24] $\delta_\gamma(rings)$ [23]
		715 s.*		720 s. 715 s. sh.		$\delta_{\gamma s}(COO^-)$ [24] $\delta_\gamma(rings)$ [25]
666 s.		−	−	−	−	$\delta_\gamma(O-C=O)$ [24]
		544 m.		530 m.	532 m.	$\delta_r(COO^-)$
		402 m. br.*	420 m.	452 m.		$\nu(Bi-O)$
431 m.	460 m.	−	−	−	−	$\delta(C-OH)$ [24]

Note. ν − stretching vibration; ν_{as} − asymmetric stretching vibration; ν_s − symmetric stretching vibration; δ − in-plane (flat) bending vibration; δ_s− scissor vibration; δ_r − pendular vibration; δ_γ − out-of-pane bending vibration; $\delta_{\gamma s}$ − symmetric out-of-plane bending vibration; δ_ω − fan vibration; s. − strong; v. s. − very strong; s. sh. − strong sharp; m. − medium; w. − weak; m. br. − medium broad; br. − broad.

*Superposition with δ_γ (of the ring) is possible.

seems to be related to the stretching vibrations $\nu(Bi-O)$ [31].

The replacement of hydrogen atom of the carboxyl group by Bi-containing cation causes characteristic changes also in the Raman spectra of the complexes in comparison with the spectra of initial benzoic acid (see Table 1): the bands of the stretching $\nu(C=O)$ and bending vibrations of the carbonyl group disappear, the bands of asymmetric $\nu_{as}(COO^-)$, symmetric $\nu_s(COO^-)$ vibrations and the band of the bending vibrations of carboxylate ion appear. In the

spectrum of bismuth oxide benzoate, also the band of stretching vibrations $\nu(Bi-O)$ appears at 420 cm^{-1} [32]. The data of IR, Raman spectra and chemical analysis of bismuth benzoates confirm the correctness of the representation of bismuth oxide benzoate as $BiOC_7H_5O_2$ and bismuth tribenzoate as $Bi(C_7H_5O_2)_3$.

The data of DTA and TG of the samples of bismuth benzoate (Fig. 2, *a*, *b*) in the air provide evidence of a number of serial endo- and exothermal stages, confirm the composition and allow verifying the possibility of ob-

taining bismuth oxide through thermal decomposition of its benzoates. The steps on the TG curve correspond to the effects on the DTA curve with the maxima indicated at the temperature curve. The process of thermal decomposition of bismuth tribenzoate (see Fig. 2, b) starts from the partial loss of the ligand (endothermic effect at 300 °C), so bismuth oxide benzoate is formed as the intermediate product. Then thermal decomposition of bismuth oxide benzoate occurs; it is accompanied by the loss of benzoate ions (endothermic effect at 360 °C), their oxidation (exothermal effect at 500 °C) and the formation of bismuth oxide. These processes correspond to the endothermic effect at 380 °C and exothermal effect at 480 °C in the thermogram of initial bismuth oxide benzoate (see Fig. 2, a). One can see that heating
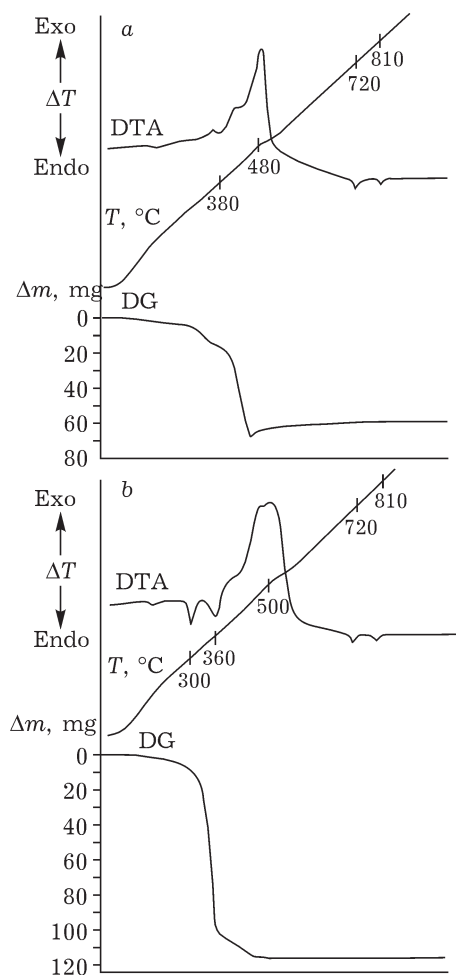
of the samples in both cases finishes with the formation of the monoclinic α-modification of bismuth oxide, which turns during further heating into the cubic face-centred high-temperature modification δ-Bi_2O_3 (endothermic effect at 720 °C), stable till the melting point of the oxide 824 °C [33] (endoeffect in the region 810−850 °C). The calculated mass loss values (65/3 and 118.5 mg) connected with the decomposition of $BiOC_7H_5O_2$ (I) and $Bi(C_7H_5O_2)_3$ (II) to Bi_2O_3 agree with those measured (64.5 (I) and 117.0 mg (II)).

The data of electron microscopic examination provide evidence that the samples of bismuth tribenzoate obtained by precipitation from perchloric solutions at 70 °C by adding benzoic acid are flat extended crystals 2−10 μm wide and 10−20 μm long (Fig. 3, a). Bismuth tribenzoate is also precipitated from nitric solutions as flat extended crystals about 30 μm long and 5−7 μm wide (see Fig. 3, b). The samples of bismuth oxide benzoate obtained by precipitation from perchloric solutions at 25 °C by adding sodium benzoate are aggregates with a size from 2 to 10 μm (see Fig. 3, c) composed of thin plate-like crystals.

For the synthesis of bismuth, it is usual to take bismuth containing nitrate solutions that are obtained by dissolving metal bismuth 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 the reaction

$$Bi_{met} + 6HNO_3 = Bi(NO_3)_3 + 3NO_2 + 3H_2O \qquad (1)$$
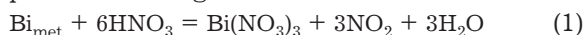
We demonstrated previously [34] that it is reasonable to prepare the solutions of bismuth nitrate from metal bismuth by its preliminary oxidation at a temperature of (600±50) °C with atmospheric oxygen according to reaction

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

Preliminary transfer of metal bismuth into oxide allows one to decrease the consumption of nitric acid by a factor of 2 and eliminate the evolution of nitrogen oxides into the atmosphere at the stage of obtaining the solutions of bismuth nitrate because the reaction of the dissolution of bismuth oxide is

$$Bi_2O_3 + 6HNO_3 = 2Bi(NO_3)_3 + 3H_2O \qquad (3)$$
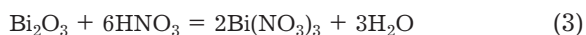
Our investigations and the data obtained by us previously on the oxidation of metal bismuth with atmospheric oxygen into oxide followed by its dissolution in nitric acid (1 : 1) allowed us to
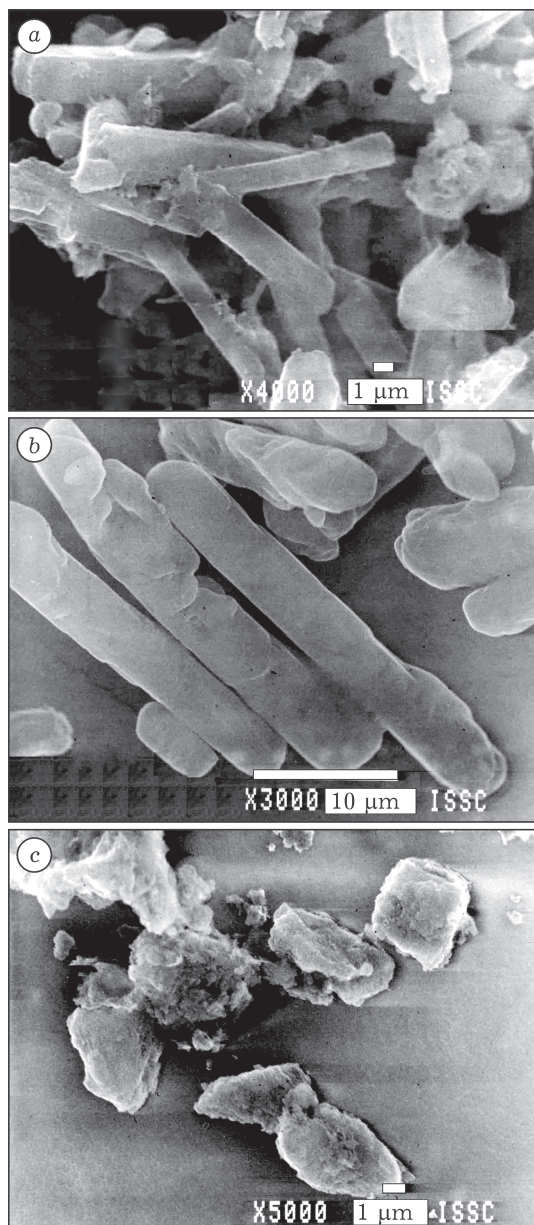

Fig. 2. Curves of thermal analysis of the samples of bismuth (III) oxide benzoate (a) and tribenzoate (b) in the air. Weighed portions: 200 mg.

Fig. 3. Photomicrographs of the samples of bismuth (III) tribenzoate (*a*, *b*) and oxide benzoate (*c*) precipitated from perchloric (*a*, *c*) and nitric (*b*) solutions after the addition of benzoic acid (*a*) and sodium benzoate (*b*, *c*). Temperature, °C: 25 (*c*), 70 (*a*, *b*).

propose the following scheme of obtaining bismuth (III) tribenzoate. Metal bismuth (1 kg) of the composition, mass %: Bi 99.99, Pb $1.2 \cdot 10^{-3}$, Cu $1.0 \cdot 10^{-4}$, Ag $2.0 \cdot 10^{-5}$, Fe $5.0 \cdot 10^{-4}$, Zn $3.0 \cdot 10^{-4}$, Cd $2.0 \cdot 10^{-5}$ was preliminarily transferred into oxide using the procedure described in [34]. Bismuth oxide was dissolved in nitric acid. The results solution (420 g/L bismuth, 62 g/L free nitric acid) was added to the solu-

tion of sodium benzoate (molar ratio of benzoate ions to bismuth $n = 3.1$), process temperature 70 °C). The precipitate was washed two times with the solution of benzoic acid (0.1 mol/L) and once with distilled water. The product was dried at a temperature of 90 °C for 6 h. The resulting bismuth (III) tribenzoate had the composition, mass %: Bi 36.51, Pb $5.0 \cdot 10^{-4}$, Cu $2.0 \cdot 10^{-6}$, Ag $3.0 \cdot 10^{-6}$, Fe $1.0 \cdot 10^{-4}$, Zn $3.0 \cdot 10^{-5}$, Cd $6.0 \cdot 10^{-6}$.

CONCLUSION

Thus, bismuth is precipitated from perchloric solutions with sodium benzoate at the molar ratio of benzoate ions to bismuth equal to 0.25–6.0, and temperature 25–70 °C, in the form of oxide benzoate having the composition $BiOC_7H_5O_2$, while with benzoic acid at 70 °C is precipitates in the form of bismuth tribenzoate $Bi(C_7H_5O_3)_3$. Washing of bismuth tribenzoate with water at 70 °C or with alcohol at 25 °C leads tot eh formation of $BiOC_7H_5O_2$. It is shown that it is reasonable to obtain bismuth tribenzoate through preliminary oxidation of metal bismuth with atmospheric oxygen, followed by the dissolution of bismuth oxide in nitric acid, the addition of the resulting solution to the solution of sodium benzoate at the molar ratio of benzoate ions to bismuth equal to 3.0–3.2, and process temperature (70±10) °C. The advantage of the proposed method is the possibility to obtain bismuth tribenzoate directly from nitric solutions from the production of its compounds excluding the stage of obtaining bismuth oxide, hydroxide or acetate. The method is ecologically safe because the evolution of nitrogen oxides at the stage of the preparation of acidic solutions is successfully avoided.

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