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> INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

## **Precipitation of Bismuth(III) Tartrates from Nitrate Solutions**

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**Abstract**—The precipitation of bismuth(III) from nitrate solutions on addition of aqueous solutions of tartaric acid and sodium tartrate was studied by X-ray phase analysis, thermogravimetry, IR spectroscopy, and chemical analysis. Conditions for the formation of  $[Bi(NO_3)(H_2O)_3]C_4H_4O_6$  and  $[Bi(C_4H_4O_6)(C_4H_5O_6)] \cdot 3H_2O$  were determined.

Bismuth(III) compounds with tartaric acid and its salts are widely used in medicine for treatment of various diseases and also in the synthesis of bismuthcontaining oxide materials [1, 2]. Usually they are prepared by precipitation of bismuth(III) from nitrate solutions with tartaric acid or its alkali metal salts [3]. As the composition of the precipitated products is sensitive to the synthesis conditions [pH of the medium, ratio of tartrate ions and bismuth(III) in the aqueous phase, temperature, etc.], and tartaric acid itself has several donor centers and four labile protons, compounds of various compositions can be formed in these systems. It was shown that bismuth(III) can form the following compounds with tartrate ions:  $BiC_4H_5O_7 \cdot nH_2O$  [3, 4],  $Bi(OH)_2Bi(OH)(C_4H_3O_6)$ [5], and Bi(C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>)(C<sub>4</sub>H<sub>5</sub>O<sub>6</sub>)  $\cdot$  3H<sub>2</sub>O [4, 6]. Reactions of these compounds with solutions of ammonia and of alkali metal hydroxides and acetates yield three-component complex compounds, both insoluble, e.g.,  $C_4H_3O_6BiM$  (M = K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, NH<sub>4</sub><sup>+</sup>) [3],  $[Bi(C_4H_4O_6)_2]NH_4 nH_2O$  [7], and soluble in water, e.g.,  $C_4H_4O_7BiNa$  [3],  $Na(BiO)_2C_4H_3O_6$  and  $Na(BiO)_3C_4H_2O_6$  [8],  $Bi(HC_4H_4O_6)_4$ , and  $Bi(OH)_3$ .  $C_4 H_4 O_6]^{2-}$  [9].

Bismuth(III) compounds are usually synthesized by hydrolytic processing of nitrate solutions obtained by dissolution of metallic bismuth in HNO<sub>3</sub>. Therefore, it is of practical interest to study the precipitation of Bi(III) tartrate from nitrate solutions of the composition similar to that of the process solutions.

In this work, we studied how the concentration of tartrate ions, temperature, and pH affect the degree of Bi(III) precipitation from nitrate solutions, and also the composition and purity of the precipitated products.

Precipitation of Bi(III) was carried out by adding aqueous solutions of sodium tartrate  $C_4H_4O_6Na_2$  or tartaric acid  $C_4H_6O_6$  to a solution of Bi(NO<sub>3</sub>)<sub>3</sub> containing  $(g l^{-1})$ : Bi(III) 440 and free nitric acid 74. The solution of Bi(NO<sub>3</sub>)<sub>3</sub> was prepared by dissolving Vi 00 grade metallic bismuth (no less than 99.98% Bi) in 9 M HNO<sub>3</sub>; its composition corresponded to solutions usually used in the technology of bismuth(III) compounds. The volume ratio of the initial and final bismuth-containing solutions was 1:10; it was adjusted by adding distilled water. The experiments were carried out in fluoroplastic vessels equipped with stirrers. The mixture was stirred for 2 h. After sedimentation for 1 h, the precipitate was filtered off, washed on the filter with distilled water, and dried in air. The X-ray phase analysis of the precipitated products was carried out on a DRON-3 diffractometer using  $CuK_{\alpha}$  radiation (rotation rate of the counter  $0.5 \text{ deg min}^{-1}$ , I = 1000). The DTA and TG curves for the samples under study were taken on an MOM derivatograph (Hungary) at a heating rate of 10 deg min<sup>-1</sup>. The IR absorption spectra in the range 400-4000 cm<sup>-1</sup> were recorded on a Specord IR-75 spectrophotometer. Samples were prepared in the form of pellets with calcined KBr. The electron micrographs of products were taken on a JSMT-20 scanning microscope with a 200 Å resolution. The specific surface area of the samples was measured by thermal desorption of argon, monitored chromatographically. Macroamounts of Bi(III) in the liquid and solid phases were determined by EDTA titration using xylenol orange as indicator, and its microamounts were determined photocolorimerically in the presence of KI. The concentrations of metal ions (Bi, Pb, Ag, Cu, Fe, Zn) were determined by the atomic absorption method on a Saturn 2M spectrophotometer. The precipitated products were



**Fig. 1.** Degree of Bi(III) precipitation *R* as a function of the molar ratio *n* of tartrate ions to Bi(III) in solution. Agents added to a bismuth-containing solution: (1, 2) tartaric acid and (3, 4) sodium tartrate. Temperature, °C: (1, 3) 23 and (2, 4) 60.

preliminarily dissolved in  $HNO_3$  (1 : 1). The concentration of nitrate ions was determined photometrically with sodium salicylate after dissolution of the precipitates by treatment with a sodium hydroxide solution (2 M) at 70–90°C.

The study of the influence of the tartaric acid concentration on the degree of bismuth precipitation R(Fig. 1, curves 1 and 2) shows that, as the concentration of tartrate ions in solution increases, the degree of bismuth(III) precipitation at  $23\pm1^{\circ}$ C first slightly decreases, passes through a minimum at the molar ratio of tartrate ions and Bi in solution n equal to 0.5, and then increases, reaching 98.8% at n = 5. Increased process temperature results in decreased degree of Bi(III) precipitation. The degree of Bi(III) precipitation at  $60\pm1^{\circ}$ C remains constant and independent of tartaric acid concentration up to n = 3, and at higher n the degree of precipitation grows, reaching 91.1% at n = 5.

According to the X-ray analysis (Fig. 2), the basic nitrates  $[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4H_2O$  (23°C) and  $[Bi_6 \cdot$  $O_4(OH)_4](NO_3)_6 H_2O$  (60°C) are formed in the system in the absence of tartrate ions. The X-ray patterns of these compounds (Fig. 2, curves 1, 2) contain the characteristic diffraction peaks: d/n 1.68, 2.11, 2.39, 2.77, 2.82, 3.30, 3.81, and 8.42 Å for the tetrahydrate and 1.51, 1.73, 2.17, 2.50, 2.84, 3.75, 4.31, and 7.37 Å for the monohydrate [10, 11]. The precipitates obtained at the initial molar ratio of tartrate ions and bismuth in solution less than 1 are X-ray amorphous; in this case, Bi(III) seems to be precipitated as a mixture of oxohydroxonitrate and nitratotartrate. At nequal to 1, diffraction peaks with d/n 2.24, 3.72, 5.57, and 10.92 Å are clearly seen in the X-ray patterns of the precipitates (Fig. 2, curve 3). This pattern does not correspond to any of the known bismuth compounds. However, according to the chemical analysis, the samples contain (%) Bi 49.00, C 9.74, H 1.42, and N 2.46; the molar ratio of Bi(III) and tartrate and nitrate ions in the precipitate is 1:1.1:1.2, which suggests that, under these conditions, a compound of the composition  $[Bi(NO_3)(H_2O)_3]C_4H_4O_6$  mainly precipitates. The possibility for its formation was reported in [12].

The precipitates obtained at  $23^{\circ}$ C and *n* no less than 2 and also at  $60^{\circ}$ C and *n* no less than 3 consist of a compound with the composition  $[Bi(C_4H_4O_6)$ .  $(C_4H_5O_6)$ ] 3H<sub>2</sub>O, which contains two different tartrate ligands, (+)-tartrate<sup>-</sup> and (+)-tartrate<sup>2-</sup>. This is confirmed by the X-ray phase and chemical analyses. The diffraction peaks characteristic of this compound  $(d/n \ 1.84, \ 2.15, \ 2.46, \ 3.31, \ 4.36, \ 6.74, \ and \ 9.08 \ \text{\AA})$  [6] are present in the X-ray pattern (Fig. 2, curve 4), and the molar ratio of Bi(III) and tartrate ions in the precipitate is 1:2 (the product contains 37.00% Bi, 17.61% C, and 2.64% H). The orthorhombic crystal structure of this compound (space group  $P2_12_12_1$ ) includes a three-dimensional network with bridging and chelating bonds of polydentate hydroxocarboxylate ligands, and the coordination number of Bi(III) is 4 [6].

The thermal (DTA, TG, DTG) analysis of Bi(III) oxohydroxonitrates and tartrates in air reveals a number of endo- and exothermic stages, demonstrating the possibility of obtaining  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> by thermal decomposition of Bi(III) tartrates. Comparison of the thermograms of the samples obtained by Bi(III) precipitation from nitrate solutions in the absence of tartaric acid (Fig. 3a) and at *n* equal to 1 (Fig. 3b) and 5 (Fig. 3c) shows that the total weight loss increases with increasing n. This is due to an increase in the content of tartrate ions in the precipitated products. The thermal analysis of bismuth(III) oxohydroxonitrate reveals stepwise dehydration, dehydroxylation, and decomposition of nitrate with the formation of Bi<sub>2</sub>O<sub>3</sub> [13]. The thermal decomposition of Bi(III) nitratotartrate starts from water removal (endothermic effect at 100°C) and decomposition of nitrate and tartrate ions (exothermic effects at 130, 240, and 320°C). Bismuth(III) tartrate trihydrate obtained at n = 5 loses weight in two stages: first water is removed (endothermic effect at 140°C), and then tartrate ions decompose with endothermic effects at 270 and 340°C. It is seen from the thermograms that heating of all the samples gives Bi<sub>2</sub>O<sub>3</sub> as the final product. The endothermic effect at 730°C is due to the polymorphous transition of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> into the high-temperature modi-



**Fig. 2.** Diffraction patterns of Bi(III) precipitates obtained from nitrate solutions by adding (1, 2) water and (3, 4) tartaric acid. (*I*) Signal intensity and ( $\theta$ ) Bragg angle. *n*:  $(1, 2) \ 0, (3) \ 1,$  and  $(4) \ 5.$  Temperature, °C: (*I*) 23 and  $(2-4) \ 60.$ 

fication  $\beta$ -Bi<sub>2</sub>O<sub>3</sub>, and the endothermic effect at 820°C is due to melting of Bi<sub>2</sub>O<sub>3</sub> [14]. To transform Bi(III) oxohydroxonitrate into the oxide, it is necessary to calcine it at a temperature of no less than 540±20°C, whereas Bi(III) tartrates can be transformed into the oxide by their thermal decomposition at 320±20°C.

The study of the effect exerted by pH of the medium on the degree of Bi(III) precipitation has shown that, at the molar ratio of tartrate ions and Bi(III) equal to 2.1, 23°C, and the concentration of  $H^+$  ions



**Fig. 3.** Thermograms of Bi(III) precipitates obtained from nitrate solutions by adding (a) water and (b, c) tartaric acid. 23°C; sample weight 200 mg. ( $\Delta m$ ) Weight loss and ( $\tau$ ) time. *n*: (a) 0, (b) 1, and (c) 5.

of 0.073, 0.34, 0.41, 0.61, 1.03, and 1.33 M the concentration of Bi(III) in solution is 20.9, 2.6, 1.0, 2.1, 11.5, and 12.8 g l<sup>-1</sup>, respectively, i.e., the maximal degree of Bi(III) precipitation (97.5%) is reached at the 0.4–0.5 M concentration of hydrogen ions. The concentration of free nitric acid in precipitation of bismuth ditartrate by adding tartaric acid to a solution of Bi(NO<sub>3</sub>)<sub>3</sub> is 0.75 M. To achieve the maximal precipitation, it is necessary to neutralize the solution by adding NaOH or NH<sub>3</sub> · H<sub>2</sub>O. However, the degree of Bi(III) precipitation sharply decreases at the concen-

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**Fig. 4.** IR absorption spectra of (1) tartaric acid, (2) sodium tartrate, (3)  $[Bi(NO_3)(H_2O)_3]C_4H_4O_6$ , and (4)  $[Bi(C_4H_4O_6) \cdot (C_4H_5O_6)] \cdot 3H_2O$ . (A) Absorption and (v) wave number.

tration of free  $HNO_3$  in solution less than 0.3 M, which may be due to formation of soluble tartratecontaining complexes. As the concentration of free  $HNO_3$  in solution increases over 0.6 M, the degree of Bi(III) precipitation as a dihydrate also decreases, and at 1.33 M H<sup>+</sup> it is as low as 70.9%.

The degree of Bi(III) precipitation as a function of the concentration of sodium tartrate is plotted in Fig. 1 (curves 3, 4), which shows that this degree first increases, passes through a maximum at the molar ratio of tartrate ions and Bi(III) of 1.6 (R = 98%), and then sharply decreases, i.e., the precipitate dissolves. Such a pattern is due to the capability of Bi(III) to form water-soluble complexes with tartrate ions. The increase in the sodium tartrate concentration initially results in the precipitation of basic Bi(III) nitrates and tartrates of various compositions. The chemical analysis has shown that the products precipitated at n = 1and 2 contain, respectively (%): Bi 49.7, Na 1.43,  $NO_{3}^{-}$  11.32 and Bi 35.0, Na 6.1 and  $NO_{3}^{-}$  17.13. The sodium-bismuth(III) molar ratio in the precipitate is 0.25 and 1.5, respectively. At n > 2 (23°C) and n > 3(60°C), the degree of Bi(III) precipitation sharply decreases, which is due to formation of water-soluble Bi(HC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>)<sup>-</sup><sub>4</sub> complex ions [9].

The IR absorption spectra of bismuth(III) tartrates were compared to those of tartaric acid and its sodium

salt. The carboxy groups in the IR spectrum of tartaric acid (Fig. 4, curve *I*) give a broad band in the range  $3300-2500 \text{ cm}^{-1}$  corresponding to O–H stretching vibrations of carboxy groups bound in dimers. A band with a maximum at 1720 cm<sup>-1</sup> corresponds to stretching vibrations of the C=O bonds of free carboxy groups. A band with well-defined maxima at 3320 and 3400 cm<sup>-1</sup> corresponds to stretching vibrations of hydroxy groups involved to various extents in the hydrogen bonding.

The IR spectrum of sodium tartrate  $C_4H_4O_6Na_2$ (Fig. 4, curve 2) contains bands of the COO<sup>-</sup> group with C–O bonds of the order 1.5 at 1610 (asymmetric stretching vibrations) and 1410 cm<sup>-1</sup> (symmetric stretching vibrations), indicating the transformation of the carboxy groups to the anionic form. A broad band with several maxima in the range 3560–3200 cm<sup>-1</sup> corresponds to hydroxy groups involved in various hydrogen bonds and to molecular water present in a certain amount in the associated form.

A similar IR pattern is observed with the compound  $[Bi(NO_3)(H_2O)_3]C_4H_4O_6$  obtained at the 1 : 1 molar ratio of tartrate ions and Bi(III) (Fig. 4, curve 3). However, along with the absorption bands of the deprotonated carboxy group (1590 and 1390 cm<sup>-1</sup>), broadened bands in the range 1400–1280 cm<sup>-1</sup> and a pronounced shoulder at 1310 cm<sup>-1</sup> are observed in the spectrum, which most likely originate from the absorption of nitrate ions. A broad band with a pronounced maximum at 3400 cm<sup>-1</sup> is due to the O–H stretching vibrations of water molecules and hydroxy groups of tartrate ions involved in hydrogen bonding.

Similar to the spectrum of tartaric acid, the IR spectrum of bismuth ditartrate (Fig. 4, curve 4) contains, along with the absorption bands of carboxylate groups (1590 and 1390 cm<sup>-1</sup>), also the bands of carboxy groups: a broad band in the range 3200–2400 cm<sup>-1</sup>, which corresponds to the stretching vibrations of OH groups of carboxylic acids involved in hydrogen bonding, and a band at 1720 cm<sup>-1</sup> of the stretching vibrations of the C=O bond in the carboxy group. This spectral pattern is quite consistent with the composition  $[\text{Bi}(C_4H_4O_6)(C_4H_5O_6)] \cdot 3\text{H}_2\text{O}.$ 

The electron micrographs (Fig. 5a) show that Bi(III) nitratotartrates obtained at 23 and 60°C consist of relatively large aggregates of the size from 3 to 40  $\mu$ m, with signs of a block structure. The aggregates consist of smaller crystals. Bismuth(III) ditartrate trihydrate obtained at 23°C consists of oriented intergrown pieces of elongated prismatic (almost needle-like) crystals of the size of about 3–10  $\mu$ m, whereas

crystals of the product obtained at an elevated temperature (60°C) have a size of  $20-60 \ \mu m$  (Fig. 5*c*).

When Bi(III) is precipitated from nitrate solutions by adding a sodium tartrate solution, an X-ray amorphous product is obtained; its aggregates, having a size of 1–5  $\mu$ m, consist of submicrometer X-ray amorphous particles (Fig. 5d). The specific surface areas of sodium tartrates obtained at 23 and 60°C are, respectively, for the nitratotartrate 0.8 and 0.7, for the ditartrate 0.6 and 0.4, and for the sodium-containing tartrate 1.5 and 1.1 m<sup>2</sup> g<sup>-1</sup>, i.e., the specific surface area of Bi(III) tartrates decreases with increasing temperature.

Bismuth(III) compounds are usually synthesized from nitrate solutions starting from Vi-1 grade bismuth which contains Ag and Pb as the main impurities. The Bi(III) tartrate  $[Bi(C_4H_4O_6)(C_4H_5O_6)]$ . 3H<sub>2</sub>O was precipitated by adding tartaric acid to a solution of Bi(NO<sub>3</sub>)<sub>3</sub> at  $23 \pm 1^{\circ}$ C and the 5 : 1 ratio of tartrate ions to Bi(III) in solution. Enlarged tests were carried out with a Bi(III)-containing solution, which was obtained by dissolving Vi-1 grade bismuth containing 0.06 wt % Ag and 1.2 wt % Pb. The mixture was stirred for 2 h and settled. The mother solution containing 0.69 g l<sup>-1</sup> of Bi(III) was separated by decanting. The precipitate of Bi(III) tartrate was washed with one portion of a nitrate solution with pH 1.0 and two portions of distilled water. The resulting Bi(III) tartrate contained (wt %) Pb 0.55, Ag  $1.5 \times 10^{-4}$ , Cu  $2.5 \times 10^{-4}$ , Fe  $1.0 \times 10^{-3}$ , and Zn  $2.5 \times 10^{-4}$ , i.e., the removal of Pb(II) from Bi(III) was inefficient. Therefore, to synthesize high-purity Bi(III) tartrate, it is necessary to use the Vi 00 grade metal (≥99.98% Bi) or to preliminarily remove impurity metal ions by precipitating Bi(III) from nitrate solutions as its oxohydroxonitrate [15]. To remove impurity metal ions from Bi(III), we diluted the initial nitrate solution by a factor of 2 with distilled water and added a 2.5 M solution of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> with stirring to the solution containing 220 g  $l^{-1}$  of Bi(III) and 37 g  $l^{-1}$  of free HNO<sub>3</sub>, until pH of the pulp became 0.9. The precipitate was washed with two portions of distilled water, and the resulting oxohydroxonitrate [Bi<sub>6</sub>O<sub>5</sub>(OH)<sub>3</sub>](NO<sub>3</sub>)<sub>5</sub> · 3H<sub>2</sub>O was dissolved in 6.0 M HNO<sub>3</sub>. The precipitation of Bi(III) ditartrate trihydrate by adding tartaric acid to the resulting solution under the above-mentioned conditions gave a product containing (wt %) Pb  $5.0 \times 10^{-4}$ ; Ag  $3 \times 10^{-6}$ ; Cu  $2 \times 10^{-6}$ ; Fe  $1.0 \times 10^{-4}$ ; Zn  $8 \times 10^{-5}$ ; and Ca, Mg, and Na  $<1.0 \times 10^{-4}$ .



**Fig. 5.** Electron micrographs of (a) nitratotartrate, (b) ditartrate, and (c) sodium-containing tartrate of Bi(III) obtained on adding (a–c) tartaric acid and (d) sodium tartrate to a solution of  $Bi(NO_3)_3$ . Temperature (°C): (a, b, d) 23 and (c) 60.

## CONCLUSIONS

(1) It is appropriate to synthesize the Bi(III) ditartrate  $[Bi(C_4H_4O_6)(C_4H_5O_6)] \cdot 3H_2O$  by its precipitation from bismuth-containing nitrate solutions by adding tartaric acid at the molar ratio of tartrate ions and

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Bi(III) in solution no less than 2,  $H^+$  concentration of 0.4–0.5 M, and temperature of  $22\pm3^{\circ}C$ .

(2) When synthesizing high-purity Bi(III) ditartrate, it is necessary to use high-purity Bi(III), or, if using technical-grade Bi(III), to preliminarily perform hydrolytic purification of bismuth by its precipitation as oxohydroxonitrate.

(3) Bi(III) is precipitated as the nitrotriaquatartrate  $[Bi(NO_3)(H_2O)_3]C_4H_4O_6$  from a solution with the 1 : 1 molar ratio of tartrate ions and Bi(III), whereas the precititation with sodium tartrate gives sodium-containing tartrates.

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