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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Precipitation of Bismuth(III) Oxobromide from Bromide Media

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Abstract—Abstract—X-ray phase analysis, thermogravimetry, IR spectroscopy, and chemical analysis were used to study bismuth(III) precipitation from nitrate solutions upon addition of aqueous solutions of hydrobromic acid or ammonium bromide, and from bismuth-containing hydrobromic acid solutions. The conditions in which bismuth(III) oxobromide of BiOBr composition is formed were determined and the possibility of obtaining a high-purity product was assessed.

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Bismuth oxobromide is used in veterinary medicine [1], in technology for manufacture of piezo-, pyro-, and ferroelectric materials, and in physical development of silver-containing photographic materials [2, 3]. This compound is obtained by dissolving bismuth oxide of reagent-grade purity in hydrobromic acid, with the subsequent dilution of the resulting solution with hot water [4, 5]. A method is known for preparation of bismuth oxobromide, in which a mannitol-containing aqueous solution of bismuth nitrate is reacted with an alkali metal bromide at pH 5.0–5.2 in the presence of a buffer mixture based on urotropin and hydrobromic acid [6].

Bismuth compounds are commonly synthesized from a metal of Vi1 brand (mass fraction of Bi \geq 98%) by dissolution of its grains in 9 M nitric acid, followed by hydrolytic purification of bismuth to remove impurity metals at pH 1.5–2.0 [7]. A disadvantage of this method is in that toxic nitrogen oxides are released into the gas phase in the stage of preparation of bismuth nitrate solutions, because the dissolution process occurs in accordance with the equation

$$Bi + 6HNO_3 = Bi(NO_3)_3 + 3NO_2^{\uparrow} + 3H_2O.$$
 (1)

It has been shown [8] that preliminary oxidation of metallic bismuth with atmospheric oxygen to give a technical-grade oxide makes it possible to reduce the expenditure of nitric acid by a factor of 2 and to eliminate release of nitrogen oxides into the atmosphere in the stage of preparation of bismuth nitrate solutions. This is so because the dissolution process is described in this case by the equation

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

Hydrobromic acid well dissolves bismuth oxide, as also does nitric acid, and the dissolution reaction has the form

$$Bi_2O_3 + 6HBr = 2BiBr_3 + 3H_2O.$$
 (3)

It is of practical interest in this context to study synthesis of bismuth(III) oxobromide directly from solutions produced by dissolution of technical-grade bismuth oxide in nitric or hydrobromic acid.

This communication reports on a study of the influence exerted by the concentration of bromide ions and the process temperature on the purity and degree of bismuth(III) oxobromide precipitation from nitrate and bromide solutions. The metal was oxidized in a stainless steel reactor equipped with a screw for melt agitation. A single batch charged into the oxidation reactor was 150-160 kg. The metal was melted at a temperature of 350° C and bismuth oxide from the preceding stage of oxidation of metallic bismuth was introduced in an amount of 20% into the melt under agitation. The temperature was raised to 600° C and the powder was agitated for 6 h. The technical-grade oxide contained 88.4% bismuth.

Product	Content, %					
	Pb	Cu	Ag	Fe	Zn	Cd
I II III IV	$\begin{array}{c} 1.08 \\ 6.2 \times 10^{-2} \\ 0.22 \\ 4.8 \times 10^{-5} \end{array}$	$\begin{array}{c} 8.7\times 10^{-3}\\ 7.5\times 10^{-4}\\ 7.8\times 10^{-4}\\ 1.0\times 10^{-6}\end{array}$	$\begin{array}{c} 5.0\times 10^{-2}\\ 3.0\times 10^{-3}\\ 9.0\times 10^{-3}\\ 2.0\times 10^{-6} \end{array}$	$5.6 \times 10^{-3} \\ 1.0 \times 10^{-3} \\ 5.2 \times 10^{-4} \\ < 1.0 \times 10^{-4}$	$\begin{array}{c} 5.8\times 10^{-4}\\ 2.0\times 10^{-5}\\ 1.2\times 10^{-5}\\ 1.0\times 10^{-5} \end{array}$	$\begin{array}{c} 27\times10^{-3}\\ 5.0\times10^{-5}\\ 3.6\times10^{-5}\\ 5.0\times10^{-6} \end{array}$

Hydrolytic processing of technical-grade bismuth oxide I to give oxobromides II-IV

Its composition (I) in terms of impurity metals is presented in the table.

A bismuth(III) nitrate solution containing 380 and 110 g l⁻¹ of Bi(III) and free nitric acid, respectively, was prepared by dissolving technical-grade oxide in 6 M nitric acid. The composition corresponded to that of solutions commonly used in the technology of bismuth compounds. A bismuth(III) bromide solution containing 385 g l⁻¹ of bismuth and 70 g l⁻¹ of free hydrobromic acid was obtained by dissolving technical-grade bismuth(III) oxide in 7 M hydrobromic acid. The volume ratio between the starting and final bismuth-containing solutions was 1 : 10. Upon addition of hydrobromic acid or an ammonium bromide solution to the bismuth nitrate solution, it was adjusted by addition of distilled water.

The bismuth-containing bromide solution was processed by its dilution with distilled water (1 : 9). This was done in glass vessels with the use of stirrers. The mixture was agitated for 20 min. After settling for 0.5 h, the precipitate was filtered off with the use of a vacuum, washed on the filter with distilled water, and dried in air. An X-ray phase analysis (XPA) of the precipitation products was made on a DRON-3



Fig. 1. Degree *R* of bismuth(III) precipitation from a nitrate solution vs. the molar ratio *n* between bromide ions and bismuth(III) in the system. Process temperature (°C): (1) 22 and (2) 90.

diffractometer with $\operatorname{Cu}_{K_{\alpha}}$ radiation, counter rotation rate of 0.5 deg min⁻¹, and I = 4000. Curves of differential thermal analysis (DTA) and thermogravimetry (TG) were measured for the samples under study on an MOM derivatograph (Hungary) at a heating rate of 10 deg min⁻¹. Electron microscopic images of the products were obtained using a JSMT-20 scanning electron microscope with a resolution of 200 Å. The specific surface area of the samples obtained was measured by the chromatographic method of thermal desorption of argon. Macroscopic amounts of bismuth(III) in the liquid and solid phases were determined by titration with a solution of Complexon III, with Xylenol Orange as indicator, and microscopic amounts, by photocolorimetry in the presence of KI. The concentrations of metals (Pb, Ag, Cu, Fe, Zn) were determined by the atomic-absorption method on a Saturn 2M spectrophotometer. The precipitation products were preliminarily dissolved in nitric acid (1:1). The concentration of nitrate ions was found by voltammetry on a renewable copper electrode [9], and that of bromide ions, on a silver electrode, after being transferred to solution by preliminary treatment with a sodium hydroxide solution (2 M) at $70-90^{\circ}$ C.

The study of the hydrolytic processing of bismuthcontaining bromide solutions demonstrated that, upon their dilution with distilled water (1:9), the degree of bismuth(III) recovery into oxobromide at 25 and 65°C is 97.9 and 96.5%, respectively. In precipitation of bismuth(III) from nitrate solutions by addition of a hydrobromic acid solution, the dependence of the degree R of metal precipitation on the molar ratio nbetween bromide ions and bismuth in solution passes through a maximum at 1.0-1.1 (Fig. 1). In this case, the degree of bismuth(III) precipitation is 99.4%. The decrease in the degree of bismuth(III) precipitation at n > 1 is due to the formation of bromide com-plexes of the type BiBr_x^{3-x} in solution [11], which hinders bismuth precipitation in the form of oxobromide. It can also be seen in Fig. 1 that raising the process temperature has virtually no effect on the degree of bismuth(III) recovery into a precipitate. It should be noted that solutions of both hydrobromic acid and ammonium bromide can be used for quantitative precipitation of bismuth(III). With ammonium bromide used as a donor of bromide ions, the degree of bismuth recovery into the precipitate somewhat increases to become 99.6% at n = 1.0.

Bismuth oxobromide has clearly pronounced diffraction peaks at d 8.10, 4.05, 3.52, 2.82, 2.77, 1.96, and 1.61 Å (Fig. 2) [12]. It follows from the results of X-ray studies that, in bismuth precipitation from nitrate solutions to which bromide ions were added, the positions of these peaks remain virtually unchanged, irrespective of the nature of the solutions used (Fig. 2, curve 1). This confirms that bismuth precipitates from these solutions as the oxobromide BiOBr in the pH range under study (0-3). X-ray studies also demonstrate that bismuth(III) precipitation from bromide solutions upon addition of water to these solutions depends both on the process temperature and on the order in which reagents are introduced. At a process temperature of 22°C and addition of a bismuth bromide solution to water, the Xray pattern of the product corresponds to bismuth oxobromide (Fig. 2, curve 2). If, however, water is added to a bismuth bromide solution (Fig. 2, curve 3) or the process is performed at an elevated temperature (90°C) (Fig. 2, curve 4), an additional reflection appears in the X-ray diffraction patterns at d = 6.32 Å. As a result of washing of these products with water, this reflection disappears. An analysis demonstrated that the washing solution contains hydrogen ions and bromide ions. This indicates that, in bismuth precipitation from bromide solutions (ratio between bromide ions and bismuth equal to 3.8), the product can capture hydrobromic acid, which can be removed in the stage of product washing with water.

DTA and TG data for bismuth oxobromide samples obtained by processing of nitrate solutions (Fig. 3a) indicate that the product is stable in a wide temperature range. On heating of bismuth oxobromide, the loss of mass begins at temperatures higher than 600°C, which is due to sublimation of bismuth in the form of bromide to give oxobromides with a Bi: Br molar ratio exceeding unity [13]. In the case of samples obtained by bismuth precipitation from bromide solutions (Fig. 3b), the loss of mass begins at 250°C and is complete at 300°C. In this case, the loss of mass is 6.3% for a product obtained upon addition of water to a bismuth-containing solution at a process temperature of 22°C and 2.7% in the case of a reverse order of addition of the reagents. When synthesis is performed at 90°C, the loss of mass by the product upon



Fig. 2. X-ray diffraction patterns of bismuth oxobromides obtained by precipitation from (1) nitrate solutions and (2-4) bromide solutions, with (2, 4) a bismuth solution added to water and (3) water added to a bismuth solution. (1) Intensity and (2θ) Bragg angle. Temperature (°C): (1) 65, (2) 22, and (4) 90.



Fig. 3. Thermograms of bismuth oxobromides obtained by precipitation from (a) nitrate and (b) bromide solutions and (c) of bismuth oxobromide formed by thermal treatment of the product at 300°C. Sample mass 300 mg. (Δm) Loss of mass and (τ) time.

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calcination is 6.7% in both cases. A chemical analysis of a product calcined at 300°C and kept in air for 10 days demonstrated that this product is pure bismuth oxobromide (its thermogram is shown in Fig. 3c). It should be noted here that the product obtained from bromide solutions has a yellowish tint, which disappears upon washing with water or calcination at 300°C.

Analysis of IR absorption spectra of bismuth oxobromides obtained by precipitation from both nitrate and bromide solutions, and of the same oxobromides calcined at 300°C, shows that all these spectra contain in the spectral range under study $(400-4000 \text{ cm}^{-1})$ only a single band associated with symmetric stretching vibrations of the Bi–O bond (510 cm⁻¹) of the A_{2u} type.

According to the results of electron-microscopic studies of hydrolysis products, bismuth oxobromide produced by precipitation from nitrate and bromide solutions has in all cases, irrespective of the order in which reagents are poured-in, the form of aggregates composed of thin-lamellar oval microcrystals with a size of $0.3-3 \,\mu\text{m}$ in the basal plane and a thickness of about 0.1 µm. On washing with water, the morphology of the initial microcrystals remains virtually unchanged. The specific surface areas of bismuth(III) oxobromides obtained at 22 and 65°C from nitrate solutions are 1.7 and 1.3 $m^2 g^{-1}$, respectively, and of those formed at 22 and 90°C from bromide solution tions, 1.9 and 1.2 $m^2 g^{-1}$. The order of introduction of the reagents has virtually no effect on the specific surface area of the product. In the case of washing with water of a bismuth oxobromide having a specific surface area of 1.2 m² g⁻¹, it increases to $3.0 \text{ m}^2 \text{ g}^{-1}$, and upon calcination at 300°C, decreases to $1.0 \text{ m}^2 \text{g}^{-1}$. A product with a specific surface area of 23 $m^2 g^{-1}$ was obtained by bismuth precipitation from dilute $[20 \text{ g } \text{l}^{-1} \text{ Bi(III)}]$ bromide solutions.

In order to synthesize bismuth(III) oxobromide of increased purity, the possibility of its purification to remove basic impurity metals in precipitation from bromide media was assessed. A processing of bismuth-containing bromide solutions diluted with water (1 : 9) at a process temperature of 65°C, with the subsequent washing of the precipitate with water at $65 \pm 5^{\circ}$ C and drying of the product at 100°C, yielded bismuth(III) oxobromide whose composition (II) is listed in the table. The results of an analysis of the product obtained indicate that processing of bismuth-containing bromide solutions does not involve effective purification of bismuth to remove lead, silver, and iron. In this context, the possibility of obtaining bismuth

oxobromide from nitrate solutions commonly used in synthesis of bismuth compounds was analyzed. Precipitation of bismuth(III) from nitrate solutions in the form of an oxobromide at a molar ratio between bromide ions and bismuth equal to 1.05, as well as its precipitation from bromide solutions, fails to provide effective purification of bismuth to remove lead and silver [see table, composition (III)].

Precipitation of bismuth from nitrate solution in the form of a compound of composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$ enables its effective purification to remove impurity metals. This process is used to synthesize special-purity bismuth(III) oxide [14]. Therefore, in order to obtain high-purity bismuth oxobromide, it is advisable to preliminarily purify bismuth nitrate solutions to remove associated metals by precipitation of bismuth in the form of an oxo hydroxonitrate, followed by its dissolution in nitric acid.

In view of the aforesaid, the variant of bismuth oxobromide synthesis by precipitation from nitrate solutions was chosen for larger-scale tests. An additional advantage of this process is that it yields solutions more concentrated in terms of bismuth in the stage of dissolution of the technical-grade oxide and enables use of stainless steel apparatus employed in synthesis of other bismuth compounds. Metallic bismuth of the Vi1 brand was used in the tests.

High-purity bismuth(III) oxobromide was synthesized by its precipitation from a bismuth nitrate solution upon addition of a hydrobromic acid solution at a molar ratio between bromide ions and bismuth equal to 1.05 and a process temperature of 65° C. The precipitate was twice washed with distilled water at 65° C and dried at 100°C. The tests yielded bismuth(III) oxobromide containing (%) 68.54 bismuth, 26.21 bromide ions, and less than 1×10^{-3} nitrate ions. The contents of impurity metals in product (IV) are listed in the table. The degree of bismuth recovery from the technical-grade oxide into oxobromide is 90.3%.

CONCLUSIONS

(1) Bismuth(III) is virtually completely precipitated as an oxobromide of composition BiOBr from bromide solutions upon their dilution with water and from nitrate solutions upon addition of bromide ions.

(2) The product obtained in processing of bromide solutions may contain hydrobromic acid, which is removed by washing of the product with water or its calcination at 300°C.

(3) To obtain high-purity bismuth oxobromide from technical-grade products, it is necessary to preliminarily purify bismuth to remove associated metals by its precipitation from nitrate solutions in the form of a compound of composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$.

REFERENCES

- 1. Polyvyannyi, I.R., Ablanov, A.D., and Batyrbekova, S.A., Vismut (Bismuth), Alma-Ata: Nauka, 1989.
- Yukhin, Yu.M. and Mikhailov, Yu.I., *Khimiya vismutovykh soedinenii i materialov* (Chemistry of Bismuth Compounds and Materials), Novosibirsk: Sib. Otd. Ross. Akad. Nauk, 2001.
- Dolgikh, V.A., Kholodkovskaya, L.N., and Popovkin, B.A., *Zh. Neorg. Khim.*, 1996, vol. 41, no. 6, pp. 970–975.
- 4. *Handbuch der praparativen anorganischen Chemie*, Bd. 3, von Brauer, G., Huber, F. et al., Eds., Stuttgart: Ferdinand, 1981.
- 5. Gmelins Handbuch der anorganischen Chemie, 8 Auflage, Wismut, Weinheim Bergstr: Chemie, 1964.

- 6. USSR Inventor's Certificate, no. 1116011.
- Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie veshchestva* (Pure Chemical Substances), Moscow: Khimiya, 1974.
- Yukhin, Yu.M., Daminova, T.V., and Smirnov, V.I., *Khim. Interesakh Ustoich. Razv.*, 1999, vol. 7, pp. 745–749.
- 9. Aleksandrova, T.P. and Kletenik, Yu.B., *Zh. Anal. Khim.*, 1994, vol. 49, pp. 615–619.
- 10. Kletenik, Yu.B., Tarasova, V.A., and Bek, R.Yu., *Zh. Anal. Khim.*, 1987, vol. 42, pp. 891–896.
- Fedorov, V.A., Kalosh, T.N., Shmyd'ko, L.I., and Mironov, V.E., *Zh. Neorg. Khim.*, 1972, vol. 17, no. 8, pp. 2089–2095.
- 12. JCPDS-International Center for Diffraction Data, 1995.
- Nurgaliev, B.Z., Popovkin, B.A., and Stefanovich, S.Yu., *Zh. Neorg. Khim.*, 1983, vol. 28, pp. 2207–2211.
- Yukhin, Yu.M., Mikhailov, Yu.I., Afonina, L.I., and Podkopaev, O.A., *Vysokochist. Veshch.*, 1996, no. 4, pp. 62–71.