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## SUBSALTS OF BISMUTH.

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The successful preparation of various subsalts of lead by the action of the vapor of methyl iodide upon lead suboxide<sup>1</sup> has suggested that this method might also lead to definite results, if applied to the suboxides of other elements, *e. g.*, bismuth.<sup>2</sup> Moreover, it has already been established by the author<sup>3</sup> that salts of bismuth, of a lower stage of oxidation than the trivalent, can exist in aqueous solution.

## Preparation of Bismuth Suboxide.

Bismuth suboxide (BiO) has been described by various workers<sup>4</sup> but it was Tanatar who first brought forward definite evidence of the chemical identity of this substance, his work being subsequently confirmed by Herz and Guthmann.<sup>5</sup> In the following work a slight modification of Tanatar's method was introduced.

The basic oxalate of bismuth, prepared according to Tanatar's method,<sup>2</sup> was decomposed in the apparatus already used by the author for the preparation of lead suboxide and subsalts.<sup>3</sup> With the aid of a 3-fall Sprengel pump for removing the gases formed during the decomposition, about 2 g. of oxalate could be converted into the suboxide in 6 to 8 hours at 250–260°. The suboxide retained small quantities of carbon dioxide very tenaciously, while at very low pressures the suboxide shows a tendency to lose oxygen. This is borne out in the following experiments.

|                                  |      |      |      |      |      |      |
|----------------------------------|------|------|------|------|------|------|
| Temperature, ° C.....            | 260  | 270  | 265  | 260  | 265  | 265  |
| Duration of the decomp., hours.. | 8    | 10   | 10   | 18   | 36   | 48   |
| Bi, %.....                       | 90.7 | 91.7 | 91.8 | 93.1 | 95.3 | 95.5 |
| Bi in BiO, calc. = 92.8%.        |      |      |      |      |      |      |

In making the suboxide as a preliminary step in the preparation of bismuth subsalts, the decomposition was never allowed to proceed longer than 8 hours, nor was the pressure allowed to fall sufficiently low to cause the removal of oxygen. The traces of carbon dioxide left behind in the suboxide were found to be completely eliminated during the subsequent treatment with the vapor of methyl iodide.

It is noteworthy that all samples prepared in this way were spontaneously oxidized on exposure to the air except those which approached pure bismuth in composition.<sup>2,5</sup>

## Preparation of Bismuth Subsals.

About 2 g. of the basic oxalate was mixed with about 4 times its weight of silica or of powdered glass, not too fine in grain. This was necessary

<sup>1</sup> *J. Chem. Soc.*, **111**, 29 (1917); **113**, 249 (1918); **115**, 109 (1919).

<sup>2</sup> Tanatar, *Z. anorg. Chem.*, **27**, 437 (1901).

<sup>3</sup> Denham, *J. Chem. Soc.*, **93**, 835 (1908).

<sup>4</sup> Schneider, *Pogg. Ann.*, **96**, 130 (1855). Heinz, *ibid.*, **63**, 55 (1844).

Weber, *ibid.*, **107**, 596 (1859). Berthelot, *J. Pharm.*, **14**, 616 (1829).

<sup>5</sup> Herz and Guthmann, *Z. anorg. Chem.*, **53**, 64 (1907).

to prevent caking, and not to keep down the temperature of the reaction as in the case of lead subiodide already described.<sup>1</sup> The apparatus used in the preparation of the subsalts of lead was again adopted without alteration, nor did any material change in the method of procedure prove necessary. After the formation of an approximately pure suboxide, about 10 cc. of pure methyl iodide was introduced into the distillation vessel, and the distillation begun at a temperature of 260–262°. Extreme difficulty was experienced in bringing the reaction between methyl iodide and the suboxide to completion. Generally, after an hour's distillation the evolution of gas entirely ceased. This should indicate that the reaction is at an end, but examination of the cooled reaction vessel showed that in nearly all cases the reaction was incomplete at this stage, the product being dark red and obviously heterogeneous. A further distillation at the original temperature gave a renewed evolution of gas, this often lasting another hour. In order to take advantage of this renewed reactivity conferred upon the reaction mixture by cooling, the distillation was carried out in two stages. Five cc. of methyl iodide was distilled through the suboxide at 260–262°, the duration of the distillation being about an hour. The reaction vessel was then cooled to room temperature, and then slowly raised again to the original temperature of distillation. An additional 5 cc. was then distilled through the reaction mixture. In some cases it was necessary to subject the reaction mixture to a yet further distillation. As it had already been established that at temperatures above 262° methyl iodide oxidizes lead subiodide<sup>1</sup> to the normal iodide, no distillation tests were carried out above this temperature. At the completion of the distillation, the distillate was cooled by liquid ammonia, the apparatus partly evacuated, the vessel containing the distillate sealed off, and the apparatus completely evacuated by means of the Sprengel pump.

**Products of the Reaction.**—As a result of the distillation the following products were isolated. (1) The reaction vessel contained roughly 2 g. of a non-volatile, brick-red powder which appeared perfectly homogeneous under the microscope. (2) Just outside the oven there appeared bright red crystals of considerable volatility. (3) The distillate was yellow whereas in the corresponding case of lead subiodide it was colorless. On admitting air into the distillate a pale yellow solid separated, the methyl iodide at the same time decolorizing.

**The Product in the Reaction Vessel.**—This non-volatile, brick-red substance was found to be perfectly stable in dry air. Analysis of this compound gave the following results.

These results agree closely with the calculated percentages for the basic subiodide,  $2\text{BiI}_2 \cdot 3\text{BiO}$ . It is of interest at this stage to note that the distillation of methyl iodide over bismuth trioxide under similar conditions leads to the formation of bismuth oxyiodide, a reddish compound, the

|       | Bi.<br>%. | I.<br>%. | O (by difference).<br>%. |
|-------|-----------|----------|--------------------------|
|       | 64.9      | 31.3     | 3.8                      |
|       | 64.8      | 31.7     | 3.5                      |
|       | 65.2      | 31.7     | 3.1                      |
|       | 64.8      | 31.9     | 3.3                      |
|       | 65.0      | 31.5     | 3.5                      |
| Mean  | 64.9      | 31.6     | 3.5                      |
| Calc. | 64.9      | 31.8     | 3.3                      |

analysis of which indicates the formula  $\text{BiOI}$  or  $\text{BiI}_3 \cdot \text{Bi}_2\text{O}_3$ . The percentage of bismuth in 2 samples of this oxyiodide was found to be 58.96 and 59.00 (calc. 59.28).

Bismuth sub-oxyiodide is non-volatile even at  $300^\circ$ . On being heated in the absence of air to a temperature of  $350^\circ$  and above, the reddish subsalt becomes dark and patchy, and does not regain its former homogeneity on cooling. Presumably, decomposition into metal and a basic tri-iodide has occurred. A saturated aqueous solution of this sub-oxyiodide gives, after filtration, a barely perceptible darkening on treatment with hydrogen sulfide, while a solution of silver nitrate produces a barely detectable opalescence. Sulfuric, acetic and hydrochloric acids, as well as sodium hydroxide, cause decomposition into metal and a more soluble trivalent bismuth salt. It is insoluble in alcohol and in an aqueous solution of potassium iodide. It reduces an acid solution of potassium permanganate.

As a further criterion of the chemical individuality of this subsalt, the conductivity of various samples was compared with that of the basic iodide,  $\text{BiOI}$ , formed as above from bismuth oxide, the method of procedure in determining the solubility being precisely as described in a previous paper.<sup>6</sup> The measured resistance of the oxyiodide was found to be by two tests  $745 \pm 15$  ohms; that of the sub-oxyiodide was  $9000 \pm 900$  ohms.

**The Red Volatile Product.**—Mention has been made of the fact that a red, volatile, crystalline product separated in the tubes leading from the oven. This occurred in all cases. In order to test whether this substance was produced during the distillation by a side reaction, or was the product of the decomposition of the sub-oxyiodide, a sample of the latter compound was sealed to the pump, evacuated, and heated to  $262^\circ$ . After prolonged evacuation no sign of such a volatile substance outside the oven could be detected.

During each distillation small quantities of these bright red crystals, rarely more than 0.04 g., were formed. In order to determine the percentage of bismuth which they contained, the crystals were weighed into a platinum crucible, covered with dil. nitric acid, evaporated to dryness and gently ignited. Control experiments performed with a similar weight of the trioxide of bismuth showed that the analysis by this method could

<sup>6</sup> *J. Chem. Soc.*, 111, 29 (1917).

be relied on to yield a result correct to 0.1 mg. The balance used was sensitive to 0.05 mg. The iodine was determined by treating the crystals with an aqueous solution of silver nitrate to which dil. nitric acid was afterwards added to dissolve out traces of metallic bismuth. The precipitate of silver iodide was gathered on a Gooch crucible, according to the ordinary procedure. Three analyses of bismuth were carried out and two of iodine showing 44.9, 44.8 and 45.0 (av. 44.9) % of bismuth, and 55.2 and 54.9 (av. 55.05) % of iodine, as compared with 45.04 % of bismuth and 54.96 % of iodine calculated. The results agree very closely with the percentage composition of  $\text{BiI}_2$ . Such a compound has been described by Bertholet,<sup>7</sup> who obtained it in the form of metallic, leafy crystals by melting together iodine and bismuth.<sup>8</sup> The following description throws doubt upon the chemical identity of the product obtained in these earlier experiments. The crystals of bismuth subiodide obtained by the distillation of methyl iodide over bismuth suboxide are of a bright red color, and form long needles in the orthorhombic system. On treatment with water freed from dissolved oxygen a solution was obtained which gave much stronger reactions for bismuth and iodine than given by the suboxyiodide. In the absence of oxygen the subiodide dissolves without decomposition in ethyl alcohol and in methyl iodide, forming in both cases a clear yellow liquid. It is also freely soluble in an aqueous solution of potassium iodide, producing a solution closely resembling in appearance that of potassium dichromate. Bismuth subiodide rapidly reduces an aqueous solution of iodine and an acid solution of permanganate. On heating above 400° it decomposes into bismuth tri-iodide which volatilizes, leaving a residue of bismuth.

**The Pale Yellow Product from the Distillate.**—The distillate of methyl iodide was yellow in color. On cooling this with liquid ammonia, a white, curdy precipitate separated, which redissolved immediately on warming to room temperature. In the absence of air this distillate remained yellow and homogeneous for 9 days at a temperature between 15° and 20°, but shortly after the admission of air or of oxygen, about 0.05 g. of a white solid separated in each experiment. In the course of a few days the color of this solid turned to a distinct yellow while the supernatant liquid lost its color. Analysis of this solid showed that in all cases bismuth, iodine and carbon were present, while its separation only in the presence of oxygen is sufficient confirmation of the presence of this element. Analyses of the bismuth and iodine content showed that the composition of the solid varies from experiment to experiment, the last two samples showing 90.3 and 85.2% of bismuth, and 5.8 and 9.4 % of iodine, respectively; and in some of the analyses the percentage of bismuth fell as low as 71% and

<sup>7</sup> Bertholet, Ref. 4.

<sup>8</sup> See also Weber, Ref. 4.

the iodine was as high as 22%. The yellow product was insoluble in alcohol and proved to be a strong reducing agent, for its addition to an aqueous solution of silver nitrate caused the precipitation of a mixture of silver and silver iodide. The above facts appear to be best interpreted on the assumptions that, (1) the distillate contains a varying quantity of the volatile bismuth subiodide carried over in the vapor of methyl iodide; (2) there is also present in the distillate bismuth dimethyl ( $\text{Bi}(\text{CH}_3)_2$ ) for it is extremely improbable that a volatile compound could exist wherein the ratio of bismuth to iodine is as high as 90.3:5.8 or even 85.2:9.4.

The first of these hypotheses was tested by inserting a short fractionating column between the reaction vessel and the condenser. The result was to make a marked reduction in the amount of iodine present in the solid, while the color of the solid became nearly white. It was also shown that bismuth subiodide, dissolved in methyl iodide, does slowly oxidize in air (oxygen) with the production of a yellow powder.

Owing to the small amount of material available it was impossible to test the second hypothesis conclusively. The percentage composition rules out the possibility that the whole of the bismuth came over in combination with iodine, and the most reasonable supposition appears to be that it distilled over in the form of a methyl compound. Bismuth trimethyl is well known, but it has been shown by Marquardt<sup>9</sup> that the halogens do not oxidize this compound, but replace the methyl groups. Hence the oxidation of bismuth trimethyl by oxygen could not yield a product possessing reducing properties sufficient to account for the reduction of silver nitrate to metallic silver.

Since the author has shown that the oxidation product of bismuth subiodide, formed by the action of oxygen upon a solution of the subiodide in methyl iodide, does not possess such reducing power, the most tenable hypothesis is that bismuth is carried over in the distillate as bismuth dimethyl, which on oxidation passes into such a compound as dimethoxy bismuth,  $\text{Bi}(\text{OCH}_3)_2$ .

### Summary.

1. Bismuth sub-oxyiodide,  $2\text{BiI}_2 \cdot 3\text{BiO}$ , a brick-red powder of considerable stability, has been isolated.
2. Bismuth subiodide,  $\text{BiI}_2$ , has been prepared as a red, volatile crystalline substance, belonging to the orthorhombic system.
3. Evidence has been adduced that bismuth dimethyl,  $\text{Bi}(\text{CH}_3)_2$ , has been isolated. It oxidizes readily and produces a strongly reducing substance, possibly dimethoxy bismuth,  $\text{Bi}(\text{OCH}_3)_2$ .

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<sup>9</sup> Marquardt, *Ber.*, 20, 1517 (1887).