[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CESIUM BISMUTH IODIDE

BY C. C. MELOCHE AND P. V. CLARK

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In studying certain reactions of cesium it was observed that a solution of hydrogen bismuth iodide when added to one of cesium nitrate gave a bright red crystalline precipitate. On analysis it was found that this compound had the empirical formula $Cs_3Bi_2I_9$ and was, therefore, identical in composition with the compound which Wells and Foote[1] had prepared by the interaction of cesium iodide and bismuth iodide. The interesting properties of this substance and its application in the determination of cesium justify a brief description.

Reagents

Cesium Nitrate.—The method of Godeffroy[2] as modified by Wells[3] was used at first for the preparation of cesium nitrate from pollucite. Later a modification suggested by Willard and Scott was employed.

Hydrogen Bismuth Iodide Solution.—This reagent was prepared by dissolving C. P. bismuth hydroxide, bismuth basic carbonate or bismuth oxyiodide in an excess of specially purified hydriodic acid and diluting. The solution was preserved in an atmosphere of hydrogen or carbon dioxide.

Preparation and Analysis.—A dilute aqueous solution of the cesium nitrate was treated dropwise in the cold with a slight excess of the hydrogen bismuth iodide solution. When the reaction was found to be complete, the precipitate was washed by decantation with 0.1 *N* hydriodic acid, transferred to a Büchner funnel, washed further with 0.1 *N* hydriodic acid, then with alcohol and finally dried at 110°.

The red compound was analyzed as follows. Five-tenths to one-gram samples were dissolved in 1:5 nitric acid and the solution boiled to remove free iodine. After cooling and diluting, the bismuth was separated as bismuth sulfide, the sulfide decomposed by hot 1:4 nitric acid and the resulting solution of bismuth nitrate used for the determination of bismuth by the phosphate method as modified by Schoeller and Waterhouse.[4]

The filtrate from the bismuth sulfide was evaporated with aqua regia to remove any ammonium salts and the cesium finally converted to cesium sulfate by evaporation with sulfuric acid, treatment with ammonium carbonate and gentle ignition.

The iodine was determined volumetrically on separate samples: 0.5 to 0.6 g. was suspended in hydrochloric acid (3:2), a little chloroform

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[1] Wells and Foote, *Am. J. Sci.*, [4] **3,** 461 (1897).

[2] Godeffroy, *Ber.*, **7,** 375 (1874).

[3] Wells, *Am. Chem. J.*, **26,** 266 (1901).

[4] Schoeller and Waterhouse, *Analyst,* **45,** 435 (1920).

added and the iodine titrated with 0.025 *M* potassium iodate solution in carbon dioxide atmosphere as recommended by Andrew.[5]

The averages of closely agreeing analyses were as follows: 20.66% Cs, 21.28% Bi and 58.15% I. The values calculated for $Cs_3Bi_2I_9$ were 20.34% Cs, 21.34% Bi and 58.32% I.

Properties.—On examination under the microscope the crystals are transparent and appear to be hexagonal. Gradual hydrolysis occurs when the compound is suspended in water at room temperature, and in boiling water the insoluble copper colored bismuth oxyiodide, together with the soluble cesium iodide and hydriodic acid, is rapidly formed. Hydriodic acid in concentrations as low as 0.05 *N* will prevent hydrolysis at 25°. The red compound dissolves to some extent in dilute hydrochloric acid and is completely decomposed by boiling 1:5 nitric acid with evolution of iodine. Strong nitric acid converts some of the iodide to iodate and causes the precipitation of white finely divided bismuth iodate.

The approximate solubility in different solvents was determined by sealing the solvent with excess of the red compound in a 200-ml. glass tube otherwise filled with carbon dioxide. After agitation for at least forty-eight hours in a thermostatic tank kept at 25 ± 0.01°, the remaining cesium bismuth iodide was allowed to settle, the glass tube opened and 10-ml. portions of the clear supernatant liquid were removed for the colorimetric determination of bismuth by the bismuth iodide method. The free iodine which was almost invariably present in the solvent at the end of the solubility determination was determined by means of 0.01 *N* thiosulfate. The results obtained are recorded in Table I.

TABLE I

APPROXIMATE SOLUBILITIES OF CESIUM BISMUTH IODIDE

Solvent at 25°	Free iodine, g. per 100 ml.		$Cs_3Bi_2I_9$ diss., g. per 100 ml.		Cs equivalent g. per 100 ml.	
0.1096 *N* hydriodic acid	<0.00066	0.0000	0.170	0.166	0.035	0.034
0.0472 *N* hydriodic acid	.0000	< .00066	.094	.082	.019	.017
Absolute alcohol	.006	.010	.00078	.00073	.00016	.00015

It will be observed that the solubility of $Cs_3Bi_2I_9$ increases with increase in concentration of hydriodic acid. The solubility in absolute ethyl alcohol corresponds to less than 0.2 mg. of cesium per 100 ml. The solubility in mixtures of absolute ethyl alcohol and absolute *n*-butyl alcohol is also very low.

The effect of drying and igniting cesium bismuth iodide at various temperatures was studied in some detail on account of the application of this data in analytical work. As a rule 0.5 to 1.0-g. samples of cesium bismuth iodide were transferred to porcelain boats and placed in a pyrex glass tube enclosed by a constant temperature electric oven. A slow

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[5] Andrew, THIS JOURNAL, **25**, 756 (1903).

current of air dried by means of concentrated sulfuric acid was passed through the glass tube. At the higher temperatures a porcelain tube heated by helically wound resistance wire was employed. The temperature was controlled by a rheostat and measured by means of a platinum iridium thermocouple. The losses at various temperatures are shown in Table II.

TABLE II

LOSS IN WEIGHT OF CESIUM BISMUTH IODIDE ON HEATING IN DRY AIR

$Cs_3Bi_2I_9$ g.	Temp., °C.	Time, hours	Loss in weight, g.	Rate of loss in weight, % per hour
0.8343	210	13.5 additional	0.00035 additional	0.003
0.8343	250	3.0 additional	0.0009 additional	0.036
1.3289	300	12.0 total	0.0625 additional	0.392
0.8237	400	19.0 additional	0.2767 total	1.768
1.5578	750	49.0 additional	1.1590 total	...

The sensible constancy in weight at 210 and at 220° after the initial loss of hygroscopic moisture, as well as the slow losses at 230° and above, are shown in Table III.

TABLE III

THE STABILITY OF CESIUM BISMUTH IODIDE AT 210°

Weight of $Cs_3Bi_2I_9$ after drying at 110°: (I) 0.8343, (II) 1.3496.

Temp., °C.	Time, hours	Loss in weight, g. (I)	(II)	Loss in weight, % per hour (I)	(II)
210	3.0 i	0.00075	0.0010	0.030	0.025
210	3.0 a	.00010	.0002	.004	.005
210	3.0 a	.00005	.00015	.002	.004
210	7.5 a	.0002	.00025	.003	.0025
220	3.0 a	.0000	.0000	.000	.000
230	3.0 a	.0004	.0002	.016	.005
240	3.0 a	.0010	.0002	.040	.005
250	3.0 a	.0009	.0013	.036	.032

i = initial heating. a = additional.

When cesium bismuth iodide was heated in dry air as above described, the color changed to a dark red or very dark brown when the temperature was 110 to 210°, but the original bright red color was restored on cooling. At temperatures above 230° loss of iodine occurred and a permanent change in color eventually took place. At first an orange-colored material was produced. After heating for sixty-two hours at 300° the residue was lemon-yellow. After heating for twenty to thirty hours at 400° a white or yellowish-white material remained. Several specimens of this white material were prepared, the percentage loss in weight observed and the iodine content determined volumetrically. The averages of closely agreeing results were as follows: loss in weight of the red precipitate, 33.65%; iodine in residue, 22.41%, referred to the red precipitate;

iodine replaced by oxygen, 35.91% of the red precipitate; iodine replaced calculated from loss in weight, 35.91% of the red precipitate; atoms of iodine replaced, 5.54. The white substance, though not of definite composition, was obviously formed by the replacement of nearly six of the nine original atoms of iodine by an equivalent of oxygen. The composition, therefore, tends toward the limit expressed by the formula $Bi_2O_3 \cdot 3CsI$, but neither the pure white color nor the sensible constancy in weight is a reliable indication that this limit has been reached.

The use of cesium bismuth iodide in the quantitative determination of cesium is being investigated.

The authors wish to express their appreciation of the interest which Professor H. H. Willard has taken in the progress of this work.

Summary

1. A new method for the preparation of cesium bismuth iodide has been described and the properties of cesium bismuth iodide, which have significance in analysis, have been studied.

2. The very low solubility in ethyl alcohol, the constancy in weight at 210°, and the quantitative reaction with standard potassium iodate have been noted.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SASKATCHEWAN]

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM CaO–Al_2O_3–SiO_2. III. THE HEAT OF HYDRATION OF CALCIUM OXIDE[1]

BY T. THORVALDSON, WELDON G. BROWN AND C. R. PEAKER

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Introduction

Several values for the heat of hydration of calcium oxide are to be found in the literature. Thomsen[2] obtained the value 15,540 calories per mole at 20° from data on the heat of solution of calcium oxide and calcium hydroxide in $HCl \cdot 300H_2O$. Berthelot[3] determined the heat of solution of calcium oxide in hydrochloric acid (one-sixth molal) at 16°, the heat of solution of calcium hydroxide in water and the heat of neutralization of a solution of calcium hydroxide by 0.5 *M* hydrochloric acid. From these results he calculated the heat of hydration of calcium oxide, obtaining the

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[1] The authors wish to acknowledge generous financial assistance from the National Research Council of Canada.

[2] Thomsen, "Thermochemische Untersuchungen," Vol. 3, **1883,** p. 248.

[3] Berthelot, *Ann. chim. phys.,* [5] **4,** 531 (1875).