XVIII.—*On the Iodides of Antimony.*

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WHEN an intimate mixture of antimony with iodine is triturated in a mortar, immediate and violent combination takes place, much heat being given out, whereby a great portion of the more volatile element is vapourised in the free state. The product of the union is antimony tri-iodide. The best method of effecting the synthesis of considerable quantities of the compound consists in gradually adding excess of finely divided antimony to iodine contained in a convenient vessel to which a gentle heat is at first applied, in order to initiate the combination. The first few additions of metal produce sufficient heat to fuse the iodine, and its further addition must be very carefully effected in order to avoid as much as possible volatilization of the haloid. When saturation has been completed, the melted product is poured off from excess of metal, and may be subjected to sublimation or cast into cylindrical bars or other convenient form.

As obtained by casting, the iodide has a dull, reddish, semi-metallic aspect, but a bar of it when broken presents a most beautifully radiated fracture and bright metallic lustre. On heating to $164\cdot4^{\circ}$ C. (corr.)* it melts, forming a thin red liquid, which at a considerably higher temperature enters into ebullition, evolving orange-coloured vapours, which condense on a cold surface to form large, thin, transparent, bright red, hexagonal plates. When the sublimation is conducted in

* In *Chem. News*, xxix, p. 255, the melting point is stated as being $165\cdot5^{\circ}$ C., which is the uncorrected temperature.

air, the iodide undergoes a slight decomposition, whereby iodine is liberated and antimony oxyiodide formed—the former manifesting itself by imparting a violet tint to the vapours.

The decomposition is rendered much more complete when the iodide is volatilised in a current of dried oxygen—the antimony burning with flame to form antimonious oxide. It does not undergo decomposition when vaporised in dried carbon dioxide or hydrogen.

Powdered antimony iodide is of a reddish-brown colour, and may be exposed to air for a long time without undergoing any perceptible change. It dissolves in boiling benzene, producing a yellow solution which on cooling deposits bright red tabular crystals having the same form as those obtained by evaporating a carbon disulphide solution of the compound. It is nearly insoluble in chloroform, and does not dissolve in turpentine or carbon tetrachloride. An attempt to form carbon hexiodide by heating SbI_3 and carbon hexchloride together, gave a negative result. When the compounds are heated to 250° or so, the iodide partially dissolves in the melted C_2Cl_6 , forming a dark brown solution which on cooling solidifies to a lemon-yellow mass, from which, on further cooling, red crystals shoot out, the yellow colour being rapidly changed to red.

The iodide is easily soluble in aqueous hydriodic acid, and the solution gives a yellow precipitate of oxyiodide when added to water. Its solution in cold fuming hydrochloric acid contains undecomposed iodide, and gives when poured into water a yellow precipitate, but a few seconds' boiling converts the whole of the antimony into trichloride, whereupon the solution gives with water a white precipitate of an oxychloride. Cold sulphuric acid ($12\text{H}_2\text{SO}_4.13\text{H}_2\text{O}$), contrary to the statement of Brandes, has little or no action upon it, but the application of a gentle heat determines a rapid decomposition, iodine being liberated and antimonious sulphate formed. Nitric acid of specific gravity 1.5 immediately decomposes it, producing nitrous vapours, free iodine, and antimony oxide. The same acid, of specific gravity 1.4, acts in a similar manner, but when a more dilute acid (of specific gravity 1.2) is poured on the iodide, it does not at first appear to act, but in a very short time a sensible amount of heat is given out and a rapid decomposition takes place. When digested with cold absolute ethyl alcohol, it dissolves partially forming a brown solution, but the greater portion is converted into yellow oxyiodide. Anhydrous ether also partially decomposes it, producing yellow oxyiodide and a dark-brown solution containing unaltered tri-iodide. Chlorine immediately converts it into antimony chloride and iodine monochloride. Treated with melted iodine monochloride it is decomposed with production of antimony trichloride and free iodine. By the action of bromine, antimony tribromide and iodine monobromide are formed.

The latter compound is a black crystalline solid, which emits an irritating and tear-exciting vapour, undergoes spontaneous sublimation in the vessels in which it is kept, and collects on the upper parts in the form of star-like clusters of flat crystals which are black by reflected, and dark red by transmitted light. It melts at 42° C. to form a reddish-brown liquid, which on distillation begins to boil at 80° — 82° , when iodine tribromide passes over and the thermometer rises to 110° — 120° , when the monobromide distils leaving a considerable residue of iodine. Iodine tribromide is a reddish-brown liquid at ordinary temperatures, boiling at 80° — 82° , and undergoing partial decomposition when distilled under ordinary pressure, producing some free bromine, iodine monobromide, and free iodine.

Lowig's iodine pentabromide does not exist.

Antimony Penta-iodide.

Van der Espt (*Arch. Pharm.* [2], cxvii, 115), states that he obtained a penta-iodide of antimony by heating the elements together in the requisite proportions. Upon repeating this chemist's experiment I obtained nothing but tri-iodide and free iodine. I attempted to form it by carefully heating SbI_3 and I_2 together, but without success. From my experiments I conclude that SbI_5 cannot be formed by the method of Van der Espt—indeed its existence is in my opinion doubtful.

Antimony Oxyiodide.

Antimony tri-iodide, or, as already stated, its solution in hydriodic acid, is decomposed by water, with formation of a yellow oxyiodide. The composition of the latter varies with the circumstances under which it is formed. The precipitate formed by pouring the hydriodic acid solution into boiling water, has a composition approximating to that required by an oxyiodide of the formula $2\text{SbI}_3 \cdot 5\text{Sb}_2\text{O}_3$, or $\text{Sb}_4\text{I}_2\text{O}_5$.

	Calculated.	Found.	
Sb	59.37	58.83	59.24
I	30.90	31.07	30.81
O (as difference) .	9.73	10.10	9.95
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The oxyiodide dissolves somewhat slowly in a hot solution of tartaric acid.