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HALIDES OF TANTALUM.[1]

BY WALTER K. VAN HAAGEN.

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The chloride alone of all the possible halides of tantalum has received more than passing attention. A bromide has been recorded but the iodide is absent from our literature. H. Rose[2] claimed to have obtained the bromide by strongly igniting a mixture of tantalic oxide and carbon in a current of carbon dioxide laden with bromine vapor. He failed to give any analytical results. He surmised that his product was the bromide. Moissan believed it was produced upon heating tantalum metal in a stream of bromine vapor.

With pure materials the conditions essential for the satisfactory preparation of tantalum pentabromide may be briefly summarized:

1. Tantalic oxide, previously strongly ignited, should be intimately mixed with an excess of pure carbon, an equal weight of the latter being a convenient and quite sufficient amount. Starch carbon answers well but it usually leaves an appreciable ash, hence pure sugar carbon is preferable. The excess of carbon indicated makes the mass sufficiently permeable to the bromine.

2. Air should be completely expelled. Raise the charge to a full red heat in a current of carbon dioxide to remove the last traces of moisture.

3. Phosphorus pentoxide is essential as the final drying agent for the carbon dioxide.

4. A high temperature must be maintained during the passage of the bromine, otherwise nearly all of it will escape unchanged.

[1] An abstract from the author's doctoral thesis (1909).

[2] *Pogg. Ann.*, 99, 87 (1856).

5. The resulting pentabromide should be fused from time to time in order that the combustion tube may not be obstructed.

It is easy to get a yield of about 70 per cent. of the theory.

The product from the above procedure was resublimed in an atmosphere of carbon dioxide. Upon analysis it showed:

			Theory.
Ta = 32.21	32.03	31.79	31.39
Br = 68.70	68.68	68.38	68.61

Tantalum pentabromide consists of yellow, elongated lamellae, curving or clinging to the tube in beautiful arborescent forms resembling frost flowers. They fuse easily to a transparent, ruby-colored liquid. Their color is suggestive of that of potassium bichromate. They may be sublimed without melting. The vapor of the bromide is yellow in color, somewhat resembling that of chlorine. The bromide melts at about 240° and begins to boil at 320°. It fumes strongly in the air. It dissolves rapidly in absolute methyl or ethyl alcohol, forming at first an amber-yellow colored liquid which soon becomes colorless. Usually the heat generated causes the alcohol to boil. These reactions certainly point to tantalic esters. Anhydrous ethyl bromide is an interesting solvent for tantalum pentabromide. When the latter is brought into this liquid heat is evolved and a reddish colored solution results. If the latter be cooled in water or evaporated in a vacuum desiccator golden yellow colored crystals separate. The solution fumes strongly in the air.

Tantalum pentabromide may be sublimed in an atmosphere of hydrogen. This is possible at a temperature just sufficient for the sublimation. At more elevated temperatures a partial reduction to the metallic state occurs. If a lower bromide of tantalum should exist such a compound would not be unlikely to appear at some stage during the reduction of the pentabromide in hydrogen. At first there seemed no evidence of this. At times, however, the sublimate appeared to be different. Indeed, it had been noticed that toward the posterior end of the tube, *i. e.*, beyond the metallic deposit, there was a slight greenish, partly almost black film. It dissolved in water with an intense green color, and in methyl and ethyl alcohol with the same color. Its analysis indicated a tantalum tribromide, but Chapin, in this Laboratory, has since demonstrated that it is not this, but that it is in reality a bromo-tantalum bromide $(Ta_6Br_{12})Br_2$.[1]

An oxybromide of tantalum was not observed.

Efforts were made both by Rose[2] and by Moissan[3] to obtain an iodide of tantalum but without avail. So the query presented itself: is it not

[1] W. H. Chapin, THIS JOURNAL, **32**, 323.

[2] *Pogg. Ann.*, **99**, 593 (1856).

[3] *Compt. Rend.*, **134**, 211–215.

possible to transpose tantalum bromide by means of a suitable iodide? Silver iodide suggested itself for this pu pose. Accordingly tantalum pentabromide was distilled through a column of granular, well-dried silver iodide in a current of carbon dioxide. A brown sublimate resulted. It contained considerable free iodine, which was carefully expelled and the residue analyzed. This analysis indicated a pentabromide with unmistakable evidences of combined iodine. How could there be free iodine unless there had been a reduction of the bromide?

Finally it was found that the potassium iodide used in the preparation of the silver iodide contained some iodate. Most likely then the reaction had proceeded as follows:

$$7TaBr_5 + 5AgIO_3 = TaI_5 + 3Ta_2O_5 + 5AgBr + 15Br_2.$$

The liberated bromine set free iodine from the silver iodide and probably from the tantalum iodide, allowing only a small amount of the latter to escape, while by far the greater portion of the bromide distilled over unchanged. This view is further supported by the fact that iodine separates when tantalum pentabromide is distilled through a layer of potassium iodate.

The next thought was to try hydrogen iodide. Accordingly tantalum pentabromide was slowly distilled in a steady stream of anhydrous hydriodic acid gas. Soon the reddish color of the bromide changed to brown, while the escape o` hydrobromic acid, together with the excess of the hydriodic acid, could be proved at the exit of the tube. Further an analysis of the dark brown product showed that only one-third of the bromide had been converted into an iodide. Therefore the experiment was repeated, about three grams of the pentabromide being distilled as slowly as possible in a brisk current of hydrogen iodide for about four hours. The product was brownish black in color and showed much iodine. Its tantalum content was found to be 22.98 instead of 22.37 per cent. as required by TaI_5. The remainder of the preparation was subjected to another distillation in hydrogen iodide and analyzed with these results:

	Per cent.	Per cent.
Ta	22.62	22.51
I	77.27	77.35

The required percentage of iodine for the pentaiodide is 77.63. These results prove the formation of an iodide, TaI_5. It sublimes in dark, nearly black lamellae, bearing a remote resemblance to iodine crystals. It fuses to a dark brown liquid. Its vapor is like that of bromine. It may be distilled in a current of carbon dioxide without the separation of iodine. It resembles the bromide in its deportment toward moist air and water. An intermediate oxyiodide was never observed.

UNIVERSITY OF PENNSYLVANIA.