The Preparation and Properties of Tellurium Dibromide.

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A convenient method is given for the preparation of tellurium dibromide by the reaction between bromotrifluoromethane and molten tellurium. Some of its properties are described. It has been used to prepare tellurium(IV) dibromide di-iodide, diamminotellurium dibromide, and some pyridine complexes. Bromotrifluoromethane is converted into hexafluoroethane.

Berzelius (*Pogg. Ann.*, 1833, **28**, 392; 1834, **32**, 1, 577) claimed to have obtained tellurium dibromide as a greenish-black crystalline mass by subliming a mixture of tellurium and tellurium tetrabromide. Carnelley and Williams (*J.*, 1880, **37**, 125), who do not describe their preparation, give for the dibromide m. p. 280° and b. p. 339°, but Brauner (*J.*, 1889, **55**, 382) found m. p. 210°. The latter prepared his material by fusing the tetrabromide with an excess of tellurium, followed by sublimation either in a vacuum or in a current of carbon dioxide. The product so obtained appeared sometimes as a black or blackish-green mass, sometimes as needles of a pale steel colour, and at other times as a black or olive-green powder.

Damiens (*Compt. rend.*, 1921, **173**, 300) showed that, although tellurium dibromide exists in the vapour state, there is no evidence of its existence on the freezing-point curve of mixtures of the constituent elements and, when normally prepared, the dibromide vapour, on condensation, decomposes to form a solid solution of the metal and its tetrabromide. On addition of ether to this product, the tetrabromide dissolves and leaves a residue of tellurium. However, later (*ibid.*, 1921, **173**, 583; *Ann. Chim.*, 1923, **19**, 44) Damiens isolated the true dibromide in the solid state (*a*) by cooling its vapour in a vacuum to —80°, and (*b*) by reducing the tellurium tetrabromide in dry ethereal solution in the dark with finely divided tellurium. The dibromide is chocolate-brown, and completely soluble in ether, from which solution it can be recovered unchanged. Disproportionation is rapid when the solid dibromide is gently heated, so Damiens was unable to determine its m. p. and b. p. He was able, however, to show that in ethereal solution tellurium dibromide combines with iodine to form red crystals of tellurium(IV) dibromide di-iodide, $TeBr_2I_2$.

It appears that other workers in this field have not handled solid tellurium dibromide but a solid solution of the element and its tetrabromide. *E.g.*, Yost and Hatcher (*J. Amer. Chem. Soc.*, 1932, **54**, 151), who have shown by vapour-density measurements that the molecule of the vapour is $TeBr_2$ up to 750°, describe tellurium dibromide as a black solid.

We describe a new method of preparing tellurium dibromide which consists of streaming bromotrifluoromethane over molten tellurium so as to obtain a black, amorphous powder which is the solid solution of tellurium in tellurium tetrabromide, and then subliming this mixture in a dry vacuum on to a surface cooled in liquid air. In this way chocolate-brown pure tellurium dibromide is deposited on the cooled surface and in a fair yield. Our product is identical with that obtained by Damiens.

From the unpleasant-smelling gaseous by-products, hexafluoroethane was isolated and in an amount expected from the reaction: $2CF_3Br + Te = C_2F_6 + TeBr_2$.

The dibromide thus obtained has a vapour which is violet at lower temperatures and pink at higher temperatures. It is readily soluble in dry diethyl ether and less readily in dry chloroform, and forms greenish-yellow solutions; these solutions are unstable and, at ordinary temperatures, tellurium is slowly deposited from them on to the walls of the containing vessel. This decomposition is accelerated if the solutions are heated; and, if a trace of moisture is admitted, the decomposition is instantaneous. In each case the solution remaining is tellurium tetrabromide.

The solid solution of tellurium in its tetrabromide was found to have m. p. 279—281° and b. p. 340°, figures in good agreement with those published by Carnelley and Williams (*loc. cit.*) for the dibromide. It seems, therefore, that their material was the solid solution and not the dibromide.

In fluorine much diluted with nitrogen, tellurium dibromide reacts at once to form first the tetrafluoride and then the hexafluoride. No evidence of a difluoride has been obtained. When the dibromide is gently heated in chlorine, bromine is liberated and black tellurium dichloride is formed which is then oxidised to the tetrachloride. Liquid bromine converts the dibromide exothermally into the tetrabromide. When ethereal solutions of the dibromide and iodine are mixed in a dry evacuated vessel, and some of the ether is then evaporated from the mixture, garnet-red crystals of tellurium(IV) dibromide di-iodide crystallise, having m. p. 323—325°, b. p. 420° (decomp.). The liquid is dark red, the vapour purple. Like the tetrabromide, the compound is unaffected by dry air but slowly absorbs moisture from the atmosphere. Water decomposes it at once with the formation of a white precipitate of tellurous acid in hydrobromic and hydriodic acids.

When ethereal solutions of tellurium(IV) dibromide di-iodide and pyridine are mixed, a new complex, dipyridinedibromodi-iodotellurium(IV), $(C_5H_5N)_2TeBr_2I_2$, is precipitated as an amorphous cream-coloured powder. It is stable in dry air, but becomes yellow in moist air, and is at once hydrolysed by water to tellurous acid.

Dipyridinedibromodi-iodotellurium(IV) dissolves in warm concentrated hydrochloric, hydrobromic, and hydriodic acid to give, on cooling, orange needles of dipyridinium dibromodichlorodi-iodotellurite, $(C_5H_5NH)_2TeCl_2Br_2I_2$, red needles of dipyridinium tetrabromodi-iodotellurite $(C_5H_5NH)_2TeBr_4I_2$, and black needles of dipyridinium hexaiodotellurite, $(C_5H_5NH)_2TeI_6$, respectively.

When ethereal solutions of tellurium dibromide and pyridine are mixed a white solid is first precipitated which rapidly blackens, precipitating tellurium and leaving dipyridinetetrabromotellurium(IV), $(C_5H_5N)_2TeBr_4$.

Tellurium dibromide does not combine with either gaseous or liquid sulphur dioxide or with hydrogen cyanide, but it disproportionates in each of the liquids. Dry ammonia, however, at laboratory temperatures is at first rapidly absorbed by tellurium dibromide and then much more slowly. The black powder remaining when the excess of ammonia is removed is diamminotellurium dibromide, $TeBr_2,2NH_3$, which is unaffected by air but loses ammonia when heated alone or with sodium hydroxide. In liquid ammonia the dibromide blackens, swells to a bulky mass, and with further liquid collapses to a black powder containing free tellurium and tellurium nitride. The liquid ammonia contains ammonium bromide. In this reaction the tellurium dibromide probably disproportionates and the tetrabromide formed then undergoes ammonolysis to form tellurium nitride (Strecker and Ebert, *Ber.*, 1925, **58**, 2527).

EXPERIMENTAL

Preparation of Tellurium Dibromide.—Bromotrifluoromethane (from Imperial Chemical Industries Limited), dried with concentrated sulphuric acid and then with phosphoric oxide, was led over molten tellurium at about 500°. The disproportionation mixture of tellurium and tellurium tetrabromide was formed as a black, amorphous powder and was distilled forward in the gas stream and collected in the first of two receivers. The flow of gas was stopped and the receivers were sealed off from the rest of the apparatus and evacuated. On distillation of the mixture of tellurium and its tetrabromide into the second receiver, which contained a surface cooled in liquid air, tellurium dibromide collected on the cold surface as a chocolate-brown, amorphous powder. Its vapour was violet at lower temperatures and pink at higher temperatures. It was unstable, and if it was heated gently or if a trace of water was admitted, it disproportionated at once, forming the black solid solution of the metal in its tetrabromide. The dibromide was completely soluble in ether, but the solution rapidly precipitated tellurium when exposed to light or boiled or when treated with a trace of moisture. It was less soluble in chloroform, and solutions in this solvent were also unstable, but the deposition of tellurium by light was slower.

When the gas issuing from the reaction vessel was cooled to approx. −180° (bromotrifluoromethane has b. p. −59°), a colourless foul-smelling liquid containing traces of tellurium was collected. The tellurium was removed from this liquid by passing its vapour through "Carbosorb" and then into a trap surrounded by liquid air. The contents of the trap were transferred to the bottom of a Podbielniak-type low-temperature fractionation column (Podbielniak, *Ind. Eng. Chem. Anal.*, 1931, **3**, 177) and fractionated, and the amounts and molecular weights of the fractions were determined. Unchanged bromotrifluoromethane and hexafluorethane, b. p. −78° (lit., −78°), made up the whole of the fractionated liquid (Found: *M*, 138·5. Calc. for C_2F_6: *M*, 138).

Reactions with Halogens.—Tellurium dibromide reacted spontaneously in fluorine diluted with nitrogen (1 : 10, by vol.) and the surface of the solid was soon coated with the tetrafluoride. On continued flow of fluorine, the tetrafluoride was rapidly oxidised to gaseous tellurium hexafluoride.

Chlorine rapidly converted gently heated tellurium dibromide first into the black dichloride and then into the tetrachloride with the liberation of bromine.

Excess of liquid bromine was added to a few g. of tellurium dibromide. A strongly exothermic reaction took place. On removal of the excess of bromine in a stream of carbon dioxide, yellow tellurium tetrabromide remained.

Mixing ethereal solutions of tellurium dibromide and iodine in an evacuated vessel and then evaporating away some of the excess of ether gave garnet-red crystals of tellurium(IV) dibromide di-iodide (Found: Te, 23·7; Br, 29·9; I, 46·6. Calc. for $TeBr_2I_2$: Te, 23·6; Br, 29·5; I, 46·9%), m. p. 323—325°, b. p. 420°. Decomposition with liberation of iodine takes place on boiling.

Pyridine Complexes of $TeBr_2I_2$.—This compound (1 mol.) and pyridine (2 mols.) were mixed in ether. *Dipyridinedibromodi-iodotellurium*(IV) was precipitated as a cream-coloured amorphous solid in almost quantitative yield [Found: C, 17·5; N, 3·6; H, 1·8; Te, 18·2; Br, 23·8; I, 35·5. $(C_5H_5N)_2TeBr_2I_2$ requires C, 17·2; N, 4·0; H, 1·4; Te, 18·3; Br, 22·9; I, 36·4%]. This compound is at once hydrolysed by water to tellurous acid. It melts with decomposition and, when it is boiled, pyridine and iodine are evolved.

Dipyridinedibromodi-iodotellurium(IV) (I) was dissolved in hot concentrated hydrochloric acid and, on cooling, orange needles of *dipyridinium dibromodichlorodi-iodotellurite* (II) crystallised [Found: C, 16·0; N, 3·8; H, 1·5; Te, 16·4; Cl, 9·6; Br, 20·3; I, 33·7. $(C_5H_5NH)_2TeCl_2Br_2I_2$ requires C, 15·5; N, 3·6; H, 1·6; Te, 16·5; Cl, 9·2; Br, 20·7; I, 32·9%]; the compound (I) in hot concentrated hydrobromic acid gave red needles of *dipyridinium tetrabromodi-iodotellurite* (III) on cooling [Found: C, 13·3; N, 3·7; H, 1·1; Te, 15·1; Br, 36·9; I, 30·3. $(C_5H_5NH)_2TeBr_4I_2$ requires C, 13·9; N, 3·3; H, 1·4; Te, 14·8; Br, 37·5; I, 29·5%]. The compounds (I), (II), and (III) with hydrogen iodide gave in each case dipyridinium hexaiodotellurite $(C_5H_5NH)_2TeI_6$, which is the most stable compound of this series (Aynsley and Hetherington, *J.*, 1953, 2802) [Found: C, 11·6; N, 2·8; H, 1·3; Te, 12·2; I, 72·3. Calc. for $(C_5H_5NH)_2TeI_6$: C, 11·4; N, 2·7; H, 1·1; Te, 12·1; I, 72·7%].

When ethereal solutions of tellurium dibromide and pyridine were mixed, a white amorphous solid was first precipitated but this at once blackened, depositing tellurium and dipyridinetetrabromotellurium(IV). A little of this was separated from the tellurium by extraction with hot pyridine and was readily identified by dissolving it in hot concentrated hydrobromic acid and crystallising out red needles of dipyridinium hexabromotellurite [Found: C, 15·8; N, 3·6; H, 1·7; Te, 16·8; Br, 62·3. Calc. for $(C_5H_5NH)_2TeBr_6$: C, 15·7; N, 3·7; H, 1·6; Te, 16·6; Br, 62·6%].

Reaction with Ammonia.—(*a*) A stream of dry ammonia was passed over tellurium dibromide at laboratory temperature. The dibromide blackened and absorption of the ammonia was rapid at first, but the reaction was not complete until the dibromide and gas had been in contact for several days. On removal of the excess of ammonia with dry nitrogen followed by exposure to phosphoric oxide in a desiccator, *diamminotellurium dibromide*, $Te(NH_3)_2Br_2$, was obtained as an amorphous black powder, unchanged when exposed to air, but readily losing ammonia when heated alone or with sodium hydroxide [Found : Te, 39·8; N, 9·0; H, 1·8; Br, 49·5. $Te(NH_3)_2Br_2$ requires Te, 39·7; N, 8·8; H, 1·9; Br, 49·7%]. (*b*) A quantity of tellurium dibromide was transferred to a fritted-glass filter in an evacuated Pyrex vessel and cooled to −50° (NH_3 has b. p. −33·5°), and then ammonia was led in. The dibromide became black and at first the gas was rapidly absorbed by the dibromide, which swelled gently, but when liquid ammonia began to appear in the vessel the bulky solid collapsed to a fine black solid on the filter. The filtrate passing through left ammonium bromide on evaporation of the excess of ammonia, and the black residue on the filter was mainly tellurium mixed with tellurium nitride. The latter was recognised by its liberation of ammonia in warm sodium hydroxide and its explosive decomposition into its elements when dried and heated.

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