

**598.** *The Preparation and Properties of Tellurium Dichloride.*

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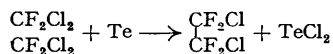
A convenient method of preparing tellurium dichloride by the reaction between Arcton 6 ( $\text{CF}_2\text{Cl}_2$ ) and molten tellurium is given. Some of its properties are described. It has been used to prepare tellurium(IV) dichloride dibromide and some pyridine complexes, but attempts to prepare tellurium(IV) dichloride di-iodide were unsuccessful. The Arcton 6 is partly converted into  $\text{C}_2\text{F}_4\text{Cl}_2$ , presumably through the free radical  $\text{CF}_2\text{Cl}$ .

PREVIOUS evidence for tellurium dichloride is a little confused. From chlorine and hot tellurium, Rose (*Pogg. Ann.*, 1831, **21**, 443) obtained a mixture of the dichloride and tetrachloride from which he believed he separated the former by fractional distillation. The formation of the dichloride in other reactions has been noted by Lenher (*J. Amer. Chem. Soc.*, 1902, **24**, 188) and by Linder and Apolant (*Z. anorg. Chem.*, 1924, **136**, 381). But Damiens (*Ann. Chim.*, 1923, **19**, 44) found no evidence of tellurium dichloride from the freezing-point curve of mixtures of the constituent elements. He concluded that it exists only as a vapour, and that on solidification it dissociates into a mixture of the element with the tetrachloride. Later Grether (*Ann. Physik*, 1936, **26**, 1) measured atomic distances in tellurium dichloride by electron diffraction in the vapour and found them to be 2.55 Å, and Dharmatti (*Proc. Indian Acad. Sci.*, 1940, **12**, A, 212) made magnetic-susceptibility measurements on the compound; neither describes the preparation. As the latter author states that his material was very unstable and that some decomposition took place before he could make his measurements, it is difficult to know what he was actually handling.

Tellurium dichloride has been described as a black, amorphous solid which does not fume in air. When molten it is black and its vapour is purple. Michaelis (*Ber.*, 1887, **20**, 2488) gives m. p. 175° and b. p. 324°, but Carnelley and Williams (*J.*, 1879, 563; 1880, 125) found m. p. 209° ± 5°, b. p. 327°.

All the above methods of preparation produce mixtures from which the dichloride has to be separated by a tedious fractionation in which it is difficult to remove the last traces of tetrachloride.

Streaming Arcton 6 (dichlorodifluoromethane,  $\text{CF}_2\text{Cl}_2$ ) over molten tellurium provides a new method of preparing tellurium dichloride, in a pure state and a good yield. This product melted sharply at 208° and boiled at 328° (corr.) in good agreement with Carnelley and Williams (*loc. cit.*). From the unpleasant-smelling gaseous by-products, small quantities of *s*-dichlorotetrafluoroethane were isolated, so, presumably the reaction involves:



and the radical  $\text{CF}_2\text{Cl}$  at least in part.

The dichloride has been described as soluble in diethyl ether. But this is not true: tellurium dichloride disproportionates rapidly into tellurium and tellurium tetrachloride in diethyl ether, dioxan, or dibutyl ether. The solutions previously described were of the tetrachloride, not the dichloride. My attempt to form a complex between tellurium dichloride and pyridine failed because disproportionation takes place in this liquid also, giving tellurium and the yellow base, dipyridinetetrachlorotellurium(IV),  $(\text{C}_5\text{H}_5\text{N})_2\text{TeCl}_4$ . Indeed I have not found a solvent in which tellurium dichloride does not disproportionate: in liquids like carbon tetrachloride it is insoluble.

When warmed in fluorine, very much diluted with nitrogen, tellurium dichloride is converted first into the tetrafluoride and then into the hexafluoride. No evidence has been obtained of the existence of a difluoride. When heated in chlorine, the dichloride is oxidised to the tetrachloride. Damiens (*loc. cit.*) found an ethereal solution of tellurium dichloride to absorb large amounts of bromine and iodine and took this as evidence for  $\text{TeCl}_2\text{Br}_2$  and  $\text{TeCl}_2\text{I}_2$  in solution, but he was unable to isolate either substance. Since tellurium dichloride disproportionates in diethyl ether, clearly Damiens must have started with a solution of the tetrachloride and not the dichloride, and the formation of either of these compounds

appears improbable. I have found that when excess of liquid bromine is added to tellurium dichloride, a strongly exothermic reaction occurs, and, on removal of the excess of bromine with carbon dioxide, the new compound tellurium(IV) dichloride dibromide,  $\text{TeCl}_2\text{Br}_2$ , is obtained as a yellow powder, m. p.  $292^\circ$ , b. p.  $415^\circ$  (corr.). The liquid is ruby-red and forms a dark-yellow crystalline mass on cooling; the vapour is orange. 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 hydrochloric and hydrobromic acids.

When ethereal solutions of tellurium(IV) dichloride dibromide and pyridine are mixed, a new complex, dipyridinedichlorodibromotellurium(IV),  $(\text{C}_5\text{H}_5\text{N})_2\text{TeCl}_2\text{Br}_2$ , 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. It melts with decomposition, liberating pyridine and tellurium dichloride.

Dipyridinedichlorodibromotellurium(IV) readily dissolves in hot concentrated hydrochloric acid, from which, on cooling, separate pale-orange needles of a second new complex, dipyridinium tetrachlorodibromotellurite,  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeCl}_4\text{Br}_2$ . When this, or dipyridinedichlorodibromotellurium(IV), is dissolved in hot concentrated hydrobromic acid and the solution cooled, red needles of dipyridinium hexabromotellurite,  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeBr}_6$ , separate. This was first prepared by Lenher (*J. Amer. Chem. Soc.*, 1900, **22**, 136) from tellurium dioxide in hydrobromic acid and pyridine. When hydriodic is substituted for hydrobromic acid, a third new complex, dipyridinium hexaiodotellurite,  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeI}_6$ , is obtained as black needles.

In an attempt to prepare the salt,  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeF}_2\text{Cl}_2\text{Br}_2$ , dipyridinodichlorodibromotellurium(IV) was evaporated with a concentrated solution of hydrofluoric acid. The first crop of crystals was red needles of  $(\text{C}_5\text{H}_5\text{NH})\text{TeBr}_6$ ; the second, after further concentration, orange needle-shaped mixed crystals of  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeBr}_6$  and  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeCl}_6$ ; the third, after still further concentration, yellow needles of  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeCl}_6$ . From this last compound, dipyridinium hexachlorotellurite, all the chlorine is replaced by bromine under the action of hot concentrated hydrobromic acid, giving red crystals of dipyridinium hexabromotellurite. Similarly, solutions of dipyridinium hexachlorotellurite and hexabromotellurite, when treated with hot concentrated hydriodic acid, yield black needles of the hexaiodo-compound. Clearly the stabilities of these complexes increase in the order chloro-, bromo-, iodo-tellurite. Attempts to prepare tellurium(IV) dichloride di-iodide were unsuccessful.

Neither gaseous nor liquid sulphur dioxide reacts with tellurium dichloride. Gaseous dinitrogen tetroxide has no immediate action, but the liquid oxidises it to tellurium dioxide, nitrosyl chloride being also formed, thus:  $\text{TeCl}_2 + \text{N}_2\text{O}_4 \longrightarrow \text{TeO}_2 + 2\text{NOCl}$ .

Ammonia, at about its temperature of condensation, is rapidly absorbed by tellurium dichloride which increases greatly in bulk. The black powder remaining when the excess of ammonia is removed is unaffected by ordinary air and contains 15% of combined ammonia, at least partly as ammonium chloride. In liquid ammonia, however, the dichloride first swells to a bulky mass, but with further liquid collapses to a fine powder. This is tellurium; the liquid ammonia contains ammonium chloride, and nitrogen is liberated. Quantitative observations show that the reaction can be represented thus:  $3\text{TeCl}_2 + 8\text{NH}_3 \longrightarrow 3\text{Te} + 6\text{NH}_4\text{Cl} + \text{N}_2$ .

#### EXPERIMENTAL

*Preparation of Tellurium Dichloride.*—Arcton 6 ( $\text{CF}_2\text{Cl}_2$ ) (from Imperial Chemical Industries Limited), dried first with concentrated sulphuric acid and then with phosphoric oxide, was led over molten tellurium contained in the first section of a 2.5-cm. Pyrex tube, constricted at intervals of about 10 cm. to furnish six compartments. A receiver was attached to the far end and was protected by a drying tube. The tellurium dichloride was distilled forward in the gas stream from section to section and finally into the receiver. In this way material entirely free from unchanged tellurium and the tetrachloride could be collected at a rate of 2 g. per hr. (Found: Te, 64.5; Cl, 35.6. Calc. for  $\text{TeCl}_2$ : Te, 64.3; Cl, 35.7%).

When the gas issuing from the receiver was cooled to  $-20^\circ$  (Arcton 6 has b. p.  $-29.8^\circ$ ),

about 1 ml. of a colourless liquid containing carbon, chlorine, fluorine, and traces of tellurium was collected. The nature and quantity of the liquid appeared to depend on the temperature of the tellurium. Fractionation gave a little liquid, b. p.  $4^{\circ}$ , which produced tetrafluoroethylene with zinc and alcohol and so was *s*-dichlorotetrafluoroethane. A higher-boiling, foul-smelling fraction containing traces of tellurium was always obtained and sometimes a fraction boiling between  $-6^{\circ}$  and  $+6^{\circ}$ : these are under examination.

*Disproportionation of Tellurium Dichloride.*—Tellurium dichloride was distilled into a tube fitted with a fritted-glass filter, and its weight was obtained. Dry diethyl ether was continuously drawn through the dichloride for  $\frac{1}{2}$  hr., followed by warm, dry nitrogen. The weight of the residue of tellurium and that of the tellurium tetrachloride in the ether corresponded to the disproportionation  $2\text{TeCl}_2 \longrightarrow \text{Te} + \text{TeCl}_4$ . When ether was added to hard lumps of tellurium dichloride they rapidly crumbled to finely divided tellurium and left tetrachloride in the ethereal layer. Behaviour was similar with dioxan and dibutyl ether.

Disproportionation occurred in dry pyridine, the products being tellurium and yellow dipyridinetetrachlorotellurium(IV). A little of this was separated from the tellurium by extraction with hot pyridine, and, although the complex was not obtained pure, it was readily identified by dissolving it in hot concentrated hydrochloric acid and crystallising out yellow needles of dipyridinium hexachlorotellurite [Found: C, 23.8; N, 5.7; H, 2.6; Te, 25.8; Cl, 42.3. Calc. for  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeCl}_6$ : C, 24.0; N, 5.6; H, 2.4; Te, 25.5; Cl, 42.6%].

*Reactions with Halogens.*—Gently warmed tellurium dichloride in fluorine diluted with nitrogen (1:9, by vol.) reacted quietly without further heating. The surface of the solid was soon coated with the tetrafluoride. When the temperature was raised or the proportion of fluorine in the gas mixture increased, the tetrafluoride was immediately oxidised to gaseous tellurium hexafluoride.

Chlorine rapidly converted molten tellurium dichloride into the tetrachloride which was collected as a snow-white crystalline mass.

Excess of liquid bromine was added to a few g. of tellurium dichloride. A strongly exothermic reaction took place. On removal of the excess of bromine with a stream of carbon dioxide, the yellow powder *tellurium(IV) dichloride dibromide* (Found: Te, 35.9; Cl, 19.5; Br, 44.9.  $\text{TeCl}_2\text{Br}_2$  requires Te, 35.6; Cl, 19.8; Br, 44.6%), m. p.  $292^{\circ}$ , b. p.  $415^{\circ}$  (corr.), remained. Slight decomposition takes place on boiling.

The following attempts failed to produce tellurium(IV) dichloride di-iodide: (a) passing iodine vapour over molten tellurium dichloride, (b) keeping tellurium dichloride in a saturated solution of iodine in carbon tetrachloride, (c) sealing tellurium dichloride and iodine in an evacuated tube, and (d) mixing ethereal solutions of tellurium dichloride dibromide and iodine.

*Pyridine Complexes of  $\text{TeCl}_2\text{Br}_2$ .*—This compound (1 mol.) and pyridine (2 mols.) were mixed in ether. The compound *dipyridinedichlorodibromotellurium(IV)* was precipitated as a cream-coloured amorphous solid in almost quantitative yield [Found: C, 23.0; N, 5.6; H, 2.2; Te, 24.5; Cl, 13.6; Br, 31.2.  $(\text{C}_5\text{H}_5\text{N})_2\text{TeCl}_2\text{Br}_2$  requires C, 23.2; N, 5.4; H, 1.9; Te, 24.7; Cl, 13.8; Br, 31.0%]. This compound is at once hydrolysed by water to tellurous acid. It melts with decomposition and, on boiling, pyridine and tellurium dichloride are evolved.

Dipyridinedichlorodibromotellurium(IV) was dissolved in hot concentrated hydrochloric acid and, on cooling, pale orange needles of *dipyridinium tetrachlorodibromotellurite* crystallised [Found: C, 20.1; N, 4.9; H, 2.3; Te, 21.5; Cl, 24.4; Br, 26.9.  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeCl}_4\text{Br}_2$  requires C, 20.4; N, 4.8; H, 2.0; Te, 21.7; Cl, 24.1; Br, 27.1%].

Both the dipyridine compound and the salt dissolve in hot concentrated hydrobromic acid and in hot concentrated hydriodic acid, giving red needles of dipyridinium hexabromo- and black needles of *hexaiodo-tellurite* respectively [Found: C, 11.5; N, 2.4; H, 1.2; Te, 12.7; I, 72.0.  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeI}_6$  requires C, 11.4; N, 2.7; H, 1.1; Te, 12.1; I, 72.6%].

An attempt to prepare  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeF}_2\text{Cl}_2\text{Br}_2$  failed. When a solution of dipyridinedichlorodibromotellurium(IV) in concentrated hydrofluoric acid was concentrated on the water-bath, red crystals of the hexabromotellurite first crystallised on cooling. These were removed and the evaporation was continued, whereupon orange crystals were obtained which appeared to be mixed crystals of the hexabromo- and hexachloro-tellurite, since the crystals were homogeneous and contained bromine and chlorine but not in the proportion required for  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeCl}_4\text{Br}_2$ . The remaining solution on further concentration and cooling left yellow crystals of the hexachlorotellurite almost entirely free from bromine. Further, the hexachlorotellurite in hot concentrated hydrobromic acid deposited the hexabromotellurite on cooling, and both the chloro- and the bromo-compound when dissolved in hot concentrated hydriodic acid gave black needles of the hexaiodotellurite on cooling.

*Reaction with Dinitrogen Tetroxide.*—Dinitrogen tetroxide, redistilled from phosphoric oxide, was condensed on a known weight of tellurium dichloride and left for some hr. Removing the excess of tetroxide left a white residue of tellurium oxide which was weighed. All the chlorine was found in the distillate as nitrosyl chloride. The quantity of tellurium dioxide formed was in accordance with the equation,  $\text{TeCl}_2 + \text{N}_2\text{O}_4 \longrightarrow \text{TeO}_2 + 2\text{NOCl}$ .

*Reaction with Ammonia.*—(a) A stream of gaseous ammonia was passed for about 1 hr. over tellurium dichloride at  $-20^\circ$ . The chloride rapidly swelled to many times its original volume. On removal of the excess of ammonia with dry nitrogen followed by exposure to phosphoric oxide in a desiccator, a black powder, unchanged when exposed to air and containing 15% of combined ammonia, was left. This substance was not, however, a pure material, and X-ray examination showed it to contain, among other things, ammonium chloride. (b) A weighed quantity of tellurium dichloride was placed on a fritted-glass filter in a Pyrex vessel, which was evacuated and cooled to  $-50^\circ$  (b. p.  $\text{NH}_3$ ,  $-33.5^\circ$ ), and then ammonia was led in. At first the ammonia was rapidly absorbed by the dichloride which swelled greatly, but when liquid ammonia began to appear in the vessel the bulky solid collapsed to a fine black solid on the filter. The ammonia filtrate passing through the filter was collected in a weighed vessel and, when the excess of ammonia had been removed from the apparatus, the black residue on the filter and the white residue from the filtrate were weighed. Elementary nitrogen was present in the ammonia leaving the reaction vessel; the black substance proved to be tellurium and the white one ammonium chloride, weights being in accordance with the equation  $3\text{TeCl}_2 + 8\text{NH}_3 \longrightarrow 3\text{Te} + 6\text{NH}_4\text{Cl} + \text{N}_2$ .

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