LXVIII.—*The Action of Hydrogen Fluoride on Compounds of Selenium and Tellurium. Part II. Tellurium Dioxide.*

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THE action of hydrofluoric acid upon tellurium dioxide was studied by Metzner (*Ann. Chim. Phys.*, 1898, **15**, 203). The oxide dissolved in the 43—55% acid. On cooling to about —50°, crystals were obtained which contained 53% of hydrogen fluoride. The solutions crystallised on evaporation to small bulk, and successive crops corresponded best with the formulæ $2TeF_4,3TeO_2,6H_2O$ and $TeF_4,TeO_2,2H_2O$, the analyses of the latter compound being the more concordant and agreeing better with the formula assigned. The mother-liquor from this preparation was treated with hydrofluoric acid " pur." (from potassium hydrogen fluoride) and cooled to — 70°. It then formed transparent crystals containing 3·8 atoms of fluorine for each atom of tellurium. This compound was regarded as TeF_4. The author remarks that its preparation in the pure state would require very concentrated acid. We have used anhydrous hydrogen fluoride throughout our investigation, but have not so far observed the crystallisation of this compound. We have, however, confined our experiments mainly to the preparation of that fluoride which is obtained at the ordinary temperature.

EXPERIMENTAL.

Tellurium, supplied by the courtesy of the Baltimore Copper Company, was dissolved in nitric acid, and the solution evaporated to dryness. The product was slightly green owing to the presence of copper, which was removed by fusion with sodium carbonate and extraction with water followed by filtration. The solution was made faintly acid with nitric acid, and the precipitated tellurous acid was filtered off, dried at 100°, heated to its melting point, and powdered.

The anhydrous hydrogen fluoride, prepared as already described (Part I, this vol., p. 167), was passed over the dioxide in a platinum boat or crucible, contained in a copper tube or copper-plated cylinder, respectively. A colourless liquid was produced and a white solid, consisting apparently of unchanged tellurium dioxide, remained. This dissolved completely in excess of hydrogen fluoride. The liquid was exposed for several days in a vacuous desiccator, covered inside with ceresin and containing calcium chloride and solid sodium hydroxide. It became slightly more viscous and remained clear.

On cooling to − 70°, it became very viscous, but no crystals appeared on stirring and rubbing. After standing for another day, it suddenly set to a mass of white crystals. This is the product A mentioned below.

The preparation was repeated with slight variations. The hydrogen fluoride vapour was passed until some of the oxide had dissolved and some had been converted into silky crystals, which adhered firmly to the crucible. The liquid was then decanted into a platinum capsule. The undissolved dioxide and the silky crystals were dissolved in more liquid hydrogen fluoride which had been condensed in a platinum bottle. Both solutions were placed at once in the desiccator described above, which was then evacuated. After about 2 days, a mass of white nodules of radiating crystalline structure separated from each solution. This is sample B.

These crystals were kept, in a desiccator, unchanged for days at atmospheric pressure. When the desiccator was evacuated over phosphorus pentoxide for a night, 0·5525 g. of the substance lost only 3 mg. But when this treatment was continued for several days (sample B1) or when the compound was kept over alkali in a desiccator for months (sample A1), the composition changed in the manner indicated by the analyses given below.

Analysis.—Since the accurate gravimetric estimation of fluoride in the presence of tellurite is difficult (Metzner, *loc. cit.*), we have devised a method of estimating it as hydrogen fluoride after hydrolysis. When a solution of tellurous acid in dilute hydrofluoric acid is titrated with alkali in the presence of *p*-nitrophenol, precipitation of tellurous acid begins at once and continues until the indicator turns yellow. When tellurous acid is suspended in water, a single drop of alkali produces this colour change. Therefore, on account of its sparing solubility, the tellurous acid gives a solution of $[H^+] = 1 \times 10^{-5}$ or even less. A weighed amount of hydrofluoric acid, when titrated in the presence of tellurous acid, required exactly the same amount of alkali as the same weight of hydrofluoric acid when titrated alone. Tellurous acid, therefore, can be disregarded at the *p*-nitrophenol end-point. Although this titration gives concordant figures, these do not, as shown in Part I (*loc. cit.*), correspond with the absolute amount of hydrofluoric acid present until multiplied by a factor 1·03.

The samples were analysed after being crushed and rubbed between filter-paper.

Tellurium was estimated as usual after precipitation by sulphur dioxide from a hydrochloric acid solution.*

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* In the volumetric analysis, the titrated liquid was proved to be free from tellurium, and the precipitate free from fluoride.

Sample A : 0·273 g. required 28·57 c.c. of *N*/10-alkali and gave 0·1805 g. of tellurium. Sample B : 0·9005 g. required 92·3 c.c. of *N*/10-alkali, and 0·382 g. gave 0·2545 g. of tellurium.

	A.	B.	A1.	B1.
% Te	66·1	66·6	68·7	70·2
% F	20·4	20·0	18·6	18·9

TeF_4,TeO_2,H_2O requires Te, 66·8; F, 20·0%. $TeF_4,TeO_2,2H_2O$ requires Te, 63·8; F, 19·1%.

The use of anhydrous hydrogen fluoride therefore leads to a compound different from either of those prepared by Metzner. In the presence of more water, more hydrated compounds would doubtless be formed. Since the only water present in our experiments was that formed in the reaction, it is evident that at least one molecule is thus produced and evaporates in the desiccator. The other molecule, if it is really eliminated, is held as water of crystallisation but has only a low vapour pressure.

We regard this compound as the least hydrated which it is possible to prepare from the dioxide and hydrogen fluoride with subsequent evaporation. It is not at present possible to decide between the formulæ TeF_4,TeO_2,H_2O, $2TeOF_2,H_2O$, and $TeOF_2,TeO_2,2HF$. In material kept in the desiccator after a long time (A1), or in a vacuum over phosphorus pentoxide (B1), the percentage of tellurium increases considerably, whilst the percentage of fluorine diminishes only slightly. These results suggest that, under the conditions employed, more water is lost than hydrogen fluoride, so that the compound behaves rather as a hydrate than as a fluoride.

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