

668. *The Fluorination of Tellurium. Ditellurium Decafluoride and Tellurium Oxyfluorides.*

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The action of fluorine on tellurium gives at $\sim 150^\circ$ exclusively the hexafluoride, at $\sim 60^\circ$ hexafluoride and some ditellurium decafluoride, and at $\sim 0^\circ$ mainly tetrafluoride. The proportion of decafluoride is increased by various solid additives; of these tellurium dioxide was the most effective. Apart from the useful control of temperature brought about by diluting the fluorine with another gas, a gaseous diluent also raises the yield, nitrogen considerably and oxygen much more. With the use of the former the oxyfluoride $\text{Te}_3\text{F}_{14}\text{O}_2$ also appears among the products, and with the latter both this oxyfluoride and a more complex one are formed.

The ditellurium decafluoride has been rigorously purified and many of its properties have been studied. Our data are in substantial agreement with those of English and Dale.⁶

The properties of $\text{Te}_3\text{F}_{14}\text{O}_2$ and the material of higher molecular weight, possibly $\text{Te}_6\text{F}_{28}\text{O}_5$, are described.

At the outset of this investigation (1951) the hexafluoride¹ was the only fluoride of sexavalent tellurium known with certainty. In 1933 Yost and Claussen² separated about 1 c.c. of liquid, m. p. -13.6° , b. p. 61.2° , from products of the reaction between tellurium and fluorine, and suggested that it might be ditellurium decafluoride. The evidence was inconclusive and, while working with one of us, Peacock³ was unable to obtain this liquid in the way prescribed, but from the action of fluorine on tellurium dioxide isolated small quantities of liquid with a range of melting points from -46° to -45° and molecular weights from 351 to 475. The quantities were too small for effective fractionation, but the liquids differed from Yost and Claussen's material in being resistant to water at 100° whereas theirs was decomposed at 85° by heat alone.

Starting from this point the present fluorination of tellurium and its oxides soon showed that, under certain conditions, products containing appreciable quantities of unequivocal decafluoride could be obtained. When notice of a Note on ditellurium decafluoride by English and Dale appeared⁴ our work had proceeded so far, and had also disclosed other new compounds, that it was continued.

The broad features of our many preparative experiments are shown in Table 1. Tellurium trioxide yielded only hexafluoride, and the dioxide, which reacts with fluorine at a

TABLE 1. *Summary of fluorination experiments.*

In furnace	Fluorine, l./hr.	Gaseous diluent, l./hr.	Furnace wall temp., °C.	Products
TeO_3	0.5—10	N_2 , 0—5	100—250	Almost entirely TeF_6
TeO_2	0.5—10	N_2 , 0—5	100—200	Volatile liquid, trace; remainder TeF_6
Te	2	N_2 , 4	40—60	Te_2F_{10} , 5—10%; TeF_6 , 80—90%
Te with Al_2O_3 , or Ni, or Cu; ratio 1 : 1	3—5	None	60—80	Te_2F_{10} , 10—16%; remainder TeF_6
Te with TeO_2 ; ratio 1 : 1	3—4	N_2 , 10	50—60	Te_2F_{10} , 25%; $\text{Te}_3\text{F}_{14}\text{O}_2$, 2%; remainder TeF_6
Te with TeO_2 ; ratio 1 : 1	3—4	O_2 , 10	50—60	Te_2F_{10} , 40—45%; $\text{Te}_3\text{F}_{14}\text{O}_2$, 5%; higher b. p. material, 0.5%; remainder TeF_6

much lower temperature, gave the same, with a trace of what is either the decafluoride or an oxyfluoride. Tellurium itself at $\sim 150^\circ$ gives exclusively the hexafluoride; at $\sim 60^\circ$ this is accompanied by decafluoride in recoverable amounts; and at $\sim 0^\circ$ the formation of solid tetrafluoride soon prevents further reaction.

¹ Prideaux, *J.*, 1906, 322.

² Yost and Claussen, *J. Amer. Chem. Soc.*, 1933, **55**, 885.

³ Peacock, Ph.D. Thesis, Univ. of Durham, 1951.

⁴ *Proc. Chem. Soc.*, 1952, 141.

Mixing the tellurium with solids (*e.g.*, alumina, nickel, copper) and adjusting the fluorine flow rate so as to maintain the reaction tube at $\sim 70^\circ$ leads to an increased proportion of decafluoride. Mixing with tellurium dioxide and using fluorine alone gives a similar result, but is attended by the production of some oxyfluoride. When, however, the fluorine is diluted with nitrogen the yield of more readily condensable products increases. This increase, consisting mainly of decafluoride, is doubled on changing the diluent from nitrogen to oxygen. The amount of oxyfluoride also rises and a little material of a still higher boiling point appears, which, in consequence, moves little beyond the hot, reaction zone. The proportion of the distinctive products depends in part upon the ratio of dioxide to tellurium, that of the decafluoride and oxyfluoride being increased as this is raised, and also considerably upon the temperature of the reacting charge and the concentration of fluorine. The evidence points to the decafluoride with its linked tellurium atoms being derived from tellurium itself where these atoms are already arranged in spiral chains.⁵ That the presence of tellurium oxide and oxygen greatly assists in the production of ditellurium decafluoride may be due to a pre-formation of the high-boiling liquids—undoubtedly oxygen-containing—which, covering the surface of the element, serve as a solvent for the fluorine and so moderate the reaction. In the oxyfluorides we believe the tellurium atoms are separated by oxygen atoms.

We tried the mixture of calcium fluoride and tellurium described by English and Dale,⁶ only to produce negligible amounts of the decafluoride, possibly because our diluent was in another form, or we had failed to realise the conditions obtaining in their particular apparatus. The larger amounts of material available and the elaborate purification which we adopted probably account for small differences between the values of some of the physical properties reported by English and Dale and those given here.

RESULTS

Products of Fluorination.—Ditellurium decafluoride. This was characterised by analysis and molecular weight determination (Found: Te, 57.1; F, 42.6%; M , 447 ± 2 . Calc. for Te_2F_{10} : Te, 57.3; F, 42.7%; M , 445). It is a colourless mobile, stable liquid, unreactive towards water, acids, and alkalis; it was purified by repeated fractional distillation of several large preparations. A summary of the physical measurements we have made is:

d_{25}^{25} , 2.839 g./c.c. (English and Dale give d_{25}^{25} 2.88 g./c.c.).

Density at 273°K , 2.9372 ± 0.0005 g./c.c.; at $T^\circ \text{K}$ (range $243\text{—}303^\circ \text{K}$), $4.0984 - 0.0042525T$ g./c.c.

Coefficient of cubical expansion (range $243\text{—}303^\circ \text{K}$), 0.00145 c.c./c.c./ $^\circ \text{C}$.

$M. p.$ $-33.7^\circ \pm 0.2^\circ \text{C}$.

$B. p.$ $59^\circ \pm 0.2^\circ \text{C}/760$ mm. (English and Dale give $54^\circ/760$ mm.).

Surface tension at 273°K , 17.6 ± 0.2 dynes/cm.; at $T^\circ \text{K}$, $\gamma_T = 49.2 \pm 0.2 - 0.11554T$ dynes/cm.

Viscosity (range -30° to $+30^\circ \text{C}$), $0.01524/(1 + 0.01365t + 0.0000175t^2)\text{P}$.

Electrical conductivity (range $293\text{—}309^\circ \text{K}$), $3.1 (\pm 0.4) \times 10^{-8}$ mhos/cm.

The low boiling point suggests a completely covalent compound and there is no evidence of association. The plot of $\gamma(M/\rho)^{\frac{2}{3}}$ against T gives a straight line of slope -3.02 , a value rather higher than would be expected for a compound of this molecular weight; its uniformity suggests a normal liquid. A critical temperature of 170° is obtained by extrapolation; this gives a ratio T_b/T_c of 0.75 which is not far removed from the usual 0.6—0.7. The viscosity exhibits no abnormality above -20° , though there is some deviation below that temperature; the plot of fluidity against specific volume is a straight line and the value of w in the Batschinski⁷ equation $v = w + c\phi$ (where v is specific volume, ϕ fluidity, and w and c constants) is 0.306, which lies within the usual range for unassociated liquids.

The infrared spectrum is being examined by Mr. R. E. Dodd and the Raman spectrum by Dr. L. A. Woodward; their findings will be published in due course. Specimens, separately prepared and purified, showed identical absorption bands in the infrared region. Very strong absorption has been found at 714, 754, and 888 and strong absorption at 723 and 740 cm.^{-1} ;

⁵ Huggins, *J. Chem. Phys.*, 1945, **13**, 37.

⁶ English and Dale, *J.*, 1953, 2498.

⁷ Batschinski, *Z. phys. Chem.*, 1913, **84**, 643.

a distribution similar to that found by Gaunt⁸ in the spectrum of tellurium hexafluoride where peaks are at 714, 752, and 888 cm^{-1} . The molecule is presumably formed by the linking of two TeF_6 groups; and these, individually, are rather like the hexafluoride molecule and would be expected to absorb at comparable frequencies. The arrangement constitutes a structure well enclosed in a sheath of fluorine atoms. Association of the polar Te-F bonds is likely to be largely prevented by the absence of space for their overlapping. This, along with the size of the molecule which tends to reduce the attractive forces, probably accounts for its monomeric character.

As already mentioned, the decafluoride is not immediately attacked by water or aqueous reagents, but it suffers slow hydrolysis during several months in contact with water, and a crust of fluorotellurates forms on the glass at the fluid interface. The pure, dry liquid has been kept in Pyrex glass for several months without showing evidence of change. It is without noticeable action on iron, copper, and nickel, and, although the vapour causes mercury to tail, the liquid seems to have little effect upon the element. Metallic sodium attacks it at the ordinary temperature with vigour, releasing tellurium and possibly forming polytellurides. Sulphur and selenium are unattacked by the liquid at its boiling point; iodine gives a magenta solution. Neither barium fluoride nor calcium fluoride retains any of the compound after being in the boiling liquid, but sodium fluoride holds some of it tenaciously. The amount is not large, and the X-ray diffraction pattern of sodium fluoride proved to be unchanged after 8 hr. under refluxing decafluoride. Presumably any compound formed effectively seals the surface layers of the salts against further penetration.

By contrast with its immiscibility and inertness in aqueous reagents, tellurium decafluoride shows high reactivity towards a wide range of organic compounds. With saturated and halogen-substituted aliphatic hydrocarbons it gives colourless solutions without appreciable reaction or loss of distinctive properties. Mono- and poly-hydric alcohols also produce colourless solutions, sometimes with a noticeable generation of heat, but these solutions no longer show the characteristic reactions of the decafluoride with the organic compounds about to be mentioned. All unsaturated and aromatic hydrocarbons tested become clear yellow. Many substituted aromatic compounds and all amines respond more vigorously, occasionally so violently as to have to be handled in dilute solution. The reactions are complex and may result in the formation of tars, but the solid products sometimes have a remarkable colour: thus catechol, α -naphthylamine, and methyldiphenylamine produce insoluble stable powders respectively green, dark blue, and black.

Tellurium oxyfluorides. We have no evidence of the formation of an oxyfluoride when tellurium, gaseous oxygen, and fluorine are used. In the presence of tellurium dioxide, however, fluorination of tellurium produces a moderate quantity of a liquid b. p. ca. 135°. When these conditions are changed by the addition of gaseous oxygen this liquid is accompanied by another in much lower yield and of much higher boiling point. At first we thought that the former was the next member of the sexivalent fluoride series Te_3F_{14} , but the evidence points to their both being oxyfluorides.

Tritellurium dioxotetradecafluoride, $\text{Te}_3\text{F}_{14}\text{O}_2$. This material has been made in lots of up to 10 c.c., and is a colourless mobile liquid, d 2.25 \pm 0.05 g./c.c. at 20°; m. p. -27°, b. p. 134.5°/755 mm.—its behaviour at these points indicates purity. Analyses show an atomic ratio Te : F of 3 : 14 but account for only 95% of the material; it seems reasonable to suppose that the remainder is oxygen, since the compound is formed only when this element is available. The molecular weight (Dumas's method) is approximately 715 and, for experimental reasons, is probably high. The Table shows that the data are in accordance with the formula suggested.

	Te, %	F, %	O, %	Te/F	M		Te, %	F, %	O, %	Te/F	M
Te_3F_{14}	59.0	41.0	—	1.44	648.8	$\text{Te}_3\text{F}_{12}\text{O}_3$	58.1	34.6	7.3	1.68	658.8
$\text{Te}_3\text{F}_{14}\text{O}_2$...	56.2	39.1	4.7	1.44	680.8	$\text{Te}_3\text{F}_{10}\text{O}_4$	60.1	29.8	10.1	2.02	636.8
Preparation	55.7	38.5	5.8	1.45	715						

The most reasonable structure is an angular one in which the tellurium atoms are separated by oxygen atoms. It may well be that this and the higher-boiling material described below are derived from such units; which may have originated in the dioxide itself since its presence appears to be necessary in the preparation. English and Dale pointed out the very high ratio, molecular weight : boiling point, displayed by tellurium decafluoride, namely 1.36, but in this compound the ratio reaches the remarkable value of 1.67.

⁸ Gaunt, *Trans. Faraday Soc.*, 1953, **49**, 1122.

The oxyfluoride distils, without decomposition or attack, in Pyrex glass. Like the decafluoride it is not readily hydrolysed. The liquid has little effect upon mercury but the vapour causes "tailing." Copper, brass, and rubber are unaffected but it dissolves and is absorbed by most greases. "Anhydrone" can be used for drying the liquid which can then be kept in Pyrex glass for long periods without evidence of attack.

Its solubility in and behaviour with organic materials are very similar to those displayed by the decafluoride.

The higher oxyfluoride. Only very small quantities of this material are produced in individual experiments (ca. 0.5 c.c.). It is a colourless, mobile liquid which can be kept in Pyrex glass at ordinary temperature. The boiling point seems to be above 300°, but it attacks Pyrex glass long before it boils. That its vapour pressure is very low follows from the fact that it distils exceedingly slowly at 20° under a high vacuum. The density is 3—3.1 g./c.c. at 20°.

Here again analysis for tellurium and fluorine leaves a deficiency of about 7% which is presumably oxygen. The molecular weight is ca. 1300. None of our determinations is claimed to be of high accuracy, but we are satisfied that the various values are of the order indicated. The data suggest that if, as we believe, the material is a single compound it should probably be represented by the empirical formula $\text{Te}_6\text{F}_{26}\text{O}_5$.

	Te, %	F, %	O, %	M
$\text{Te}_5\text{F}_{22}\text{O}_4$	56.9	37.3	5.8	1120
$\text{Te}_6\text{F}_{26}\text{O}_5$	57.1	36.9	6.0	1340
$\text{Te}_7\text{F}_{30}\text{O}_6$	57.3	36.6	6.2	1559
Preparation	56.6	36.0	7.4	1270, 1300, 1470. Mean 1350

EXPERIMENTAL

Preparation of Sexavalent Tellurium Fluorides.—The reactions summarised in Table I were carried out on the solids in nickel tube furnaces connected to a train of Pyrex-glass traps by means of brass unions furnished with neoprene rings. The apparatus was thoroughly dried by repeated evacuation and heating before fluorine, appropriately diluted and previously cooled to -180° to remove condensable impurities, was admitted. The products were condensed at -180° and, after the flow of fluorine was stopped, but before the train of traps was sealed off, the reaction-tube temperature was raised to 150° to allow the nitrogen stream to carry forward the less volatile products. The material thus collected was freed from most of the hexafluoride by keeping it at -60° in one trap connected to another at -180° , the pressure in the system being 10^{-2} mm. Before the trap at -180° was detached, the residue was allowed to warm to -50° . Afterwards it was transferred, in 10 c.c. lots, to an air-cooled reflux column, 23 cm. \times 3 mm. fitted throughout its length with a spiral of cupronickel wire (36 s.w.g.), and provided at the head with a thermocouple in a narrow well. Total reflux was maintained for 5 min. to expel hexafluoride after which distillation was allowed to proceed until the take-off temperature became steady. From this point a reflux ratio of about 3 : 1 was maintained and successive fractions boiling at 59° were collected. The apparatus was a closed system thus enabling the fractions to be transferred to break-seal storage bulbs without coming into contact with the air. As soon as the boiling point began to rise the distillate was rejected and this was continued until a second steady boiling temperature of 134° was reached. Excessive reflux, causing the column to flood, was avoided by now surrounding the column with a paper tube. The temperature remained steady at the higher boiling point until the still was empty. Vapour-density measurements on the successive fractions at each of the steady boiling points showed that the materials were uniform and presumably of high purity. A careful examination of the hexafluoride head fraction, made by distilling it in a Podbielniak column, failed to disclose any impurity.

Trap-to-trap distillation, with rigorous temperature control, was also used in the purification of the decafluoride. In some instances the hexafluoride was removed by its selective hydrolysis. For this purpose the crude product was first condensed on ice at -180° and then allowed to warm slowly to room temperature: afterwards the unhydrolysed layer was separated, dried on "Anhydrone," and distilled.

The very high-boiling material collected from the reaction tube itself was not easy to fractionate. At 20° , under a pressure of 10^{-3} mm., it distilled extremely slowly; only 0.5 c.c. of liquid was collected during 6 hr. in a trap immersed in liquid oxygen.

Measurement of the Physical Properties.—For vapour-density measurements, the Dumas method using "Pyrex" bulbs was employed for both Te_2F_{10} and $\text{Te}_3\text{F}_{14}\text{O}_2$. More accurate figures for the decafluoride were obtained by weighing the vapour at 80—100 mm. in bulbs of

30—300 c.c. capacity. The samples were freed from more volatile material as thoroughly as possible, and taps were avoided since grease absorbs the fluoride.

The apparent molecular weight of the very high-boiling product was determined on a modified Victor Meyer apparatus operating at 40—50 mm. and a bulb temperature of 150°. The accuracy was $\pm 8\%$.

The density of Te_2F_{10} was obtained by use of a calibrated bulb with a capillary stem.

Temp. ($^{\circ}\text{K}$)	296	289	275.5	261.7	247.5	236.2
Density (g./c.c.)	2.8390	2.8673	2.9255	2.9855	3.0436	3.0916

The surface tension was measured by using two capillary tubes of different, known diameters mounted with the liquid in a sealed vessel.⁹

Temp. ($^{\circ}\text{K}$)	311	296.2	274.5	258	257
Surface tension (dynes cm^{-1}) (a)	12.94	15.07	17.51	19.25	—
(b)	—	14.85	—	—	19.67

(a and b refer to different pairs of capillaries.)

The determination of the viscosity has been described elsewhere.¹⁰ The values ranged from 26.66 mP at 14.55° to 11.17 mP at 69.30°.

The cell and the method of measurement used in the determination of conductivity will be described in a later communication.

The infrared spectrum was examined on a Grubb-Parsons S3 single-beam infrared spectrometer, standard technique being used. It was necessary to have the potassium bromide windows of the cell extremely dry; this was effected by keeping them at a pressure of 10^{-4} mm. for a week.

Materials.—Both tellurium and its oxides, derived from AnalaR telluric acid, and also commercial grades of these materials were used without significant difference in result. The fluorine was obtained from a 10 A Imperial Chemical Industries cell. In experiments made without oxygen the halogen stream was run to waste for some time before beginning, and the nitrogen was scrubbed four times with concentrated alkaline pyrogallol.

Analyses.—Tellurium was determined as the element after prolonged reduction of a solution in 1 : 3 hydrochloric acid by means of hydrazine and sulphur dioxide. The fluorine, separated as described by Huckabay, Welch, and Metler,¹¹ was precipitated and weighed as lead chlorofluoride.

The preparation of solutions suitable for analysis from the tellurium fluorides was difficult. It was achieved by dissolving them in concentrated alcoholic sodium hydroxide containing 10% of pyridine. This solution was then converted into a 1 : 3 hydrochloric acid solution for the determination of tellurium, or used directly in the distillation procedure for fluorine.

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⁹ Mills and Robinson, *J.*, 1927, 1823.

¹⁰ Hetherington and Robinson, *J.*, 1956, in the press.

¹¹ Huckabay, Welch, and Metler, *Analyt. Chem.*, 1947, **19**, 154.