

Reactions of Tellurium Hexafluoride with Alcohols: Preparation and Properties of Mono- and Di-alkoxotellurium(vi) Fluorides

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The compounds $\text{Te}(\text{F})_5\text{OR}$ (I; R = Me, Et, Prⁿ, Prⁱ, Buⁿ, Buⁱ, or Bu^s) and $\text{TeF}_4(\text{OR})_2$ (II; R = Me, Et, Prⁿ, or Prⁱ) have been synthesised by the reaction of tellurium hexafluoride with the corresponding alcohol. The asymmetric molecules $\text{TeF}_4(\text{OMe})\text{OR}$ (III; R = Et, Prⁿ, or Prⁱ) have been synthesised by the reaction of the alkoxotellurium pentafluoride with methanol. Chemical and physical properties of these molecules are discussed.

UNTIL recently tellurium hexafluoride had been little investigated, but in the last few years it has been shown to undergo many reactions. It is a weak Lewis acid, reacting with trimethylamine to form the complex $\text{TeF}_6 \cdot 2\text{NMe}_3$,¹ and with caesium fluoride to produce

$\text{Cs}_2[\text{TeF}_8]$.² Tellurium hexafluoride has also been used as a starting material to prepare other tellurium(vi)

¹ E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 1957, **79**, 2975.

² E. L. Muetterties, *J. Amer. Chem. Soc.*, 1957, **79**, 1004.

fluorides. It reacts with (dialkylamino)trimethylsilanes to produce a variety of compounds including dialkylaminotellurium pentafluorides $\text{Te}(\text{F})_5\text{NR}_2$ and bis(dialkylamino)tellurium tetrafluorides $\text{TeF}_4(\text{NR}_2)_2$.³ The reaction of tellurium hexafluoride with methanol produces the mono- and di-methoxy-derivatives $\text{Te}(\text{F})_5\text{OMe}$ and $\text{TeF}_4(\text{OMe})_2$,⁴ but with trimethylsilanol tellurium hexafluoride forms $\text{Te}(\text{F})_5\text{OH}$.⁵

RESULTS AND DISCUSSION

Reactions between tellurium hexafluoride and some simple alcohols have been studied in detail and the products characterised. The latter were shown to depend on the relative concentrations of the alcohols and tellurium hexafluoride, and also on the base used to remove

$\text{Te}(\text{F})_5\text{OH}$] were prepared using sodium fluoride, but the time for complete reaction increased with the number of carbon atoms in the alcohol. Thus, methanol formed (I; R = Me) in a few hours, but the corresponding reaction with ethanol took 3–4 d and the propanol and butanol reactions were not complete after 1 week. Because the b.p.s of compounds (I) (Table) and the corresponding alcohols were close to each other, they were difficult to separate and this method is, therefore, only useful for preparing the (I; R = Me).

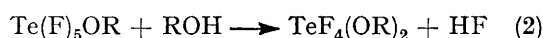
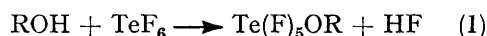
The other compounds (I) and those of (II) were most easily prepared using py to remove hydrogen fluoride formed according to equations (1) and (2). When the reactions were complete with molar concentrations of alcohol, tellurium hexafluoride, and py in the ratio

B.p.s ($\theta_c/^\circ\text{C}$), yields (%), analyses (%), and i.r. (cm^{-1}), ^1H (τ), and ^{19}F n.m.r. spectra for the alkoxotellurium fluorides

Compound	B.p. (P/mmHg)	Yield	Analyses						$\bar{\nu}$ (Te-F)	^1H N.m.r.†	^{19}F N.m.r. spectra (CFCl_3)		
			Found			Calc.					$\delta_A/$ p.p.m.	$\delta_B/$ p.p.m.	$J(\text{AB})$ /Hz
$\text{Te}(\text{F})_5\text{OMe}$	58	75	5.1	1.6	*	4.7	1.2	37.4	720	5.75, $J(\text{HF}_B)$ 1 Hz	+45.7	+58.2	179
$\text{Te}(\text{F})_5\text{OEt}$	78	73	9.6	2.1	34.9	9.0	1.9	35.4	720	5.4(2), 8.55(3)	+44.3	+55.6	179
$\text{Te}(\text{F})_5\text{OPr}^n$	96	74	12.0	2.5	34.2	12.8	2.5	33.7	720	5.45(2), 8.15(2), 8.95(3)	+44.4	+56.3	181
$\text{Te}(\text{F})_5\text{OPr}^i$	88	70	12.4	2.8	33.7	12.8	2.5	33.7	715	4.9(1), 8.55(6)	+42.5	+52.6	181
$\text{Te}(\text{F})_5\text{OBu}^n$	82(200)	66	17.0	3.5	32.5	16.2	3.0	32.0	715	5.45(2), 8.1—8.8(4), 9.0(3)	+44.0	+55.6	179
$\text{Te}(\text{F})_5\text{OBu}^i$	88(400)	52	16.8	3.2	31.4	16.2	3.0	32.0	720	5.7(2), 7.95(1), 9.0(6)	+43.2	+55.1	181
$\text{Te}(\text{F})_5\text{OBu}^s$	89(400)	60	16.4	3.1	32.5	16.2	3.0	32.0	715	5.05(1), 8.3(2), 8.55(3), 9.0(3)	+42.0	+52.3	182
$\text{TeF}_4(\text{OMe})_2$	88(150)	63	9.5	2.5	27.5	9.0	2.3	28.6	680	5.85 $J(\text{HF}_B)$ 1 Hz	+51.0	+61.7	155
$\text{TeF}_4(\text{OEt})_2$	89(50)	65	16.2	3.5	26.0	16.3	3.4	25.8	690	5.55(4), 8.65(6)	+46.5	+54.9	158
$\text{TeF}_4(\text{OPr}^n)_2$	93(20)	65	22.9	4.7	23.4	22.5	4.8	23.6	690	5.75(4), 8.30(4), 9.1(6)	+46.9	+56.0	158
$\text{TeF}_4(\text{OPr}^i)_2$	78(15)	67	23.0	4.9	23.4	22.5	4.8	23.6	670	5.1(2), 8.65(12)	+42.9	+49.1	162
$\text{TeF}_4(\text{OMe})(\text{OEt})$	56(20)	63	12.2	2.5	27.3	12.9	2.9	27.1	680	5.9(3), 5.5(2), 8.65(3)			Complex
$\text{TeF}_4(\text{OMe})(\text{OPr}^n)$	86(50)	63	16.2	3.4	24.6	16.3	3.4	25.8	675	5.9(3), 5.65(2), 8.25(2), 9.0(3)			Complex
$\text{TeF}_4(\text{OMe})(\text{OPr}^i)$	65(20)	65	17.1	4.0	25.0	16.3	3.4	25.8	690	5.95(3), 5.0(1), 8.65(6)			Complex

* The compound $\text{Te}(\text{F})_5\text{OMe}$ is too volatile for F analysis. † The number of H atoms is given in parentheses.

hydrogen fluoride which is formed according to equations (1) and (2). The alkoxotellurium pentafluorides, (I), were the only products formed when the reactions were



carried out in the presence of sodium fluoride, whereas the dialkoxotellurium tetrafluorides, (II), were produced in the presence of anhydrous sodium carbonate. When pyridine (py) was used the reaction was more complex, since both the mono- and di-alkoxy-compounds and, in the presence of excess of py, the alkylpyridinium salts $[\text{Rpy}][\text{Te}(\text{F})_5\text{O}]$ and $[\text{Rpy}][(\text{RO})\text{Te}(\text{F})_4\text{O}]$ were isolated. The latter were formed because alkoxotellurium fluorides are strong alkylating agents (comparable in alkylating power with dialkyl sulphates) and they will be discussed, together with other alkylating products, elsewhere.⁶

All compounds (I), except the tertiary alkoxy-derivatives [(I; R = Bu^s) decomposes into iso-butene and

2 : 2 : 1, the products were (I) together with small quantities of (II) from which they can be purified by distillation. However, when the ratio was 2 : 1 : 1, only compounds (II) were formed. Mixed alkoxy-compounds $\text{RO}(\text{R}'\text{O})\text{TeF}_4$, (III), were prepared by reacting (I) with the alcohol R'OH in the presence of py. Higher yields for the alkoxy-methoxy-derivatives $\text{MeO}(\text{RO})\text{TeF}_4$ were obtained when (I) reacted with methanol rather than (I; R = Me) with the alcohol, since in the latter reaction the methylpyridinium salt $[\text{Mepy}][\text{Te}(\text{F})_5\text{O}]$ was also formed.⁶

The alkoxotellurium fluorides are colourless, volatile, powerful-smelling liquids which are insoluble in water and soluble in many organic solvents. Some of the physical properties of the compounds are listed in the Table. The ^1H n.m.r. spectra were in agreement with those expected for the appropriate alkoxy-groups and, in some cases, fine structure due to HF coupling was observed. ^{19}F N.m.r. spectra of compounds (I) were analysed as typical AB_4 patterns similar to other pentafluorotellurium(VI) compounds³ in which one position of

³ G. W. Fraser, R. D. Peacock, and P. M. Watkins, *J. Chem. Soc. (A)*, 1971, 1125.

⁴ A. Clouston, R. D. Peacock, and G. W. Fraser, *Chem. Comm.*, 1970, 1197

⁵ G. W. Fraser and J. B. Millar, *J.C.S. Chem. Comm.*, 1972, 1125.

⁶ G. W. Fraser, unpublished work.

the octahedron is occupied by another atom. The spectra of the symmetrical compounds (II) were analysed as typical A_2B_2 spectra, confirming that the alkoxo-groups occupy *cis*-positions in the octahedron. In some cases, a small single line was also observed which may have been due to the *trans*-isomer, but integration of the spectra showed that these compounds never occurred in more than a few percent concentration. In the asymmetric compounds (III), two of the fluorine atoms are no longer magnetically equivalent and since the spectra were more complex, as would be expected for an A_2BC system, they were not analysed.

I.r. spectra of the compounds in the vapour or liquid states were measured. Compounds (I) exhibited a strong absorption at *ca.* 720 cm^{-1} and this is assigned to a Te-F stretching vibration, in good agreement with that found in other compounds of the type $\text{Te}(\text{F})_5\text{X}$.³ In compounds (II), a strong absorption occurred at 680 cm^{-1} and this has also been assigned to a Te-F stretching vibration. The difference in frequency of these two intense bands means that a compound can be readily identified as (I) or (II) by means of its i.r. spectrum.

EXPERIMENTAL

¹H and ¹⁹F N.m.r. spectra were obtained on a Perkin-Elmer R10 (60 MHz) spectrometer, using tetramethylsilane and trichlorofluoromethane as internal-reference standards. I.r. spectra were recorded on a Perkin-Elmer model 457 spectrometer in the region $4\ 000\text{--}400\text{ cm}^{-1}$ with potassium-bromide windows.

Tellurium hexafluoride was prepared from tellurium powder and fluorine according to the reported procedure.⁷ All other materials were obtained from commercial sources; the alcohols and pyridine were distilled and dried over molecular sieves before use and sodium fluoride and anhydrous sodium carbonate were dried in an oven at $300\text{ }^\circ\text{C}$ and stored in desiccators until required.

Reactions of Alcohols with Tellurium hexafluoride in the presence of Sodium Fluoride.—Methanol. Methanol (1.3 g) and tellurium hexafluoride (10 g) were condensed at $-196\text{ }^\circ\text{C}$ into a reaction tube (400 cm^3) containing sodium fluoride (*ca.* 10 g). The tube was warmed to room temperature and left overnight, after which the volatile materials (MeOTeF_5 and a little unreacted TeF_6) were removed under vacuum and methoxotellurium pentafluoride, (I), was purified by distillation. Analytical data for this and other compounds are given in the Table. When a similar reaction was completed with an excess of MeOH, the reaction products were (I; R = Me) and unreacted methanol.

Other alcohols. The reactions were carried out in a similar manner to that described above. In all cases the reactions

were slow and did not reach completion overnight, the products being (I), unreacted tellurium hexafluoride, and alcohol. This method was not so convenient as the one using py and was little used to make compounds (I).

Reactions of Alcohols with Tellurium Hexafluoride in the Presence of Anhydrous Sodium Carbonate.—The reactions were carried out in a similar manner to those described above, using an alcohol : tellurium hexafluoride ratio of 2 : 1. The dialkoxotellurium tetrafluorides, (II), produced were purified by distillation under reduced pressure.

Reactions of Alcohols with Tellurium Hexafluoride in the Presence of Pyridine.—(a) *Preparation of compounds (I).* Methanol (1.3 g) and tellurium hexafluoride (10 g) were condensed into a reaction vessel (400 cm^3) containing py (1.6 g). The vessel was warmed to room temperature and left overnight. Compound (I; R = Me) was removed under vacuum and separated from the small quantity of (II; R = Me) by distillation. The other compounds (I) were prepared similarly.

(b) *Preparation of compounds (II).* Methanol (1.3 g) and tellurium hexafluoride (5 g) were condensed into a reaction vessel (400 cm^3) containing py (1.6 g). The vessel was warmed to room temperature and left overnight. Compound (II; R = Me) was removed under vacuum and distilled under reduced pressure. The other compounds (II) were prepared in a similar manner but, because of their low volatility, they distilled slowly under vacuum. Carbon tetrachloride (20 cm^3) was added to the reaction vessel and pyridinium fluoride removed from the mixture by extraction with very dilute hydrochloric acid. The carbon tetrachloride layer was dried over sodium sulphate; carbon tetrachloride was then removed by distillation under vacuum and compound (II) purified by distillation under reduced pressure.

Preparation of Unsymmetrical Dialkoxotellurium Tetrafluorides, (III).—Compound (I; R = Et) (3 g) was dissolved in carbon tetrachloride (10 cm^3) and methanol (0.4 g) added. The mixture was cooled to $-20\text{ }^\circ\text{C}$ and py (0.4 g) added dropwise. Pyridinium fluoride was removed by extraction with very dilute hydrochloric acid and the carbon tetrachloride layer separated and dried over sodium sulphate. Carbon tetrachloride was then removed by distillation under vacuum and the (III; R = Et) purified by distillation under reduced pressure. The other compounds (III) were prepared similarly.

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⁷ R. Campbell and P. L. Robinson, *J. Chem. Soc.*, 1956, 3454.