Reaction of Tetratellurium(2+) Bis(hexafluoroarsenate), $Te_4(AsF_6)_2$, and Hexatellurium(2+) Bis(hexafluoroarsenate), $Te_6(AsF_6)_2$, with Tetrafluoroethylene. The Preparation of Bis(perfluoroethyl) Mono- and Di-telluride

By **C. David Desjardins, Harvey L. Paige, Jack Passmore,*** and **Peter Taylor,** Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada

Solid $Te_4(AsF_6)_2$ and $Te_6(AsF_6)_2$ react with tetrafluoroethylene at 100 °C to give $(C_2F_5)_2Te_x$ (x = 1 or 2) and $C_4F_9TeC_2F_5$. In sulphur dioxide solution $Te_4(AsF_6)_2$ and tetrafluoroethylene yield $C_2F_5TeC_3F_6C(O)F$ in addition to products found for the neat reactions. $C_2F_5SeTeC_2F_5$ and $C_2F_5TeHgTeC_2F_5$ have also been prepared. Compounds were identified by their mass spectra, and by ^{19}F n.m.r. in the case of the perfluoroalkyl tellurides.

TETRAFLUOROETHYLENE reacts with $S_8(AsF_6)_2$ and $S_{16}(AsF_6)_2$ [1,2] to give bis(perfluoroethyl) polysulphides,[3] and with $Se_8(AsF_6)_2$ and $Se_8(Sb_2F_{11})_2$ to yield bis(perfluoroethyl) di- and tri-selenides.[4] We now report the results of the corresponding reaction of tetrafluoroethylene with $Te_4(AsF_6)_2$ and $Te_6(AsF_6)_2$ yielding bis(perfluoroethyl) mono- and di-tellurides. With the exception of bis(perfluoromethyl) ditelluride, made in small quantities by the reaction of perfluoromethyl radicals on a tellurium mirror,[5] perfluoroalkyls of tellurium(II) have not been previously prepared as far as we are aware. Perfluoroaryl derivatives of tellurium have been reviewed.[6] A preliminary communication of this work has been reported.[7]

EXPERIMENTAL

Apparatus.—Techniques used in this work have been described.[3,4] ^{19}F N.m.r. spectra were obtained on a Varian Associates HA 60 spectrometer operating at 56·4 MHz. V.p.c. analysis were obtained as in ref. 4 except the stationary phase used was Kel-F wax (Applied Science Laboratories) on 45/60 mesh Chromasorb W. Retention times (with respect to air) for $(C_2F_5)_2Te_2$, $C_2F_5TeSeC_2F_5$, $C_2F_5TeC_3F_6C[O]F$, $C_4F_9TeC_2F_5$, and $(C_2F_5)_2Te$ were 8·8, 4·7, 3·5, 2·2, and 0·6 min respectively with a 1 µl sample.

Reagents.—C_2F_4 (Columbia Organic Chemicals), tellurium 99·99% (Ventron Alfa Products), fluorine, and chlorine (Matheson Co.) were used without further purification. Sulphur dioxide (Matheson Co.) was dried over calcium hydride and redistilled before use. Arsenic pentafluoride was prepared by fluorination of arsenic trifluoride (Ozark–Mahoning). $Te_4(AsF_6)_2$ and $Te_6(AsF_6)_2$ were prepared according to ref. 8, and C_2F_5SeCl from chlorine and $C_2F_5SeSeC_2F_5$ as described in ref. 9.

Reaction of Solid $Te_4(AsF_6)_2$ *with* C_2F_4.—In a typical experiment $Te_4(AsF_6)_2$ (9·38 g, 10·57 mmol) was treated with an excess of C_2F_4 (*ca.* 15 atm) for 11 days at 100 °C in a Monel reactor (40 ml). The volatile products contained C_2F_4, C_2F_6, a yellow-red liquid (8·29 g), and AsF_3 (2·25 g, 80·6% of the arsenic). The yellow liquid was separated by freezing out the AsF_3 and decanting off the tellurides into an isolatable side-arm. Arsenic trifluoride was unambiguously identified by its physical properties and i.r. spectrum. A v.p.c. analysis of the yellow-red liquid showed it contained three major components. These three compounds were isolated on a preparative scale by v.p.c. and identified by mass spectroscopy. The distribution of products was 87% $(C_2F_5)_2Te$, 0·5% $C_4F_9TeC_2F_5$, and 12·2% $(C_2F_5)_2Te_2$. Mass spectra of the bulk liquid mixture also showed traces of $(C_4F_9)_2Te$ and $C_4F_9Te_2C_2F_5$. The yellow-red liquid incorporates 38% of the available fluorine from AsF_6^- (*i.e.* 3 fluorines per AsF_6^-) and 58% of the available tellurium. An unidentified reddish brown solid (2·78 g) was also obtained. The reaction was also carried out at 80 °C; lower yields were obtained [8·82 g $Te_4(AsF_6)_2$ yielded 3·32 g tellurides], and the distribution of products was different [56·5% $(C_2F_5)_2Te$ and 43·5% $(C_2F_5)_2Te_2$]. Traces of $(C_4F_9)_2Te$, $C_4F_9TeC_2F_5$, and $C_4F_9Te_2C_2F_5$ were also detected.

The exact yields of tellurides varied from reaction to reaction, even though conditions were kept constant. In general, however, increasing the temperature increased the overall yield of tellurides but decreased the proportion of ditelluride. Increase in pressure of C_2F_4 increased the rate of reaction and the yield increased as a function of time.

Reaction of Solid $Te_6(AsF_6)_2$ *with* C_2F_4.—In a typical reaction $Te_6(AsF_6)_2$ (6·11 g, 5·34 mmol) was treated with an excess of C_2F_4 (*ca.* 15 atm) in a Monel reaction vessel for 10 days at 100 °C. The volatile products contained C_2F_4, C_2F_6, AsF_3 (1·1 g, 80% of the available arsenic), and a yellow-red liquid (2·22 g). A v.p.c. analysis of the latter showed that it contained 41% $(C_2F_5)_2Te_2$, 56·5% $(C_2F_5)_2Te$, and 1·9% $C_4F_9TeC_2F_5$. Small traces of other material were

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also observed. Molecular ions attributable to the above species were observed in the mass spectrum as well as traces of $(C_4F_9)_2Te$ and $C_4F_9Te_2C_2F_5$. 23% Of the available fluorine and tellurium were incorporated into the tellurides. A grey solid (4·1 g) was also obtained. Its *X*-ray diffraction powder photograph showed that it contained elemental tellurium.

Reaction of $Te_4(AsF_6)_2$ *with* C_2F_4 *in* SO_2.—$Te_4(AsF_6)_2$ (9·34 g, 10·52 mmol) was dissolved in sulphur dioxide (12 g) in a Monel vessel. Excess of C_2F_4 was added (*ca.* 15 atm) and the mixture heated at 100 °C for 12 days. The volatile products were C_2F_4, C_2F_6, SO_2, traces of CO, OSF_2, and a carbonyl-containing species [which, from the position of the CO peak in the i.r. region, is probably $C_3F_7C(O)F$], AsF_3, (1·91 g, 69% of the available arsenic), and a yellow-red liquid (3·37 g). An unidentified solid mixture (6·1 g) remained which contained small amounts of white crystalline TeF_4. V.p.c.–mass spectra of the yellow-red liquid showed it contained 43% $(C_2F_5)_2Te$, 40% $(C_2F_5)_2Te_2$, 13% $C_4F_9TeC_2F_5$, 3·5% $C_2F_5TeC_3F_6C(O)F$, and traces of $(C_4F_9)_2Te$, $C_4F_9Te_2C_2F_5$, and $C_2F_5TeC_3F_7$. 17% Of the available fluorine and 26% of the available tellurium were incorporated into the tellurides. The reaction was also carried out at 80 °C and gave the same products with a similar overall yield. A v.p.c.–mass spectrum study showed the distribution to be 20% $(C_2F_5)_2Te$, 71% $(C_2F_5)_2Te_2$, 2% $C_4F_9TeC_2F_5$, 7% $C_2F_5TeC_3F_6C(O)F$, and similar trace products.

Bis(perfluoroethyl) Monotelluride.—This compound is a pale yellow liquid, whose vapour pressure in the range $-22·8$ to 0 °C is described by the equation $\log_{10} p(\text{mmHg}) = 8·4 - 1850/T$. The molar heat of vaporisation was 8470 cal mol^{-1}, the extrapolated b.p. 64°, Trouton's constant 25 cal mol^{-1} K^{-1} (Found: C, 12·9; F, 51·75; Te, 34·8. Calc. C, 13·13; F, 51·97; Te, 34·90%). The analysis was performed by Alfred Bernhardt, West Germany.

Bis(perfluoroethyl) Ditelluride.—This compound is a reddish liquid, which readily decomposes in light to give the monotelluride and tellurium. Tellurium was also deposited on transfer in the vacuum line. It was however stable in the dark at -18 °C during a period of months. Vapour-pressure measurements were unreliable due to monotelluride formation. The vapour pressure at 25 °C is *ca.* 4·6 mmHg.

Bis(perfluoroethyltellurio)mercury.—A mixture of bis(perfluoroethyl)mono- and di-tellurides was agitated with mercury in a Monel vessel for several days. The monotelluride was condensed out of the reaction vessel, and the $(C_2F_5Te)_2Hg$ was separated from elemental mercury by extraction with acetone.

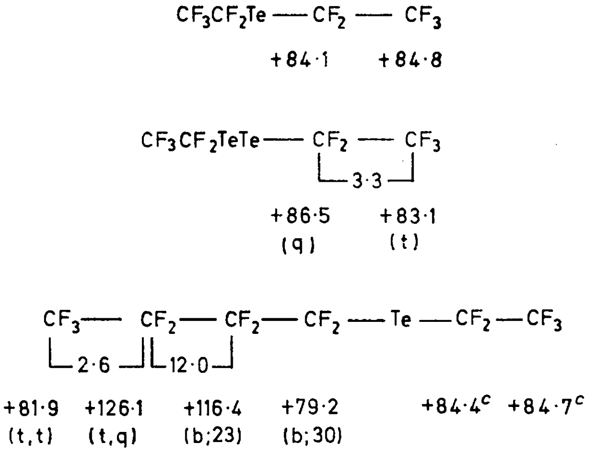
Bis(perfluoroethyl) Selenide Telluride.—A slight excess of C_2F_5SeCl was condensed into $(C_2F_5Te)_2Hg$ after which the mixture was warmed up to room temperature and then set aside for 30 min. Reaction took place rapidly, giving a yellow liquid and a white solid. A v.p.c. analysis of the liquid showed it to contain $C_2F_5SeTeC_2F_5$ (60%), $C_2F_5Se_2C_2F_5$ (34%), and $C_2F_5Te_2C_2F_5$ (6%). A v.p.c.-purified sample of $C_2F_5SeTeC_2F_5$ was shown by v.p.c. to decompose slightly when set aside for two weeks at -18 °C to give diselenide and ditelluride.

RESULTS AND DISCUSSION

Solid $Te_4(AsF_6)_2$ reacts with gaseous tetrafluoroethylene at 80 and 100 °C to give arsenic trifluoride, bis(perfluoroethyl) mono- and di-tellurides, lesser amounts of perfluoro(n-butyl ethyl) monotelluride, as well as traces of bis(perfluoro-n-butyl) monotelluride, and perfluoro(n-butyl ethyl) ditelluride. Substantially the same results are given using solid $Te_6(AsF_6)_2$ as a reactant. The relative proportion of bis(perfluoroethyl) monotelluride increases with reaction temperature, presumably by thermal elimination of a tellurium atom from the ditelluride. Increase in temperature also increases the yield of perfluoro-n-butyl derivatives. A similar increase in yield of perfluoro-n-butyl compounds on increase of reaction temperature was observed in the analogous reactions of tetrafluoroethylene and $Se_8(AsF_6)_2$.[4]

Bis(perfluoroethyl) mono- and di-telluride and perfluoro(n-butyl ethyl) monotelluride were isolated and characterized by their ^{19}F n.m.r. spectra (see Table), and mass and i.r. spectra [see Supplementary Publication No. 21215 (3 pp.)].* Other trace products were identified from mass spectra but not isolated. The mass spectra contain molecular ions and fragments with the appropriate isotopic distribution that are consistent with the given formulations. Small but variable amounts of bis(perfluoroethyl) monotelluride are observed in the spectra of bis(perfluoroethyl) ditelluride, and may come from trace impurities or by loss of tellurium in the mass spectrometer.

^{19}F N.m.r. of perfluoroalkyl tellurides [a]



[a] In p.p.m. from CCl_3F used as an internal standard. [b] Broad and unresolved peak, width at half peak height given in Hz. [c] Complex splittings.

Bis(perfluoroethyl) ditelluride has chemical shifts and coupling constants given in the Table, although the spectrum is more complicated than that expected from a simple A_2X_3 system. It may be that the methylene fluorines are non-equivalent. Additional complexity also is observed for $(C_2F_5)_2Se_2$ and $(C_2F_5)_2S_2$.[10] It may be that there is some coupling across the Group VI atoms, and/or there may exist preferred rotamers giving rise to complications in the spectra. It is noted that there is coupling between the CF_3 and CF_2 in different C_2F_5 groups in $(C_2F_5)_2O$, $(C_2F_5)_2NCF_3$, and $(C_2F_5)_3N$,[11] and

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* For details of the Supplementary Publications scheme, see Notice to Authors No. 7, *J.C.S. Dalton*, 1973, Index issue.

[10] Unpublished results.

[11] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution N.M.R. Spectroscopy,' Pergamon Press, Oxford, 1966, vol. 2.

complex spectra were observed for $(C_2F_5)_2SF_2$,[12] and $(C_2F_5)_2SeF_2$.[10] The spectrum of bis(perfluoroethyl) monotelluride is very complex and there is most probably second-order coupling between the CF_3 and CF_2 fluorine atoms. The chemical shifts and coupling constants for perfluoro(n-butyl ethyl) monotelluride (see Table) are similar to those for bis(perfluoroethyl) telluride (C_2F_5 portion), and various straight-chain perfluorocarbon sulphides [13] (C_4F_9 portion).

Tetrafluoroethylene reacts with $Te_4(AsF_6)_2$ in sulphur dioxide solution at 100 °C to give products similar to those found in the neat reaction as well as relatively small amounts of $C_2F_5TeC_3F_6C(O)F$. The carbonyl compound was isolated in small quantities by v.p.c. The i.r. spectrum of the compound shows the presence of a carbonyl group, and the mass spectrum is consistent with the given formulation of the compound. The analogous reaction of tetrafluoroethylene with $Se_8(AsF_6)_2$ gave the carbonyl compound $C_2F_5Se_2CF_2C(O)F$ in *ca.* 40% yield.[4]

The reactivity of tetrafluoroethylene towards polyatomic cations studied so far is in the order, sulphur > selenium > tellurium. It appears that the more electrophilic the cation [1,2] the greater the ease of reaction. The mechanism of the tetrafluoroethylene–$Te_4(AsF_6)_2$ reaction may first involve addition of C_2F_4 to the π bond present in the Te_4^{2+} ion,[8,14] followed by steps similar to those suggested [3,4] for the $S_8(AsF_6)_2$ and $Se_8(AsF_6)_2$ reactions with tetrafluoroethylene. The structure of Te_6^{2+} is at present not known, although it probably contains a localized or delocalized π bond allowing for a similar addition of tetrafluoroethylene.

When reagent grade tellurium containing selenium impurity was used to prepare $Te_4(AsF_6)_2$, products of its reaction with tetrafluoroethylene included $C_2F_5SeSeC_2F_5$ and $C_2F_5SeTeC_2F_5$. The latter mixed selenium–tellurium compound was also prepared by the reaction of bis(perfluoroethyltellurio)mercury, with perfluoroethylselenium monochloride. Both $(C_2F_5Te)_2Hg$ and $C_2F_5SeTeC_2F_5$ were characterized by their mass spectra. The isotopic distribution found in both parent ions and fragments agreed with the calculated distributions.

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