SYNTHESIS OF BIS-PENTAFLUOROTELLURIUMOXIDE FLUOROCARBONS

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SUMMARY

    Xenon bis-pentafluorotelluriumoxide, $Xe(OTeF_5)_2$, reacts
with fluoroolefins to form fluorocarbons containing two TeF_5O
substituents. Olefins studied include tetrafluoroethylene,
perfluoropropylene, and perfluorocyclopentene. Yields of
these adducts are high (71-82%). Details of the synthesis
and characterization of these new fluorocarbons are presented.

INTRODUCTION

    Recently we reported [1] on the addition of TeF_5OX
(X=F,Cl) to fluoroolefins to produce TeF_5O- substituted
fluorocarbons, a new class of compounds.

$$TeF_5OX + \, \underset{}{>}C=C\underset{}{<} \longrightarrow TeF_5O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X$$
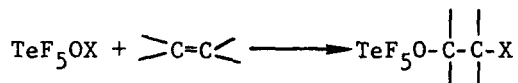
The excellent stability of these materials prompted an in-
vestigation of other routes to similar derivatives with a
greater number of TeF_5O- substituents. It is well estab-
lished that $Xe(OTeF_5)_n$ (n=2,4,6) compounds decompose under
thermal or photolytic conditions [2,3] to give TeF_5O radicals
which combine to form the corresponding peroxides. Since
fluorine radicals similarly produced from xenon fluoride
have often been successfully reacted with organic substrates
to prepare fluoro-derivatives [4], it seemed worthwhile to
attempt to trap the TeF_5O radicals with olefins. We now
report that bis-TeF_5O substituted fluorocarbons are obtained
from these reactions.

EXPERIMENTAL

Volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon FEP U-traps, 316 stainless steel bellows-seal valves, and a Heise Bourdon tube-type gauge. The synthetic reactions employed here were usually conducted in stainless steel cylinders. Infrared spectra were recorded on a Perkin Elmer Model 283 spectrophotometer using cells equipped with AgBr windows. Raman spectra were recorded at ambient temperature on a Cary Model 83 spectro-photometer with the use of the 488-nm exciting line of an Ar ion laser. Sealed Pyrex mp capillaries were used as sample containers. ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM390 spectrometer with internal $CFCl_3$ as a standard with a negative chemical shift being upfield from $CFCl_3$. Literature methods were used to prepare XeF_2[5] and TeF_5OH[3] which were then reacted to form $Xe(OTeF_5)_2$[6]. Olefins used were commercial products (PCR Research Chemicals).

Synthesis of 1,2-Pentafluorotelluriumoxide Tetrafluoroethane

A 100 ml Teflon FEP ampoule was loaded with $Xe(OTeF_5)_2$ (2.66 mmol) in the glove box. From the vacuum line C_2F_4 (4.00 mmol) was condensed into the ampoule at $-196^{\circ}C$ which was then warmed to ambient temperature for 2.5 d. At that point the volatile products were removed and separated by fractional condensation at -45 and $-196^{\circ}C$. The low temperature trap contained mainly Xe(2.45 mmol) plus some $TeF_5OCF_2CF_3$[1] and a little CF_3COF. The material retained at $-45^{\circ}C$ was a white solid which melted to a colorless liquid (mp$-14^{\circ}C$) with a vapor pressure of 5 mm at $0^{\circ}C$ and 17 mm at $20^{\circ}C$. It was identified as $(TeF_5O)_2C_2F_4$ on the basis of its vapor density molecular weight (g/mol; 573 Found, 577.2 calc.) and spectroscopic properties (see text). Since white powdery $(C_2F_4)_n$ was also produced and remained in the ampoule it was not possible to determine by visual inspection if all the $Xe(OTeF_5)_2$ had reacted. Therefore a second increment of C_2F_4(2.27 mmol) was added and allowed to react for 1 d as before. Nearly all the C_2F_4

was recovered but an additional 0.12 mmol of $(TeF_5O)_2C_2F_4$ was obtained. Overall the yield of the bis-TeF_5O compound was 82% (2.18 mmol) based on the limiting reagent, $Xe(OTeF_5)_2$. When this reaction was carried out in stainless steel vessels the amount of C_2F_4 polymerized was much higher, leaving most of the $Xe(OTeF_5)_2$ unreacted after the first treatment with C_2F_4.

Synthesis of 1,2-Pentafluorotelluriumoxide Hexafluoropropane

A 30 ml stainless steel Hoke cylinder was loaded with $Xe(OTeF_5)_2$(2.66 mmol) in the glove box. From the vacuum line $CF_3CF=CF_2$(3.00 mmol) was condensed into the cylinder at $-196^\circ C$ which was warmed to ambient temperature and then placed in an oven at $100^\circ C$ for 3 d. Separation of the products was accomplished by fractional condensation in a series of U-traps cooled at -30, -78, and $-196^\circ C$. No residue remained behind in the cylinder. The trap cooled at $-196^\circ C$ contained mainly Xe(2.8 mmol) plus some $CF_3CF=CF_2$ and a small amount of R_fCOF type material. The $-78^\circ C$ trap contained $TeF_5OCF_2CF_2CF_3$ and $TeF_5OCF(CF_3)_2$(0.15 mmol total) [1]. Retained at $-30^\circ C$ was a clear, colorless liquid (which remained liquid at $-78^\circ C$) with a vapor pressure of 3 mm at $0^\circ C$ and 11 mm at $20^\circ C$. This material was identified as $TeF_5OCF_2CF(OTeF_5)CF_3$ on the basis of the material balance of the reaction and its spectroscopic properties. The yield was 79% (2.10 mmol). During three weeks at ambient temperature no interaction of $Xe(OTeF_5)_2$ and $CF_3CF=CF_2$ was observable.

Synthesis of 1,2-Pentafluorotelluriumoxide Perfluorocyclopentane

In the same manner as described for the preceding example, $Xe(OTeF_5)_2$(2.94 mmol) and C_5F_8(3.20 mmol) were reacted at $100^\circ C$ for 7 d. In addition to the desired product and unreacted C_5F_8, the main by-products consisted of Xe(3.1 mmol) and $TeF_5OC_5F_9$(0.2 mmol)[1]. In the fractional condensation 1,2$(TeF_5O)_2C_5F_8$ was retained at $-23^\circ C$. It was a colorless liquid with a vapor pressure of 2-3 mm at $20^\circ C$ and was further

identified spectroscopically. The yield of the bis-TeF_5O
compound was 71% (2.09 mmol). When this reaction was examined
after 5 d at $100^{\circ}C$ the yield was 63% while in another experiment
conducted at $60^{\circ}C$ for 5 d only about 4-5% reaction of the
$Xe(OTeF_5)_2$ had occurred.

RESULTS AND DISCUSSION

     The transfer of the TeF_5O- groups from $Xe(OTeF_5)_2$ to
olefins can be described by the general equation:

$$Xe(OTeF_5)_2 + {>}C{=}C{<} \longrightarrow TeF_5O{-}C{-}C{-}OTeF_5 + Xe$$
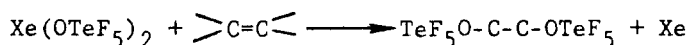
Yields in these reactions ranged from 71-82% and probably
would have been higher except that the limiting reagent,
$Xe(OTeF_5)_2$, apparently contained some $FXeOTeF_5$ [6] as an
impurity due to incomplete conversion of XeF_2 to $Xe(OTeF_5)_2$.
The reaction of this mixed ligand Xe compound with the
olefins accounts for the observed, low yields of the known
mono-TeF_5O adducts [1] consistently observed as by-products.

     The order of reactivity of the three olefins is $CF_2{=}CF_2{>}{>}$
$CF_3CF{=}CF_2{>}C_5F_8$. This is in keeping with a free radical attack
on the double bond wherein the degree of reactivity can be
correlated with steric and polar factors [7]. For comparison,
the closely related XeF_2 did not react with $CF_3CF{=}CF_2$ at
room temperature [8]. Other examples of analogous XeF_2-
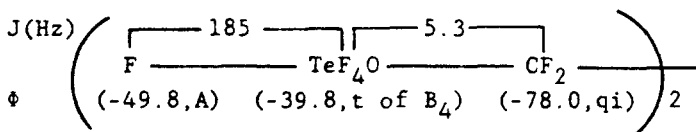fluoroolefin reactions are not known.

     All of the $(TeF_5O)_2R_f$ compounds are colorless liquids and
gases and are thermally stable to at least the $100^{\circ}C$ reaction
temperature. They have been stored for months at ambient
temperature in glass or stainless steel with no evidence of
decomposition. In addition to their identification on the

basis of the observed formation material balance, the new
compounds have been characterized spectroscopically. Most
useful in this regard is ^{19}F NMR spectroscopy. The TeF_5O-
group gives rise to AB_4 type NMR spectra owing to the magnetic
inequivalence of the axial fluorine compared to the four basal
fluorines. Thus the group might be better written as $FTeF_4O$-.
All the ^{19}F NMR spectra of the $(TeF_5O)_2R_f$ and the previously
reported TeF_5OR_f analogues [1] are similar to one another and
the narrow range of chemical shifts and coupling constants for
the TeF_5O- group is indicative of the close chemical similarity
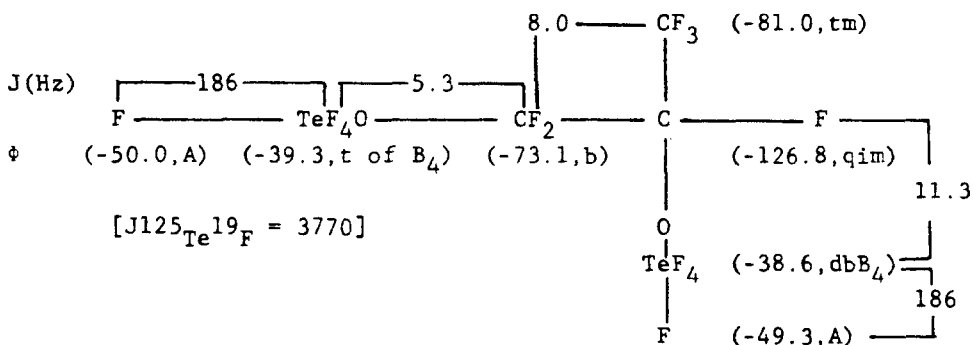of these compounds. Table I provides a summary of the ^{19}F NMR
data.

Examination of the NMR values with respect to area
ratios, chemical shifts, and multiplicities clearly
revealed the presence of two TeF_5O- groups in each
compound. For the symmetrical olefins these groups
were magnetically equivalent while for the unsymmetrical
$CF_3CF=CF_2$, the two TeF_5O- substituents were readily
distinguishable. However, it was not possible to
distinguish if cis or trans TeF_5O- substitution
prevailed with C_5F_8. For the ten mono- and bis-TeF_5O
substituted fluorocarbons prepared thus far, the range
of AB_4 chemical shifts observed is: A = -49.0 to -53.9
and B_4 = -38.3 to -42.6 ppm.

The vibrational spectra for the $(TeF_5O)_2R_f$ compounds
are given in Table II and the infrared and Raman spectra
of the propyl compound are shown in Figure 1. The expected
intense infrared absorptions attributable to C-F and C-O
stretching motions are present. In addition, in all cases
strong infrared bands are present at about 745, 720, and
320 cm^{-1} which are due to $\nu_{as}TeF_4$, $\nu TeF'$, and δTeF_4
respectively [1,9,10]. In the case of $TeF_5OCF_2CF(OTeF_5)CF_3$
two bands attributable to XF' are observed at 722 and 716
cm^{-1} confirming the slightly different molecular environment
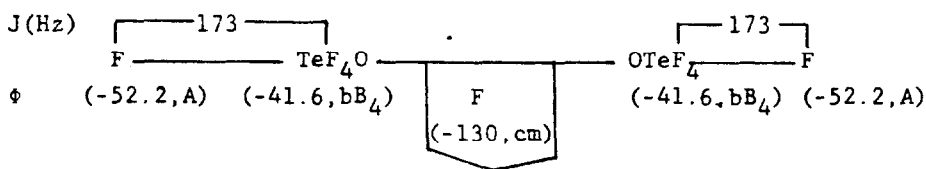of the two TeF_5- groups.

TABLE I

^{19}F NMR DATA[a]

J(Hz) ┌───── 185 ─────┐┌──── 5.3 ────┐
Φ (F ─────────── TeF$_4$O ─────────── CF$_2$ ───)$_2$
   (-49.8,A)   (-39.8,t of B$_4$)   (-78.0,qi)

    [J125$_{Te}$19$_F$ = 3770]

                                   8.0 ───── CF$_3$ (-81.0,tm)

J(Hz) ┌─────186─────┐┌──── 5.3 ────┐   │
Φ F ─────────── TeF$_4$O ─────────── CF$_2$ ─── C ─────── F ───┐
   (-50.0,A)   (-39.3,t of B$_4$)   (-73.1,b)   │   (-126.8,qim) │
                                                       11.3
    [J125$_{Te}$19$_F$ = 3770]   │
                                        O
                                      TeF$_4$ (-38.6,dbB$_4$)   186
                                        │
                                        F   (-49.3,A)

                                              [J125$_{Te}$19$_F$ = 3750]

J(Hz) ┌─────173─────┐   ┌──173──┐
Φ F ─────────── TeF$_4$O ───┐   ┌─── OTeF$_4$ ───────F
   (-52.2,A)   (-41.6,bB$_4$)   │ F │   (-41.6,bB$_4$) (-52.2,A)
                         (-130,cm)

                  [J125$_{Te}$19$_F$ = 3780]

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[a] CFCl$_3$ internal reference, negative chemical shift being upfield from the reference. Φ = chemical shift (ppm, multiplicity); where b-broad, c-complex, d-doublet, t-triplet, qi-quintet, and m-multiplet. Area ratios measured for these resonances agreed with the given assignments.

TABLE II

VIBRATIONAL SPECTRA OF $(TeF_5O)_2R_f$ COMPOUNDS

	Obsd. Freq., cm^{-1} (rel. intens.)[a]					
	$TeF_5OCF_2CF_2OTeF_5$		$TeF_5OCF_2CF(OTeF_5)CF_3$		$c\text{-}C_5F_8(OTeF_5)_2$	
Assign.	IR(gas)	Raman(liq.)	IR(gas)	Raman(liq.)	IR(gas)	Raman(liq.)
ν_{CC}		1355(0.6)p				
						1358(0.1)
ν_{CF}	1312 vw		1330 vw	1333(0.1)	1312 m	1310(0.2)p
	1280 vw	1298(0.06)	1293 w	1295(0.3)p	1263 m	1266(0.4)p
	1205 vs	1215(0.04)	1248 vs	1245(0.05)	1224 vs	1224(0.1)
	1190 sh	1185(0.08)p	1188 s	1183(0.06)		
			1172 s	1179(0.01)p	1165 ms	1165(0.1)p
	1105 vs	1103(0.06)p	1138 s	1137(0.03)p		
ν_{CO}	930 vw	928(0.02)p	1005 m	1005(0.1)p		1045(0.1)dp
	905 vw	896(0.09)p	992 m	993(0.05)p	987 vs	990(0.3)p
	885 vw	880(0.04)	888 vw	860(0.06)	875 vw	880(0.1)p
		835(0.03)p	825 vw	825(0.06)p		
	795 vw	758(0.07)p	785 vw			
$\nu_{as}TeF_4$	745 vs	742(0.15)p	747 vs	748(0.4)p	746 vs	744(0.3)p
$\nu TeF'$	720 vs	722(0.7)p	722 s	720 sh,p		
		704(2.2)p	716 s	715(2.2)p	713 m	712(2.3)p
$\nu_s TeF_4$	675 vw	676(10)p		678(10)p		678(10)p
		665 sh,p		665 sh,dp		
		620(0.05)p	630 vw	628(0.4)p		
		575(0.13)p		564(0.3)p	595 w	590(0.3)p
		550(0.15)p				510(0.2)p
	520 vw	530(0.2)p		525(0.15)p		408(0.1)p
						355(0.4)p
δFTe_4	320 s	315(0.8)dp	323 s	318(0.6)dp	319 s	316(0.7)dp
				290(0.4)p		
$\delta_{as}TeF_4$		265(0.9)dp		265(0.6)dp		265(0.5)dp
						245(0.2)
		178(0.4)p		175(0.5)p		168(1.1)p
		155(0.05)p		152(0.3)p		
		125 sh		125(0.6)p		133(0.2)
		110(0.6)p				115(0.4)p

[a]Uncorrected Raman intensities (peak heights)

In the Raman spectra, by far the most intense peak is the polarized band near 677 cm^{-1} which has no infrared counterpart and is readily assigned to $\nu_s TeF_4$[9,10]. Two depolarized bands near 317 and 265 cm^{-1} are assigned respectively to $\delta FTeF_4$ and $\delta_{as}TeF_4$. The second most intense Raman peak occurs at about 710 cm^{-1}, is polarized and is assigned

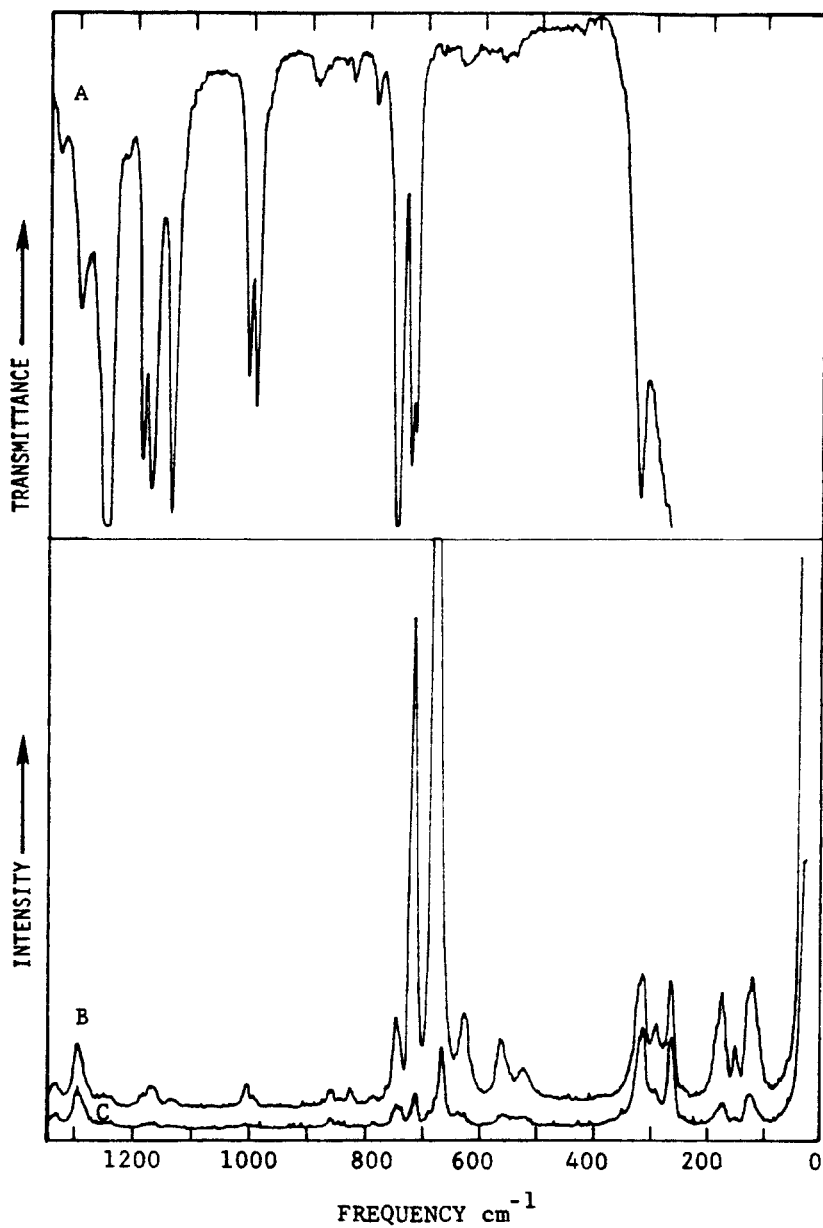Fig. 1. Vibrational Spectra of TeF₅OCF₂CF(OTeF₅)CF₃: Trace A, infrared spectrum of the gas (3 mm in 10 cm cell, AgBr windows); Traces B and C, Raman spectra of the liquid in a Pyrex capillary with the incident polarization parallel and perpendicular, respectively.

to νTeF'. For the highly symmetrical $TeF_5OC_2F_4OTeF_5$ a
splitting of νTeF into two bands is observed, attributable
to in phase and out of phase coupling of the two TeF'
stretching modes. The in phase motion gives rise to the
strong Raman band at 710 cm^{-1} which has no infrared counter-
part. The out of phase motion gives rise to the strong
infrared band at 720 cm^{-1} with a weak Raman counterpart
at 722 cm^{-1}. Again for the ethane derivative, the highly
symmetric nature of the compound is evidenced by a moderately
strong polarized Raman band at 1355 cm^{-1}. This peak is
assigned to ν_{CC} and occurs at 1228 cm^{-1} in CF_3CF_3[11]. The
constant intensity and narrow frequency range of the bands
assigned to the TeF_5- group serve as readily identifiable
characteristics of the TeF_5O- substituted fluorocarbons.
Therefore the vibrational spectra are wholly in accord with
the formulation of these new materials as $(TeF_5O)_2R_f$ moieties.

CONCLUSIONS

This study has shown that the reaction of $Xe(OTeF_5)_2$
with fluoroolefins is a useful high yield route to the
previously unknown $(TeF_5O)_2R_f$ compounds. These materials are
stable fluids comparable to the known mono-TeF_5O examples.

ACKNOWLEDGEMENT

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