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REACTIONS OF PENTAFLUOROTELLURIUM HYPOHALITES WITH FLUOROOLEFINS

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SUMMARY

Both pentafluorotellurium hypochlorite, TeF_5OCl, and hypofluorite, TeF_5OF, react with fluoroolefins to form TeF_5O- containing fluorocarbons, a new class of compounds. In the case of TeF_5OF, yields of the adducts are high (60-86%) but are lower (22-30%) with TeF_5OCl. In the latter case extensive chlorofluorination of the olefin occurs. Olefins studied include $CF_2{=}CF_2$, $CF_3CF{=}CF_2$, $CF_2{=}CFCl$, and perfluorocyclopentene. Details of the synthesis and characterization of these new fluorocarbons are presented.

INTRODUCTION

Examples of the addition of SF_5OX (X=F,Cl) to fluoroolefins to give SF_5O- containing fluorocarbons have been known for some time [1-4]. However in the case of the related SeF_5OX and TeF_5OX compounds, only one SeF_5OF-olefin adduct has been reported [5] and no SeF_5OCl or TeF_5OCl addition reactions have appeared. Recently we developed an improved synthesis of TeF_5OCl [6] and discovered a synthetic route to the previously unknown TeF_5OF [7]. With those materials in hand it was of interest to study their reactions with fluoroolefins as a possible route to TeF_5O- substituted fluorocarbons. In this paper we report that TeF_5O- containing fluorocarbons are obtained from these addition reactions.

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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 AgCl, AgBr, or CsI windows. The ^{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 $CFCl_3$.

The TeF_5OF employed herein was prepared from $Cs^+TeF_5O^-$ and $FOSO_2F$ by reaction at -45°C [7]. The TeF_5OCl was prepared by reacting TeF_5OH and $ClOSO_2F$ at temperatures below and up to ambient [6]. Olefins employed were commercial materials (PCR Research Chemicals).

General prodedure: Typically a 30 ml stainless steel Hoke cylinder was cooled to -196°C and measured amounts of reactants were successively condensed into the cylinder from the vacuum line. The closed cylinder was allowed to slowly warm to ambient temperature in either a cold empty Dewar or one partially filled with dry ice. Since the TeF_5OCl-olefin reactions gave low yields under these conditions due to an uncontrollable side reaction, more moderate conditions were also examined for these systems. These included slower warming from -196°C in a dry ice block cooled to -196°C, slow addition of the olefin vapor to liquid TeF_5OCl held at -78°C, and the use of C_2F_5Cl as solvent at -78°C. The yields of TeF_5O- adducts remained at 20-30%. Numerical data for the synthesis reactions are shown in Table I.

After the desired reaction time, usually 1-2 days, the reactor was cooled to -196°C and any noncondensable gas present was removed. While rewarming to ambient temperature the condensable products were separated by fractional condensation in a series of U-traps on the vacuum line. The

TABLE I

REACTION PARAMETERS

Reactants (mmol)	Trapping Temp. °C	Products (% yield)[a]	Vap. Dens. (g/mol) Calc.	Vap. Dens. (g/mol) Found
TeF_5OF(1.42) $CF_2=CF_2$(2.30)	-112	$TeF_5OCF_2CF_3$(60) TeF_6, $(C_2F_4)_n$	357.6	355
TeF_5OF(0.65) $CF_3CF=CF_2$(0.81)	-95	$TeF_5OC_3F_7$(78) TeF_6	407.6	404
TeF_5OF(1.65) c-C_5F_8(1.78)	-45	$TeF_5OC_5F_9$(86) TeF_6	469.6	467
TeF_5OF(0.41) $CF_2=CFCl$(0.47)	-112	$TeF_5OC_2F_4Cl$(67) TeF_6, CF_3CF_2Cl	374.1	371
TeF_5OCl(2.58) $CF_2=CF_2$(3.07)	-112	$TeF_5OCF_2CF_2Cl$(30) CF_3CF_2Cl(70), $(TeF_4O)_n$	374.1	372
TeF_5OCl(2.59) $CF_3CF=CF_2$(2.78)	-95	$TeF_5OCF_2CFClCF_3$(22) i-C_3F_7Cl(73), $(TeF_4O)_n$	424.1	426

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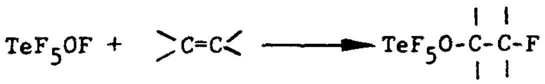
[a] Recovered olefin not included. Yield based on limiting reagent.

desired products were retained at the temperature shown in Table I, and a lower temperature trap and a higher temperature trap were used to remove by-products or unreacted materials. One or more repetitions of the fractionation procedure were used to complete the purification. Product identification was based on the observed material balance of the synthetic reaction, vapor density molecular weight determination, ^{19}F NMR spectroscopy, and infrared spectroscopy.

RESULTS AND DISCUSSION

The additions of TeF_5OF to fluoroolefins are described by the general equation.



$$TeF_5OF + \rangle C{=}C\langle \longrightarrow TeF_5O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}F$$

Yields in these reactions ranged from 60-86%. The products are all colorless liquids and gases which are thermally stable and can be recovered unchanged after 16 hours at 95°C in stainless steel vessels. Several months storage at ambient temperature has not resulted in any detectable decomposition. In addition to their identification on the basis of material balance and vapor density measurements, these new compounds have been spectroscopically characterized.

The most powerful tool 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 $FTeF_4O$-. The diverse appearance of the complex spectra possible for AB_4 systems has been illustrated for a number of SF_5- containing compounds [8]. However, all of the ^{19}F NMR spectra of the new TeF_5OR_f compounds 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 II provides a summary of the ^{19}F NMR data.

TABLE II

^{19}F NMR data[a]

J(Hz)		185		5.5		2.3			
	F		TeF_4O		CF_2		CF_3		
Φ	-49.7(A)		-40.0(t of B_4)		-80.2(cm)		-87.4(t)		
J(Hz)		179		5.3		1.45			
	F		TeF_4O		CF_2		CF_2Cl		
Φ	-49.5(A)		-40.2(t of B_4)		-78.0(qi,t)		-73.1(t)		
J(Hz)		180		5.4		0.9		8.1	
	F		TeF_4O		CF_2		CF_2		CF_3
Φ	-53.9(A)		-42.6(t of B_4)		-76.6(cm)		-132.8(t)		-84.6(t)
							9.5		
J(Hz)		185		5.4		6.7		6.7	
	F		TeF_4O		CF_2		CFCl		CF_3
Φ	-49.7(A)		-39.9(t of B_4)		-71.7(cm)		-139.7(s)		-79.2(t,d)
J(Hz)		180		6.6		1.7			
	F		TeF_4O		CFCl		CF_3		
Φ	-49.0(A)		-38.3(d of B_4)		-69.5(qi,q)		-85.8(d)		
					2.2				
J(Hz)		∿185		∿11		2.2			
	F		TeF_4O		CF		$(CF_3)_2$		
Φ	-53.4(A)		-41.8(bB_4)		-132.7(bqi)		-84.3(s)		
J(Hz)		∿180							
	F		TeF_4O		C_5F_9				
Φ	-50.7(A)		-40.0(bB_4)		-131.6(cm)				

[a] $CFCl_3$ internal reference, negative shift being upfield from the reference. Φ = chemical shift, ppm (multiplicity); where b-broad, c-complex, d-doublet, t-triplet, q-quartet, qi-quintet, s-sextet, and m-multiplet. The $J^{125}Te^{19}F$ coupling constants observed varied in the range of 3750-3780 Hz. The area ratios measured for these resonances agreed with the given assignments.

Examination of the NMR values with respect to area ratios, chemical shifts, and multiplicities clearly revealed the presence of the TeF_5O- group in each compound. In addition these spectra also showed that when TeF_5OF reacted with unsymmetrical olefins both isomers possible from a non-regiospecific addition were formed.

$$TeF_5OF + CF_3CF{=}CF_2 \longrightarrow TeF_5OCF_2CF_2CF_3(70) + TeF_5OCF(CF_3)_2(30)$$

$$TeF_5OF + CF_2{=}CFCl \longrightarrow TeF_5OCFClCF_3(60) + TeF_5OCF_2CF_2Cl(40)$$

The numbers in parentheses represent the per cent of that isomer in the mixture. Using appropriate computer programs [9], it is possible to analyze and compute the second order spectra. This is illustrated in Figure 1 for one of the isomers from the TeF_5OF and C_3F_6 reaction. The B_4 part of the spectrum consists of two complex unsymmetrical doublets, one of which is well resolved. The well resolved doublet arises from the B_4 part of the TeF_5O- group in the n-propyl isomer with the further splitting into triplets being due to the adjacent CF_2 group. Ignoring this CF_2-TeF_4 coupling, the basic B_4 spectrum was computed and is shown in Figure 1 below the measured spectrum. Also illustrated is the observed and calculated A-portion of the spectrum. Two nine line patterns are present, the more intense one being due to the apical F of the more abundant $TeF_5OCF_2CF_2CF_3$ isomer. An excellent match of calculated and measured peaks is again apparent. These data therefore confirm the presence and nature of the two isomeric products.

Nearly identical product ratios of normal to iso isomers have been reported for the related hypofluorites, $FOClO_3$[10] and CF_3OF[11] in reactions with $CF_3CF{=}CF_2$. This lack of a directed addition can be interpreted in terms of relatively non-polar O-F bonds and a free radical reaction mechanism. The high yields obtained for the TeF_5OF—fluoroolefin reactions are in contrast to those experienced with lighter element hypofluorite-olefin systems. Thus CF_3OF[12], SF_5OF[1], and SeF_5OF[5] addition reactions are difficult to control and the latter gave no SeF_5O- containing compound with $CF_3CF{=}CF_2$.

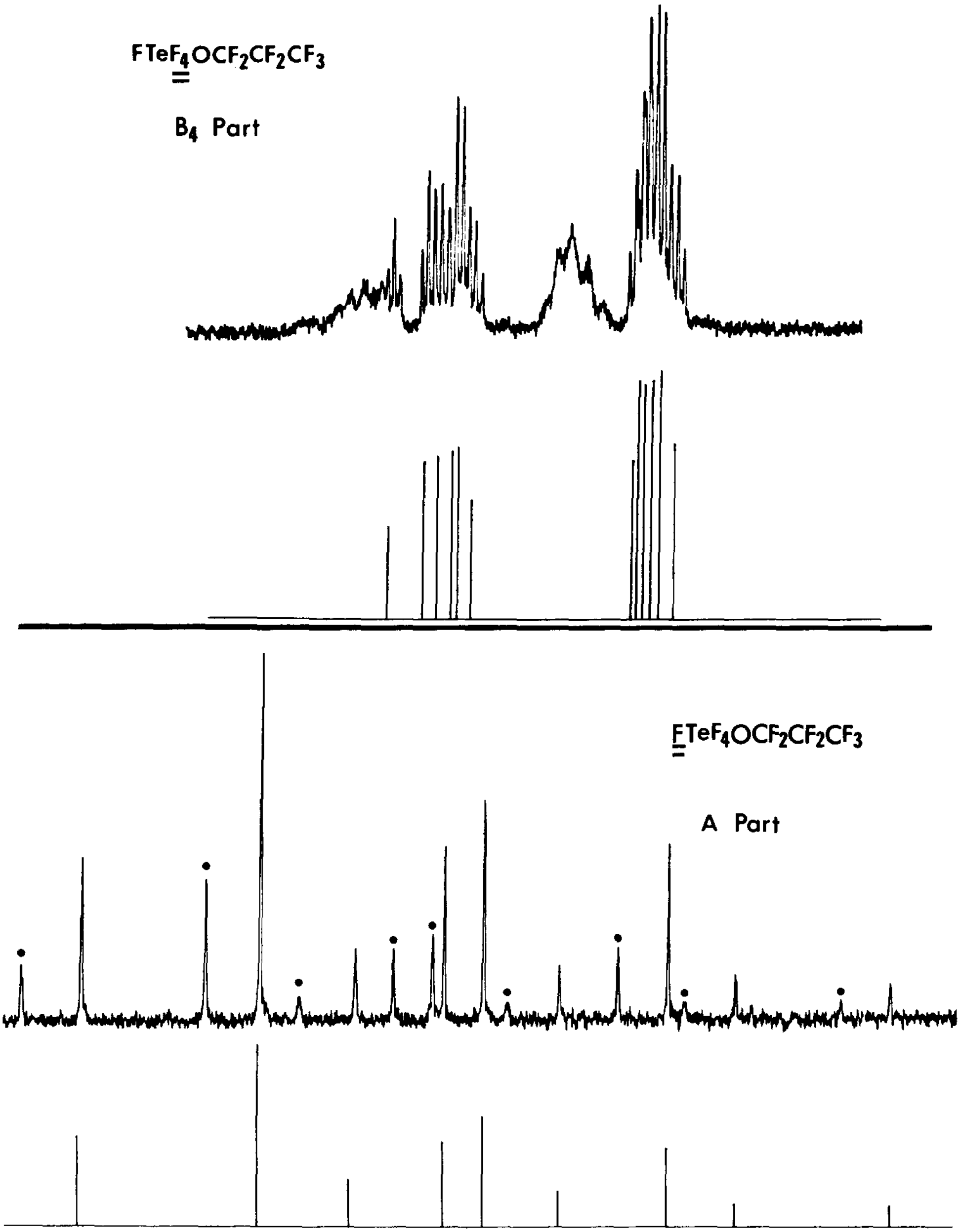


Fig. 1. Observed ^{19}F NMR spectrum of a mixture of $TEF_5OCF_2CF_2CF_3$ and $TeF_5OCF(CF_3)_2$ and the calculated A and B part of the n-propyl isomer. •Lines due to isopropyl isomer.

Since one of the characteristic reactions of covalent hypochlorites is their facile addition to olefins [13], it was anticipated that this reaction would also occur with TeF_5OCl. This was realized but the yields of the adducts were relatively low (22-30%) and the main products were the result of chlorofluorination of the olefin as shown in the equations.

$$TeF_5OCl + CF_2{=}CF_2 \longrightarrow TeF_5OCF_2CF_2Cl + CF_3CF_2Cl + (TeF_4O)_2$$

$$TeF_5OCl + CF_3CF{=}CF_2 \longrightarrow TeF_5OCF_2CFClCF_3 + (CF_3)_2CFCl + (TeF_4O)_2$$

The lower thermal stability of TeF_5OCl and its easy decomposition to ClF and 'TeF_4O' can account for the observed products. Monomeric 'TeF_4O' is unstable and was observed in the form of its nonvolatile, liquid dimer [14]. Attempts to moderate the TeF_5OCl addition reaction by slow mixing of the starting materials at -78°C or the use of a solvent, C_2F_5Cl, at -78° were not successful.

With the unsymmetrical olefin, $CF_3CF{=}CF_2$, and TeF_5OCl only one isomer was formed as shown by the NMR data in Table II. This behavior is comparable to the addition of $ClOClO_3$ to $CF_3CF{=}CF_2$[15] but differs from CF_3OCl which gave both isomers [11].

The infrared spectra for the TeF_5OR_f compounds are given in Table III. In addition to the expected strong bands due to C-F and C-O stretching motions there are intense absorptions attributable to the TeF_5- group. In all cases strong bands are present at about 745,720, and 325 cm^{-1} which are due to $\nu_{as}TeF_4$, $\nu TeF'$ and δTeF_4, respectively [7,16]. Their constant intensity and narrow frequency range serve as readily identifiable characteristics of TeF_5O- substituted fluorocarbons. Therefore the infrared spectra are wholly in accord with the formulation of these new materials as TeF_5OR_f moieties.

TABLE III

Infrared spectra of TeF_5OR_f compounds[a]

	$TeF_5OCF_2CF_3$	$TeF_5OCF_2CF_2Cl$	$TeF_5OCFClCF_3$[b]	$TeF_5OCF_2CFClCF_3$	$TeF_5OCF(CF_3)_2$ and $TeF_5OCF_2CF_2CF_3$	$c\text{-}C_5F_9OTeF_5$
ν_{C-F}					1350 w	
		1310 w	1320 w		1320 w	1321 s
				1297 ms	1300 w	
				1268 s	1265 sh	1279 ms
	1247 vs		1245 vs	1241 vs	1245 vs	1224 vs
	1190 vs	1198 vs			1210 m	
		1182 vs		1177 s	1170 s	1166 ms
		1128 s	1130 s	1136 ms	1145 s	
ν_{C-O}	1110 vs		1105 vs			
				987 s	1005 s	988 vs
		981 s	968 s	973 s		
$\nu_{as}XF_4$	745 vs	743 s	743 s	744 s	754 s	744 vs
$\nu XF'$	722 s	724 s	708 m	721 s	723 s	711 ms
δXF_4	328 s	324 s	322 s	325 s	322 s	319 s

[a] Band position cm^{-1}. Intensity: s, strong; m, medium; w, weak; v, very; sh, shoulder.

[b] Difference spectrum obtained by subtracting values for $TeF_5OCF_2CF_2Cl$ from a mixture of $TeF_5OCF_2CF_2Cl$ and $TeF_5OCFClCF_3$.

CONCLUSIONS

This study has shown that reactions of $TeF_5OX(X=F,Cl)$ with fluoroolefins are useful routes to the previously unknown class of TeF_5OR_f compounds. These materials are stable fluids comparable to the known SF_5O- and CF_3O- analogues.

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