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REACTIONS OF TeF_5OCl WITH FLUOROCARBON IODIDES AND SYNTHESIS OF CF_3OTeF_5

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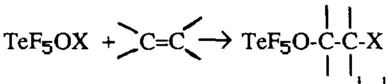
SUMMARY

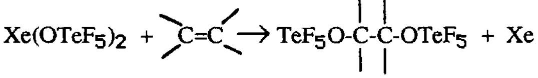
The low temperature reaction of TeF_5Cl with the fluorocarbon iodides, CF_3I, C_2F_5I, n-C_3F_7I, and i-C_3F_7I results in the formation of $R_fI(OTeF_5)_2$ adducts. Except for the trifluoromethyl derivative these are stable, colorless compounds. The trifluoromethyl adduct decomposes above -78°C to give the previously unknown CF_3OTeF_5. The perfluoroethyl and n-propyl adducts decompose at 120°C or under UV radiation giving $C_2F_5OTeF_5$ and n-$C_3F_7OTeF_5$, respectively. These reactions constitute a new synthesis of primary R_fOTef_5 compounds. Attempts to extend this synthesis to secondary fluorocarbon iodides were unsuccessful.

INTRODUCTION

Reactions of TeF_5OX (X=Cl,F) and $Xe(OTeF_5)_2$ with fluoroolefins are direct paths to TeF_5O- substituted fluorocarbons [1-3].



$$TeF_5OX + \rangle C{=}C\langle \longrightarrow TeF_5O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}X \tag{1}$$



$$Xe(OTeF_5)_2 + \rangle C{=}C\langle \longrightarrow TeF_5O\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}OTeF_5 + Xe \tag{2}$$

Because of the potentially useful properties of these derivatives it was of interest to investigate additional synthetic approaches, thus broadening the availability of the R_fOTeF_5 compounds. One promising approach involved the displacement of iodine from R_fI compounds

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using TeF_5OCl. This technique had previously been successfully employed to produce fluorocarbon fluorosulfates by the displacement of halogen from R_fHal species using $ClOSO_2F$ [4,5].

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 reactions 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 spectrophotometer with the use of the 488-nm exciting line of an Ar ion laser, and a premonochromator for the elimination of plasma lines. To avoid decomposition, the Raman spectrum of the yellow solid, $I(OTeF_5)_3$, was recorded at -140°C on a Spex Model 1403 spectrophotometer using the 647-nm exciting line of a Kr ion laser. Sealed quartz tubes, 3mm OD, or 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 negative chemical shifts being upfield from $CFCl_3$. Literature methods were used to prepare TeF_5OCl [6]. The fluorocarbon iodides were commercial products (PCR Research Chemicals and Columbia Organic Chemicals) which were stirred with Cu turnings and/or distilled before use.

<u>TeF_5OCl-R_fI Reactions.</u> A tared cylinder was cooled to -196°C and measured quantities of R_fI and TeF_5OCl were successively condensed in. The closed cylinder was placed in a dewar containing a liquid N_2-dry ice slush and this was allowed to warm slowly from -196 to -78°C in a dry ice chest. Monitoring the progress of the reaction at -78°C was accomplished by removing and measuring the evolved Cl_2 or other products volatile at -78°C. After a period of time at -78°C, the reaction mixtures were warmed slowly to ambient temperature to complete the oxidative addition reaction. For CF_3I the resulting adduct was unstable and decomposed above -78°C to give CF_3OTeF_5 (trapped at -126°C on fractionation) and other products. For the other fluorocarbon iodides, all volatile materials were removed at room temperature. In the cylinders remained the colorless addition compounds of composition, $R_fI(OTeF_5)_2$. These were low melting solids or liquids, $C_2F_5I(OTeF_5)_2$, 30-31°C; n-$C_3F_7I(OTeF_5)_2$, 49-51°C, and i-$C_3F_7I(OTeF_5)_2$, 16 - 17°C.

<u>$R_fI(OTeF_5)_2$ Decomposition Reactions.</u> In the dry box, a tared cylinder was loaded with a weighed amount of the $R_fI(OTeF_5)_2$ compound. The cylinder was then evacuated, closed and placed in an oven at 115-120°C for several hours. After recooling to ambient temperature, the contents of the reactor were separated by fractional condensation, measured, and identified by their infrared and ^{19}F NMR spectra. In addition to the R_fOTeF_5 product

generally obtained (see text), the significant volatile products were R_fI and some R_fF. Lesser amounts of TeF_6 and TeF_5OTeF_5 [7] were sometimes encountered. Left behind in the cylinder was crude $I(OTeF_5)_3$ identified by infrared and Raman spectroscopy [8] and usually present in 80-90% yield based on the disproportionation reaction shown below. For the photolytic decomposition of $R_fI(OTeF_5)_2$, Pyrex reactors were loaded in the dry box, evacuated, and irradiated with a Hanovia 100W Utility Lamp. In addition to $I(OTeF_5)_3$, the photolysis products contained variable amounts of the coupling product R_fR_f, and for i-$C_3F_7I(OTeF_5)_2$ isomers of C_6F_{14} and C_3F_7I.

RESULTS AND DISCUSSION

The reaction of TeF_5OCl and R_fI compounds occurs at low temperature in high yield according to (3).

$$2\,TeF_5OCl + R_fI \longrightarrow R_fI(OTeF_5)_2 + Cl_2 \tag{3}$$

R_f = CF_3, C_2F_5, n-C_3F_7, and i-C_3F_7

These $R_fI(OTeF_5)_2$ compounds are new compounds, except for the CF_3- derivative. The latter has previously been reported [9] from the ligand exchange reaction in (4)

$$CF_3IF_2 + 2HOTeF_5 \longrightarrow CF_3I(OTeF_5)_2 + 2HF \tag{4}$$

which required a large excess of $HOTeF_5$ and a solvent to obtain complete conversion.

Data on the $R_fI(OTeF_5)_2$ formation reaction (3) are summarized in Table I. Except for $CF_3I(OTeF_5)_2$, these oxidative addition products are all stable at ambient temperature and are low melting solids or a liquid. In analogy, the hypochlorites $ClOSO_2F$ [5], $ClOClO_3$ [10], and $ClONO_2$ [11] also react with fluorocarbon iodides to give the corresponding iodine III adducts in high yields. However, these compounds are generally not stable at ambient temperature. The fluorosulfate [5] and perchlorate [10] decompose according to (5)

$$R_fI(OX)_2 \longrightarrow R_fOX + IOX \qquad X{=}SO_2F, ClO_3 \tag{5}$$

whereas the nitrate [11] decomposes in a multistep reaction summarized by equation (6).

$$10\,CF_3I(ONO_2)_2 \longrightarrow 5CF_3I + 5CF_2O + 10\,N_2O_5 + I_2 + IF_5 + I_2O_5 \tag{6}$$

Thus, it appears that the $R_fI(OTeF_5)_2$ compounds are another example of the ability of the TeF_5O- group to stabilize relatively unstable oxidation states [12].

TABLE I

$R_fI(OTeF_5)_2$ synthesis and decomposition data

R_fI Type Compd., mmol	TeF_5OCl mmol	Temp. max. °C	Time	R_f-$OTeF_5$ Product		Percent Yield[a]	Other Products
CF_3I, 0.91	1.85	-78	4d	$CF_3I(OTeF_5)_2$	I	~80	Cl_2, CF_4, TeF_6
C_2F_5I, 1.10	2.58	25	3d	$C_2F_5I(OTeF_5)_2$	II	95	Cl_2, TeF_5OCl, TeF_5OH
n-C_3F_7I, 2.56	5.62	25	2d	n-$C_3F_7I(OTeF_5)_2$	III	94	Cl_2, TeF_5OCl, TeF_5OH
i-C_3F_7I, 2.56	4.73	25	2d	i-$C_3F_7I(OTeF_5)_2$	IV	97	Cl_2, TeF_5OCl, TeF_5OH
I, ~0.7		25	2h	CF_3OTeF_5		17	CF_3I, CF_4, $(TeF_4O)_n$, $I(OTeF_5)_3$
II, 0.24		115	21h	$C_2F_5OTeF_5$		78	C_2F_5I, $I(OTeF_5)_3$
III, 0.30		115	26h	n-$C_3F_7OTeF_5$		30	nC_3F_7I, C_3F_8, TeF_6, TeF_5OTeF_5, $I(OTeF_5)_3$
III, 0.37		25,UV	18h	n-$C_3F_7OTeF_5$		77	nC_3F_7I, C_6F_{14}, $I(OTeF_5)_3$
IV, 0.66		120	10h				i-C_3F_7I, $CF_3C(O)CF_3$, C_6F_{14}, TeF_5OTeF_5, $I(OTeF_5)_3$
IV, 0.53		25,UV	16h				C_6F_{14}, i-C_3F_7I, $I(OTeF_5)_3$

[a] Yield based on the limiting reagent and for the decomposition reactions on the stoichiometry: $2\ R_fI(OTeF_5)_2 \rightarrow R_fOTeF_5 + R_fI + I(OTeF_5)_3$.

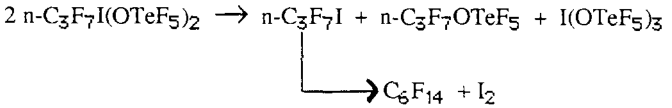
Thermal decomposition of these compounds takes place below 25°C for the methyl compound and at 115-120°C for the ethyl and n-propyl derivatives (7).

$$2R_fI(OTeF_5)_2 \rightarrow R_fOTeF_5 + R_fI + I(OTeF_5)_3 \qquad (7)$$

$R_f = CF_3, C_2F_5$, and $n\text{-}C_3F_7$

The high yields of $I(OTeF_5)_3$ in (7) demonstrates again the stabilizing effects of the TeF_5O- group on I (III). Furthermore, this mode of decomposition contrasts sharply with that noted for reaction (6) and to some extent with that for reaction (5).

The $R_fI(OTeF_5)_2$ compounds can also be decomposed by UV photolysis. For the n-propyl compound reaction (8) was observed.



$$2\ n\text{-}C_3F_7I(OTeF_5)_2 \rightarrow n\text{-}C_3F_7I + n\text{-}C_3F_7OTeF_5 + I(OTeF_5)_3; \quad n\text{-}C_3F_7I \rightarrow C_6F_{14} + I_2$$

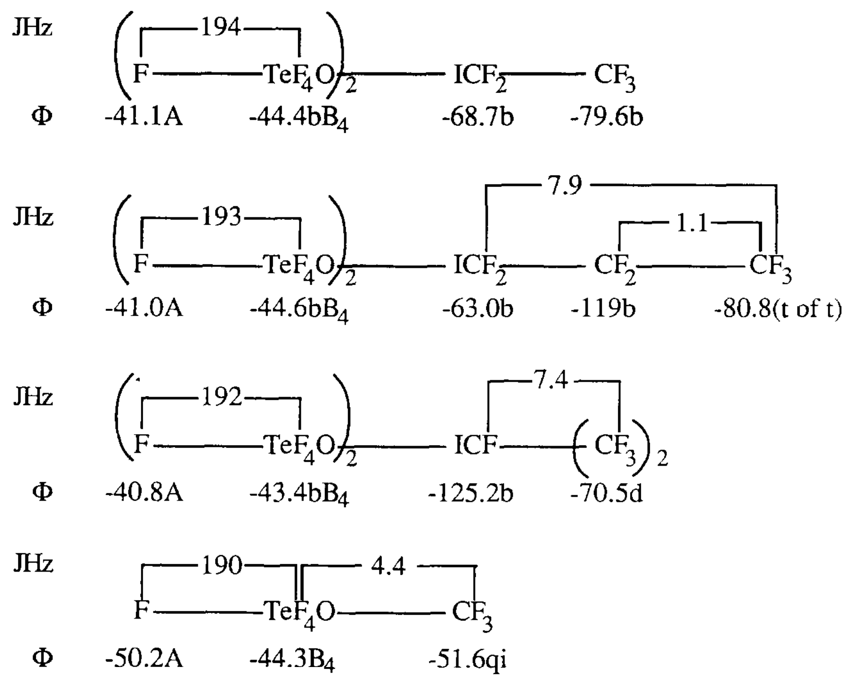
(8)

Except for the secondary decomposition of $n\text{-}C_3F_7I$, this process emulates the thermal reaction (7).

For $i\text{-}C_3F_7I(OTeF_5)_2$, neither photolysis nor thermal decomposition resulted in the formation of any R_fOTeF_5 derivative. It is noteworthy that the decomposition of $i\text{-}C_3F_7I(OSO_2F)_2$ and $i\text{-}C_3F_7I(OClO_3)_2$ also did not produce $i\text{-}C_3F_7OSO_2F$ [5], or $i\text{-}C_3F_7OClO_3$ [10], respectively. Therefore, it appears that for $X=TeF_5$, SO_2F, or ClO_3, the R_fOX synthesis from R_fI and ClOX is limited to primary R_fI compounds.

Table II lists the ^{19}F NMR data for the new compounds. Data for $C_2F_5OTeF_5$ and $n\text{-}C_3F_7OTeF_5$, prepared by other routes, have previously been reported [1]. The TeF_5O- groups give rise to AB_4 type spectra which are very similar for compounds of the same structural type. For CF_3OTeF_5, the observed chemical shifts are within the A= -49 to -54 and B_4 = -38 to -45 ppm range, found [1-3] for other R_fOTeF_5 moieties. For the $R_fI(OTeF_5)_2$ compounds the observed chemical shifts for the B_4 part are again in this region but the A part is shifted downfield to about -41 ppm. A similar shift of the A resonances from the high to the low field side of the B_4 resonances has also been noted for a series of inorganic TeF_5O- derivatives [13]. This change in the relative shifts of A and B_4 is due to the differences in the bonding environment of the TeF_5O- groups in the $R_fI(OTeF_5)_2$ and R_fOTeF_5 compounds.

TABLE II
^{19}F NMR data^a



^{a}CFCl$_3$ internal reference, negative shift being upfield from the reference. Φ = chemical shift, ppm (multiplicity; where b = broad; d = doublet, t = triplet, and qi = quintet. The area ratios measured for these resonances agreed with the given assignments. $J_{^{125}Te^{19}F}$ = 3640-50 Hz for the $R_fI(OTeF_5)_2$ compounds.

For the fluorine on carbon resonances there is remarkably little change in the chemical shifts on going from R_fI to $R_fI(OTeF_5)_2$, except for the CF resonance of the secondary fluorine in the isopropyl compound which is shifted from Ø = -149 in i-C_3F_7I [14] to Ø = -125 in i-$C_3F_7I(OTeF_5)_2$. This downfield shift might be caused by steric factors.

The vibrational spectra for the $R_fI(OTeF_5)_2$ compounds are given in Table III. In the infrared spectra, strong bands associated with νCF_n (1320 - 1130 cm^{-1}), νCC(1060 - 850 cm^1), and δCF_n (820 - 785 cm^{-1}) motions are characteristic for fluorocarbon species. In addition, strong infrared bands at about 740, 710, and 325 cm^{-1} are attributable

TABLE III

Vibrational spectra of $R_fI(OTeF_5)_2$ compounds

	Obsd. Freq. cm^{-1} (rel. intens.)[a]					
	$C_2F_5I(OTeF_5)_2$[b]		$nC_3F_7I(OTeF_5)_2$[b]		$iC_3F_7I(OTeF_5)_2$[c]	
Assign.	IR	Raman	IR	Raman	IR	Raman
	1323 s	1320(0.1)	1320 s	1326(0.6)	1293 s	1300(0.1)
	1245 vs	1235(0.1)	1260 s		1250 s	1250(0.1)
νCF			1225 s			
	1132 s	1130(0.2)	1153 s		1162 m	1165(0.2)
			1055 m	1060(1.8)		
νCC			1030 sh		962 m	
	890 s	887(0.6)	850 sh		861 m	875(1.2)
			814 w	820(0.5)		
δCF_n	805 s	800(1.0)	786 s	793(1.2)	800 m	800(0.9)p
	732 sh	731(0.6)	730 s	728(1.9)		748(2.3)p
$\nu_{as}TeF_4$	740 s	742(0.9)	740 s	745(0.4)	745 s	
$\nu TeF'$	710 s	710(1.9)	710 s	710(2.7)	710 s	715 sh
$\nu sTeF_4$		692(3.3)		695(4.1)		700(4.7)p
				655(2.1)		
νTeO	635 m	643(4.7)	629 m	640(3.0)	630 m	648(5.9)p
			620 sh	625(1.9)		
	583 w		595 m	598(0.8)		
	548 w	545(0.3)	531 m	535(0.3)	543 w	541(0.9)
			512 w			
$\nu_{as}IO_2$	465 ms		453 ms		465 m	
ν_sIO_2		440(4.8)		458(6.6)		455(3.9)p
		382(0.7)		380(1.0)		
		369(1.0)				
		353(0.9)				350(0.5)p
$\delta FTeF_4$	325 s	330(1.0)	325 s	325(1.0)	320 s	327(1.2)dp
$\delta OTeF_4$		305(1.0)		302(1.1)		300(0.6)dp
$\delta_{as}TeF_4$	265 w	271(0.5)	265 mw			
				265(8.0)		
νCI		240(10)				238(10)p
				238(5.0)		
		205(1.3)		165(3.7)		190(0.7)p
δCIO_2		135(7.8)		138(10)		135(8.3)p
				112(1.7)		
				92(5.0)		95(3.1)p

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[a] Uncorrected Raman intensities (peak heights); [b] solid; [c] liquid

to $\nu_{as}TeF_4$, $\nu TeF'$, and $\delta FTeF_4$, respectively, of the TeF_5O-group. These assignments are the same as those given for R_fOTeF_5 [1-3] and TeF_5X [15, 16] compounds. Two additional medium to strong intensity infrared bands are present for these compounds at about 630 and 460 cm^{-1}. The higher frequency band is assigned to νTeO which appears in the region 720 - 700 cm^{-1} in $(TeF_5O)_2R_f$ compounds [3], at 616 cm^{-1} in TeF_5OF [15], and at 625 cm^{-1} in $I(OTeF_5)_3$ [8]. For the 460 cm^{-1} band of the $R_fI(OTeF_5)_2$ compounds, no comparable band was observed in other R_fOTeF_5 or TeF_5X species. This band is then assigned to an iodine oxygen stretching mode which is found at 434 cm^{-1} in $I(OTeF_5)_3$ [8].

Raman counterparts are present for many of these strong infrared bands, i.e. νCF_n; νCC; δCF_n; $\nu_{as}TeF_4$; $\nu TeF'$; and $\delta FTeF_4$, and, as expected, they are relatively weak. For R_fOTeF_5 compounds, a Raman band at 675 cm^{-1} is dominant [3] and arises from ν_sTeF_4. For the $R_fI(OTeF_5)_2$ compounds, this band appears at about 695 cm^{-1}, but it is no longer the strongest Raman band. The two strongest Raman bands now occur at about 265 - 240 cm^{-1} and at 135 cm^{-1}. For the higher frequency band, an assignment is made as νCI, which occurs at 280 - 260 cm^{-1} in simple R_fI compounds [17] and which is expected to be a very intense Raman band. The intense band at 135 cm^{-1} is attributed to the skeletal bending mode, δCIO_2. This agrees well with the most intense Raman band observed for $I(OTeF_5)_3$ at 134 cm^{-1} [8] and which probably arises from the δOIO_2 motion. Medium intensity Raman bands are present corresponding to the νTeO and ν_sIO_2 motions whose infrared couterparts have been mentioned. Thus all the spectroscopic data, including ^{19}F NMR, are in agreement with the formulation of these materials as $R_fI(OTeF_5)_2$.

The infrared spectrum of CF_3OTeF_5 exhibits bands at 1263(s); 1233(s); 1192(vs); 743(s); 710(m); and 324(s) cm^{-1}. Comparable νCF_n vibrations are found for CF_3OSF_5 at 1274(s), 1243(s) and 1202(vs) cm^{-1} [18]. In the case of $C_3F_7OTeF_5$ its infrared spectrum was previously reported [1] for a 70:30 mixture of n- and iso-$C_3F_7OTeF_5$. The spectrum of pure n-$C_3F_7OTeF_5$ isolated in this study exhibits bands at 1338(w), 1250(vs), 1229(m), 1186(m), 1170(m), 1010(m), 754(s), 726(m), and 331(m) cm^{-1}.

CONCLUSIONS

It has been found that the reaction of TeF_5OCl with R_fI compounds proceeds at low temperature to furnish $R_fI(OTeF_5)_2$ derivatives in high yield. These adducts were thermally and photolytically decomposed, yielding in the case of the primary fluorocarbon compounds, the corresponding R_fOTeF_5 compounds. This two step sequence represents a new process for preparing R_fOTeF_5 type materials.

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