# REACTIONS OF TeF$_5$OCl WITH FLUOROCARBON IODIDES AND SYNTHESIS OF CF$_3$OTeF$_5$

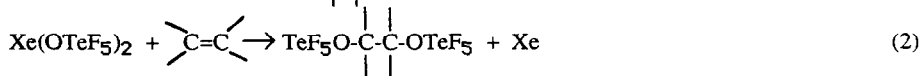CARL J. SCHACK AND KARL O. CHRISTE

Rocketdyne, a Division of Rockwell International Corporation, Canoga Park, California 91303 (USA)

## SUMMARY

The low temperature reaction of TeF$_5$OCl with the fluorocarbon iodides, CF$_3$I, C$_2$F$_5$I, n-C$_3$F$_7$I, and i-C$_3$F$_7$I results in the formation of R$_f$I(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$_3$OTeF$_5$. The perfluoroethyl and n-propyl adducts decompose at 120°C or under UV radiation giving C$_2$F$_5$OTeF$_5$ and n-C$_3$F$_7$OTeF$_5$, respectively. These reactions constitute a new synthesis of primary R$_f$OTef$_5$ compounds. Attempts to extend this synthesis to secondary fluorocarbon iodides were unsuccessful.

## INTRODUCTION

Reactions of TeF$_5$OX (X=Cl,F) and Xe(OTeF$_5$)$_2$ with fluoroolefins are direct paths to TeF$_5$O- substituted fluorocarbons [1-3].

$$\text{TeF}_5\text{OX} + \text{\textbackslash C=C/} \longrightarrow \text{TeF}_5\text{O-C-C-X} \tag{1}$$

$$\text{Xe(OTeF}_5)_2 + \text{\textbackslash C=C/} \longrightarrow \text{TeF}_5\text{O-C-C-OTeF}_5 + \text{Xe} \tag{2}$$

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$_f$OTeF$_5$ compounds. One promising approach involved the displacement of iodine from R$_f$I compounds

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.

TeF5OCl-RfI Reactions. 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.

RfI(OTeF5)2 Decomposition Reactions. 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 $i\text{-}C_3F_7I(OTeF_5)_2$ 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).

$$2\ TeF_5OCl\ +\ R_fI\ \longrightarrow\ R_fI(OTeF_5)_2\ +\ Cl_2 \tag{3}$$
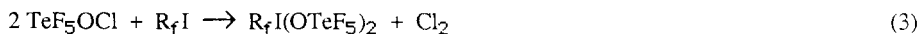
$R_f\ =\ CF_3,\ C_2F_5,\ n\text{-}C_3F_7,\ \text{and}\ i\text{-}C_3F_7$

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)

$$CF_3IF_2\ +\ 2HOTeF_5\ \longrightarrow\ CF_3I(OTeF_5)_2\ +\ 2HF \tag{4}$$
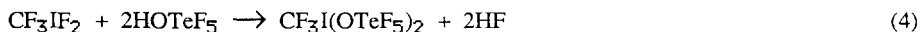
which required a large excess of $HOTeF_5$ and a solvent to obtain complete conversion.

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)

$$R_fI(OX)_2\ \longrightarrow\ R_fOX\ +\ IOX \qquad\qquad X{=}SO_2F,\ ClO_3 \tag{5}$$
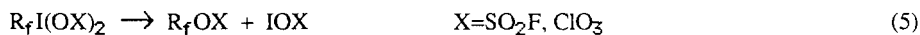
whereas the nitrate [11] decomposes in a multistep reaction summarized by equation (6).

$$10\ CF_3I(ONO_2)_2\ \longrightarrow\ 5CF_3I\ +\ 5CF_2O\ +\ 10\ N_2O_5\ +\ I_2\ +\ IF_5\ +\ I_2O_5 \tag{6}$$
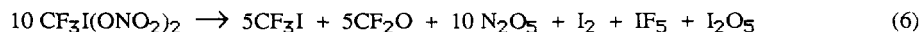
Thus, it appears that the $R_fI(OTeF_5)_2$ compounds are another example of the ability of the $TeF_5O$- group to stabilize relatively unstable oxidation states [12].

TABLE I

$R_fI(OTeF_5)_2$ synthesis and decomposition data

| $R_fI$ Type Compd., mmol | $TeF_5OCl$ mmol | Temp. max. °C | Time | $R_fOTeF_5$ 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: $2 \ R_fI(OTeF_5)_2 \rightarrow R_fOTeF_5 + R_fI + I(OTeF_5)_3$.
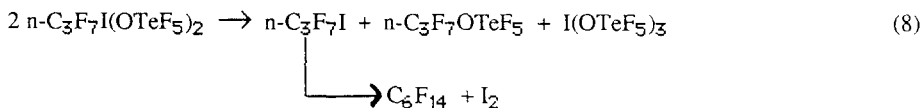
Thermal decomposition of these compounds takes place below 25°C for the methyl compound and at 115-120°C for the ethyl and n-propyl derivatives (7).

$$2R_fI(OTeF_5)_2 \rightarrow R_fOTeF_5 + R_fI + I(OTeF_5)_3 \tag{7}$$
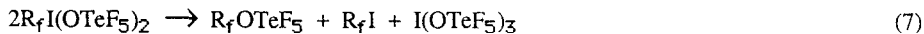
$R_f = CF_3, C_2F_5,$ and n-$C_3F_7$

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.

$$2 \text{ n-}C_3F_7I(OTeF_5)_2 \rightarrow \text{n-}C_3F_7I + \text{n-}C_3F_7OTeF_5 + I(OTeF_5)_3 \tag{8}$$
$$\longrightarrow C_6F_{14} + I_2$$

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

For i-$C_3F_7I(OTeF_5)_2$, neither photolysis nor thermal decomposition resulted in the formation of any $R_fOTeF_5$ derivative. It is noteworthy that the decomposition of i-$C_3F_7I(OSO_2F)_2$ and i-$C_3F_7I(OClO_3)_2$ also did not produce i-$C_3F_7OSO_2F$ [5], or i-$C_3F_7OClO_3$ [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-$C_3F_7OTeF_5$, 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]

JHz $\left(\overset{\displaystyle\lceil\!-\!194\!-\!\rceil}{F\!-\!\!-\!\!-\!TeF_4O}\right)_2$ — $ICF_2$ — $CF_3$

Φ  $\quad$ -41.1A $\quad$ -44.4bB$_4$ $\qquad$ -68.7b $\quad$ -79.6b

JHz $\left(\overset{\displaystyle\lceil\!-\!193\!-\!\rceil}{F\!-\!\!-\!\!-\!TeF_4O}\right)_2$ — $\overset{\lceil\!-\!-\!7.9\!-\!-\!\rceil}{ICF_2}$ — $\overset{\lceil\!-\!1.1\!-\!\rceil}{CF_2}$ — $CF_3$

Φ  $\quad$ -41.0A $\quad$ -44.6bB$_4$ $\qquad$ -63.0b $\quad$ -119b $\quad$ -80.8(t of t)

JHz $\left(\overset{\displaystyle\lceil\!-\!192\!-\!\rceil}{F\!-\!\!-\!\!-\!TeF_4O}\right)_2$ — $\overset{\lceil\!-\!7.4\!-\!\rceil}{ICF}$ — $(CF_3)_2$

Φ  $\quad$ -40.8A $\quad$ -43.4bB$_4$ $\qquad$ -125.2b $\quad$ -70.5d

JHz $\overset{\lceil\!-\!190\!-\!\rceil\lceil\!-\!4.4\!-\!\rceil}{F\!-\!\!-\!\!-\!TeF_4O\!-\!\!-\!\!-\!CF_3}$

Φ  $\quad$ -50.2A $\quad$ -44.3B$_4$ $\qquad$ -51.6qi

[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. $J_{125\text{Te}^{19}\text{F}}$ = 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 $\nu CF_n$ (1320 - 1130 cm$^{-1}$), $\nu CC$(1060 - 850 cm$^1$), and $\delta CF_n$ (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) |
| $\nu CF$ | | | 1225 s | | | |
| | 1132 s | 1130(0.2) | 1153 s | | 1162 m | 1165(0.2) |
| | | | 1055 m | 1060(1.8) | | |
| $\nu CC$ | | | 1030 sh | | 962 m | |
| | 890 s | 887(0.6) | 850 sh | | 861 m | 875(1.2) |
| | | | 814 w | 820(0.5) | | |
| $\delta CF_n$ | 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) | | |
| $\nu TeO$ | 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 | |
| $\nu_sIO_2$ | | 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 | $\big\{$ 265(8.0) | | |
| $\nu CI$ | | 240(10) | | $\big\}$ 238(5.0) | | 238(10)p |
| | | 205(1.3) | | 165(3.7) | | 190(0.7)p |
| $\delta ClO_2$ | | 135(7.8) | | 138(10) | | 135(8.3)p |
| | | | | 112(1.7) | | |
| | | | | 92(5.0) | | 95(3.1)p |

[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 $\nu TeO$ 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. $\nu CF_n$; $\nu CC$; $\delta CF_n$; $\nu_{as}TeF_4$; $\nu TeF'$; 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 $\nu_s TeF_4$. 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 $\nu CI$, 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, $\delta CIO_2$. 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 $\delta OIO_2$ motion. Medium intensity Raman bands are present corresponding to the $\nu TeO$ and $\nu_s IO_2$ 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 $\nu CF_n$ 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.

## ACKNOWLEDGMENT

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