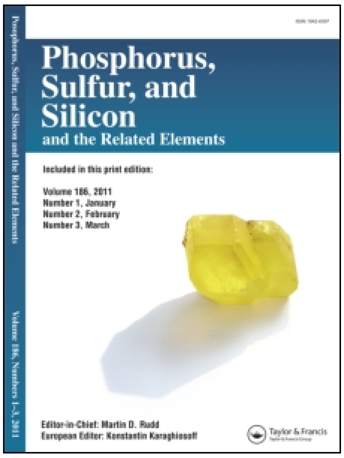

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On Perfluoroalkyl Tellurium Compounds

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On Perfluoroalkyl Tellurium Compounds

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This paper summarizes the present state of the preparations and chemical properties of perfluoroalkyl, mainly trifluoromethyl tellurium compounds. $Te(CF_3)_2$ is a reactive educt for trifluoromethyl transfer reactions in inorganic and organic syntheses. $CF_3TeTeCF_3$ is used as a starting material for preparations of CF_3Te compounds, e.g. $Hg(TeCF_3)_2$, CF_3TeI. The pyrolysis of $(CH_3)_3SnTeCF_3$ gives difluoro telluroketone. $Te(CF_3)_2$ is easily oxidized to yield trifluoromethyl tellurium(IV) derivatives. The preparations and properties of many compounds of the composition $(CF_3)_2TeX_2$ are described. Nucleophilic trifluoromethylation of $(CF_3)_2TeCl_2$ yields tetrakis(trifluoromethyl) tellurium(IV).

Keywords: perfluoroalkyl tellurium; preparations; properties

INTRODUCTION

Organo tellurium compounds are subject of many investigations in elementorganic and organic chemistry. One central field of our investigations in perfluoroorgano element chemistry is the chemistry of perfluoroalkyl tellurium compounds. These derivatives are investigated by our group for approximately 20 years more or less intensively. In most cases, non- and perfluorinated tellurium derivatives exhibit absolutely different properties which may be explained by different polarizations of the carbon tellurium bonds. For methyl compounds, polarizations such as

$$\overset{\delta+}{CH_3}\text{-}\overset{\delta-}{Te} \text{ and } \overset{\delta-}{CF_3}\text{-}\overset{\delta+}{Te}$$

can be formulated. As a consequence $(CH_3)_2Te$ behaves as a Lewis base, whereas $Te(CF_3)_2$ must be suggested as a Lewis acid. Already 50 years ago, Emeléus regarded the CF_3 group as a pseudohalogen. Under radical conditions CF_3 groups react comparable to the halogens as CF_3 radicals; under polar conditions CF_3 groups behave as anions although no "naked" CF_3 anions have been detected so far. The favoured reaction way, radical or polar, strongly depends on the central atom of a trifluoromethyl element compound, although transitions are fluent.

In this paper, I mainly confine to CF_3Te derivatives to survey the chemical properties of these compounds with special respect to our own results. In the case of special interest, I will also include the higher homologous perfluoroalkyl tellurium compounds and in some cases also the pentafluorophenyl tellurium derivatives. However, many of the investigations described here did not have come to final results.

PREPARATION OF TRIFLUOROMETHYL TELLURIUM COMPOUNDS

The first trifluoromethyl tellurium compound had been described already in 1963 by Bell, Pullman and West[1]. They obtained $Te_2(CF_3)_2$ from the reaction of CF_3 radicals, thermally generated from hexafluoroacetone, with a tellurium mirror:

$$2\,Te + CF_3COCF_3 \xrightarrow{\Delta} Te_2(CF_3)_2 + CO$$

In 1975 Denniston and Martin[2] irradiated a mixture of $(CH_3)_2Te$ and R_fI ($R_f = CF_3, C_2F_5$) and detected CH_3TeR_f and $Te(R_f)_2$ as reaction products by ^{19}F NMR spectroscopy:

$$(CH_3)_2Te + R_fI \xrightarrow{h\cdot\nu} CH_3TeR_f + Te(R_f)_2 + CH_3I \quad (R_f = CF_3, C_2F_5)$$

The reactions of CF_3 radicals, generated from discharge reactions of C_2F_6, with $TeBr_4$ or Te yielded $Te(CF_3)_2$ and $Te_2(CF_3)_2$ in small amounts (Lagow et al.[3,4], Schmeißer et al.[5]):

$$C_2F_6 + Te\,/\,TeBr_4 \longrightarrow Te(CF_3)_2 + Te_2(CF_3)_2$$

All these reactions did not give amounts of $Te_x(CF_3)_2$ ($x = 1, 2$) on a preparative scale.

The first synthesis of perfluoroalkyl tellurium compounds in large amounts was reported by Passmore et al.[6,7] via the reaction of $Te_4[AsF_6]_2$ and C_2F_4:

$$Te_4[AsF_6]_2 + C_2F_4 \longrightarrow Te(C_2F_5)_2 + Te_2(C_2F_5)_2 + \ldots$$

However, it is very difficult to reproduce this method. The authors also described some chemical properties of the new compounds and the oxidations to Te(IV) and Te(VI) derivatives.

We found a convenient route to prepare $Te(CF_3)_2$ via the thermal reaction of a 1:1 mixture of $Hg(CF_3)_2$ and $TeCl_4$[8]:

$$Hg(CF_3)_2 + TeCl_4 \xrightarrow{\Delta} Te(CF_3)_2 + Te(CClF_2)_2 + HgCl_2 + Te +$$

$Te(CF_3)_2$ is isolated by low temperature distillation. In 1988 Morrison et al. modified this reaction[9].

On the basis of the results of Denniston and Martin[2] we reinvestigated the reaction of $(CH_3)_2Te$ with perfluoroiodoalkanes in the presence of $(C_2H_5)_3N$ and were able to synthesize the higher homologous perfluoroalkyl tellurium compounds[10]:

$$\begin{tikzcd}(CH_3)_2Te + R_fI + (C_2H_5)_3N \arrow[r, "h\cdot\nu"] & CH_3TeR_f + [(C_2H_5)_3NCH_3]I \arrow[d, "R_fI"] \\ & Te(R_f)_2 + Te_2(R_f)_2 + \ldots\end{tikzcd}$$

$(R_f = CF_3, C_2F_5, C_3F_7, C_6F_5)$

In absence of $(C_2H_5)_3N$, CF_3I reacts with $(CH_3)_2Te$ at -78 °C under irradiation mainly to the telluronium salt $[(CH_3)_2TeCF_3]I$ which is thermally stable up to +70 °C. At higher temperature CH_3TeCF_3 and CH_3I are formed[11]:

$$\begin{tikzcd} CF_3I + (CH_3)_2Te \arrow[r, "h\cdot\nu", "-78\,^{\circ}C"'] & {[(CH_3)_2TeCF_3]I + \ldots} \arrow[d, "+70\,^{\circ}C"] \\ & CH_3TeCF_3 + CH_3I \end{tikzcd}$$

A different suitable approach for the synthesis of $Te(R_f)_2$ is the reaction of Na_2Te with R_fI in THF[12]:

$$Na_2Te + 2\,R_fI \longrightarrow Te(R_f)_2 + 2\,NaI \quad (R_f = C_2F_5, C_6F_5)$$

However, the solvent cannot be quantitatively separated from the product.

In 1987 we reported the first preparative method to obtain $CF_3TeTeCF_3$[13]. When $Te(CF_3)_2$ is irradiated in furan the CF_3 radicals mainly react with furan to form trifluoromethylfurans and the $TeCF_3$ radicals dimerize to form $CF_3TeTeCF_3$.

Finally, Haas et al. reported in 1996 three methods for the preparation of perfluoroorgano tellurium compounds[14]:

$$Hg(R_f)_2 + 3\,Te \xrightarrow{Cu} Te(R_f)_2 + Te_2(R_f)_2 + \ldots$$

$$Hg(R_f)I + 3\,Te \xrightarrow{Cu} Te(R_f)_2 + Te_2(R_f)_2 + \ldots$$

$$R_fI + Te + Cu \longrightarrow Te(R_f)_2 + Te_2(R_f)_2 + CuI$$

$(R_f = \text{perfluoroalkyl}, C_6F_5)$

$Te(CF_3)_2$ is a pale yellow liquid (b.p. 22.5 °C, m.p. -123 °C; molecular structure determined by electron diffraction[15]). $Te_2(CF_3)_2$ is an oily red liquid (b.p. ca. 120 °C, m.p. -70 °C; X-ray structure:

monoclinic space group $P2_1/a$[16]). Both compounds can easily be identified by their mass spectra and ^{19}F and ^{125}Te NMR spectra. They are easily oxidized by air but not hydrolysable.

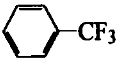
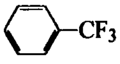
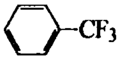
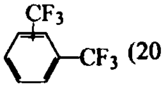
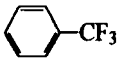
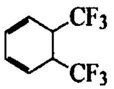
TRIFLUOROMETHYLATION REACTIONS WITH $Te(CF_3)_2$

For trifluoromethylation reactions under radical conditions in elementorganic and organic syntheses mainly CF_3I and $Hg(CF_3)_2$ are used. Both compounds had been prepared by Emeléus et al. for the first time more than 50 years ago[17,18]. In order to check the reactivity of $Te(CF_3)_2$, we compared numerous reactions of $Te(CF_3)_2$, CF_3I and $Hg(CF_3)_2$ with unsaturated organic compounds[19-22]. The reactions were carried out with mixtures of the pure compounds and initiated either by heating or by irradiation. As an example the thermal reactions with benzene are compared which demonstrate the high reactivity of $Te(CF_3)_2$ (Table 1). At comparable conditions $Hg(CF_3)_2$ yields only traces of trifluoromethylbenzene, CF_3I only about 1%, but $Te(CF_3)_2$ reacts quantitatively. The main product is $C_6H_5CF_3$, but also disubstitution takes place as well as addition reactions to the aromatic ring.

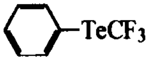
A survey of proton substitution reactions is presented in Table 2. All reactions gave trifluoromethylated mixtures of isomers in one-pot reactions in most cases in high yields.

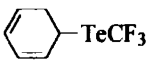
Ganja and Morrison[23] described reactions of $Te(CF_3)_2$ with the elements iodine, sulfur, selenium, phosphorus and arsenic at 220 °C giving the corresponding trifluoromethyl element compounds in good to excellent yields: CF_3I (97%), $S(CF_3)_2$ (92%), $Se(CF_3)_2$ (92%), $P(CF_3)_3$ (70%) and $As(CF_3)_3$ (46%). With antimony only small amounts of $Sb(CF_3)_3$ are formed. Good results were also achieved with $SeBr_4$ ($Se(CF_3)_2$, 98%), PI_3 ($P(CF_3)_3$, 65%) and AsI_3 ($As(CF_3)_3$, 88%).

TABLE 1. Thermal reactions of $Hg(CF_3)_2$, CF_3I and $Te(CF_3)_2$ with benzene

Molar ratio CF_3 cpd. : C_6H_6	temp. / °C	Products (yields / %)
1 $Hg(CF_3)_2$ + 12,82	150	 (< 1)
1 CF_3I + 0,93	150	 (1)
1 $Te(CF_3)_2$ [a] + 1,53	150	 (31) +  (20)[b]
		+  (8) +  (16)[c]
		+ Te containing products [d]

[a] quantitative reaction of $Te(CF_3)_2$; [b] 2% o-, 10% m-, 8% p-;

[c] 8% cis, 8% trans; [d] spectroscopic evidence of 



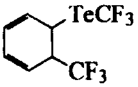
(cis / trans) and 

TABLE 2. Thermal one-pot reactions of $Te(CF_3)_2$ with selected organic compounds

educt	product	yield / %
cyclohexene	$1,2\text{-}(CF_3)_2C_6H_{10}$	85.2
pyridine	$CF_3\text{-}C_5H_4N$	57
furan	$CF_3\text{-}C_4H_3O$	74.2
fluorobenzene	$CF_3\text{-}C_6H_4F$	73
chlorobenzene	$CF_3\text{-}C_6H_4Cl$	87
bromobenzene	$CF_3.C_6H_4Br$	100
iodobenzene	$CF_3\text{-}C_6H_4I$	88
trifluoromethylbenzene	$(CF_3)_2\text{-}C_6H_4$	75
toluene	$CF_3\text{-}C_6H_4CH_3$	56
$p\text{-}C_6H_4(CH_3)_2$	$CF_3\text{-}C_6H_3(CH_3)_2$	73
mesitylene	$CF_3\text{-}C_6H_2(CH_3)_3$	10
phenol	$CF_3\text{-}C_6H_4OH$	26
p-t-bu-phenol	$CF_3\text{-}C_6H_3C(CH_3)_3OH$	31
uracil	$5\text{-}CF_3\text{-uracil}$	15

We found that $Te(CF_3)_2$ and metal alkyls equilibrate in solutions at room temperature, e. g.:

$$Te(CF_3)_2 + (CH_3)_2M \rightleftharpoons CH_3TeCF_3 + CH_3MCF_3$$
$$\rightleftharpoons (CH_3)_2Te + M(CF_3)_2 \ (M = Zn, Cd)$$

The equilibria can easily be shifted to the right or left side varying the stoichiometry. Thus, we isolated e. g. CH_3TeCF_3, CH_3MCF_3 or

$M(CF_3)_2$ in preparative amounts[24]. Via these reactions also the higher homologous perfluoroalkyl element and perfluorophenyl element compounds can be prepared.

REACTIONS OF $CF_3TeTeCF_3$

Only few chemical properties of $CF_3TeTeCF_3$ are reported. We investigated the reaction of $Te_2(CF_3)_2$ and some metals. Only in the case of Hg and Cd we were able to isolate the corresponding CF_3Te metal compounds[13]:

$$M + CF_3TeTeCF_3 \rightleftharpoons M(TeCF_3)_2 \quad (M = Hg, Cd)$$

$Hg(TeCF_3)_2$ was obtained as a yellow, water sensitive powder which decomposes at 77 °C to give the starting materials. $Cd(TeCF_3)_2$ was isolated as an oily brown unstable liquid. Silver does not react with $Te_2(CF_3)_2$ while copper reacts at above 100 °C to form elemental Te and $CuCF_3$ compounds.

When equimolar amounts of $Te_2(CF_3)_2$ and iodine are reacted in $CHCl_3$, n-pentane or thf CF_3TeI is quantitatively formed[16,25]:

$$CF_3TeTeCF_3 + I_2 \rightleftharpoons 2\ CF_3TeI$$

The compound cannot be isolated from the solution without decomposition neither by crystallization nor by low temperature vacuum distillation of the solvent; the resulting decomposition products were identified as Te, CF_3I and TeI_4. CF_3TeI is identified by spectroscopic methods and some reactions. In the NMR spectra a strong dependence of the ^{19}F and the ^{125}Te chemical shifts and the coupling constant $^2J(^{125}Te,^{19}F)$ on the donor number of the solvent is observed which proves a significant donor acceptor interaction. Some reactions demonstrate the high synthetic potential of CF_3TeI:

$$2\,CF_3TeI + Hg(SeCF_3)_2 \longrightarrow 2\,CF_3TeSeCF_3 + HgI_2$$

$$2\,CF_3TeI + Hg(NSO)_2 \longrightarrow 2\,CF_3TeNSO + HgI_2$$

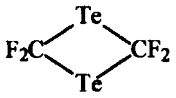
$$CF_3TeI + LiR \longrightarrow RTeCF_3 + LiI \quad (R = -C{\equiv}C{-}C_6H_5, -C(CH_3)_3)$$

$$CF_3TeI + AgSCN \longrightarrow CF_3TeSCN + AgI$$

$$CF_3TeI + LiSC_6F_5 \longrightarrow CF_3TeSC_6F_5 + LiI$$

The mercury compound $Hg(TeCF_3)_2$ reacts with $(C_2H_5)_2AlI$ to form the first difluorotelluroketone $F_2C{=}Te$ which is separated at 77 K as a deep violet, transient, amorphous material. The telluroketone is thermally unstable and dimerizes to cyclic $(F_2CTe)_2$ (dec. at 106 °C)[25,26].

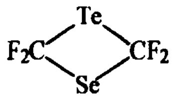
$$Hg(TeCF_3)_2 + 2\,(C_2H_5)_2AlI \longrightarrow F_2C{=}Te + HgI_2 + 2\,(C_2H_5)_2AlF$$

$2\,F_2C{=}Te \longrightarrow$ 

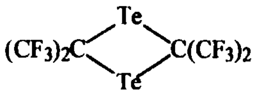
A more convenient preparation of the telluroketone is the pyrolysis of $(CH_3)_3SnTeCF_3$:

$$\begin{tikzcd}
CF_3TeTeCF_3 + 2\,(CH_3)_3SnH \arrow[r] & 2\,(CH_3)_3SnTeCF_3 + H_2 \arrow[d, "280\ ^\circ C"] \\
(F_2CTe)_2 & F_2C{=}Te \arrow[l, "2x"']
\end{tikzcd}$$

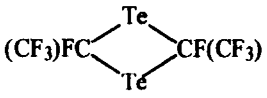
The fluorine atoms of the dimer can be substituted by chlorine and bromine using boron halides. A mixture of $F_2C{=}Te$ and $F_2C{=}Se$ forms the cyclic compound shown below.



Similarly, pyrolysis of some other $(CH_3)_3SnTeR_f$ ($R_f = C_2F_5$, i-C_3F_7)[14, 27] yield cis / trans derivatives.



and



Haas et al. also reported that the stannyl tellurium compound is excellently suited for $TeCF_3$ group transfer reactions[28]:

$$(CH_3)_3SnTeCF_3 + ArC(O)Cl \longrightarrow ArC(O)TeCF_3 + (CH_3)_3SnCl$$

BIS(TRIFLUOROMETHYL) TELLURIUM(IV) COMPOUNDS

In 1974 and 1985 Passmore et al. described some oxidation reactions of $Te(C_2F_5)_2$ and $Te_2(C_2F_5)_2$ with ClF, XeF_2 and Cl_2 to yield pentafluoroethyl tellurium(IV) and (VI) halides[29, 30]:

$$Te_2(C_2F_5)_2 + ClF \longrightarrow C_2F_5TeF_3 + \text{traces of } C_2F_5TeClF_4 + TeClF_5$$

$$Te_2(C_2F_5)_2 + XeF_2 \longrightarrow C_2F_5TeF_3 \text{ (quant., m.p. 95 °C, X-ray)}$$

$$Te(C_2F_5)_2 + ClF \longrightarrow (C_2F_5)_2TeF_2 \text{ (m.p. 4 °C)}$$

$$Te(C_2F_5)_2 + ClF \xrightarrow{r.t.} trans\text{-}C_2F_5TeClF_4 + trans\text{-}(C_2F_5)_2TeF_4 + TeClF_5$$

$$Te(C_2F_5)_2 + XeF_2 \longrightarrow (C_2F_5)_2TeF_2 \text{ (quant.)}$$

$$Te(C_2F_5)_2 + Cl_2 \longrightarrow (C_2F_5)_2TeCl_2$$

They also reported that $C_2F_5TeF_3$ and $(C_2F_5)_2TeF_2$ form 1:1 adducts with CsF and with SbF_5.

We investigated oxidation reactions of $Te(CF_3)_2$ with some oxidizers. $Te(CF_3)_2$ reacts with ambient air, oxygen and ozone to form a white solid, nearly insoluble in common organic solvents. Analysis, NMR, mass and vibrational spectra proved the existence of a $CF_3Te(IV)$ compound, probably polymeric bis(trifluoromethyl) tellurium oxide[31]:

$$Te(CF_3)_2 + \tfrac{1}{2} O_2 \longrightarrow [(CF_3)_2TeO]_x$$

The m.p. is above 350 °C; the product is not hydrolysable, but soluble in HF to give $(CF_3)_2TeF_2$. With trifluoroacetic anhydride an equilibrium with $(CF_3)_2Te(OCOCF_3)_2$ is formed. The reaction with conc. HCl primarily yields CF_3TeCl_3 and after addition of CsCl as the final product $Cs_2[TeCl_6]$:

$$\begin{array}{l}[(CF_3)_2TeO] + 3\,HCl \longrightarrow CF_3H + CF_3TeCl_3 + H_2O \\ \hspace{17em}\downarrow CsCl, HCl \\ \hspace{16em} Cs_2[TeCl_6] + CF_3H\end{array}$$

Low temperature fluorination of $Te(CF_3)_2$ with elemental fluorine, XeF_2, ClF or BrF_3 yields $(CF_3)_2TeF_2$ as the main product[32]. $(CF_3)_2TeF_2$ is isolated as a white hydrolysable solid (subl. 65 °C; m.p. in a sealed tube 185 °C). The high m.p. compared to 4 °C for $(C_2F_5)_2TeF_2$[30] is surprising. The reaction of $Te(CF_3)_2$ with excess ClF proceeds via a primary oxidative addition to form the intermediate $(CF_3)_2TeClF$ followed by a comproportionation of Cl^+ and Cl^-:

$$Te(CF_3)_2 + ClF \longrightarrow (CF_3)_2TeClF \xrightarrow{+ClF} (CF_3)_2TeF_2 + Cl_2$$

The intermediate could only be detected in the ^{19}F NMR spectra. In solution it equilibrates with the difluoride and the dichloride:

$$2\,(CF_3)_2TeClF \rightleftharpoons (CF_3)_2TeF_2 + (CF_3)_2TeCl_2$$

All isolation attempts effected a shift of the equilibrium to the right side.

We succeeded in growing single crystals of $(CF_3)_2TeF_2$ (monoclinic space group C2/c)[33]. The surrounding of the Te atom can roughly be described as a trigonal bipyramid with two CF_3 groups and the non-bonding electron pair in the equatorial plane. The asymmetric unit of the crystal contains one and a half $(CF_3)_2TeF_2$ molecules. Intermolecular Te···F and F···F distances are found which are significantly shorter than the sum of the corresponding van der Waals radii.

The oxidation reactions of $Te(CF_3)_2$ with Cl_2 and Br_2 yield the bis(trifluoromethyl) tellurium dihalides, $(CF_3)_2TeCl_2$ and $(CF_3)_2TeBr_2$[31].

$$Te(CF_3)_2 + Cl_2 \xrightarrow{r.t.} (CF_3)_2TeCl_2 \xrightarrow{exc.Cl_2} CF_3TeCl_3 + CF_3Cl$$

$(CF_3)_2TeCl_2$ (m.p. 93-95 °C) reacts with excess chlorine to give CF_3TeCl_3. The reaction of $Te(CF_3)_2$ with bromine at room temperature only yields decomposition products. Therefore, low temperature and dilute solutions are necessary:

$$Te(CF_3)_2 + Br_2 \xrightarrow[-78\,^\circ C]{CCl_3F} (CF_3)_2TeBr_2 \quad (m.p.\ 106\text{-}107\,^\circ C)$$

The reactions of $Te(CF_3)_2$ with iodine or iodosuccinimide did not give any evidence for trifluoromethyl tellurium(IV) iodides. We only observed the formation of TeI_4 and CF_3I. The reaction probably proceeds via extremely unstable $(CF_3)_2TeI_2$:

$$Te(CF_3)_2 + I_2 \longrightarrow \{(CF_3)_2TeI_2\} \xrightarrow{I_2} CF_3I + TeI_4$$

We also investigated the interactions of bis(trifluoromethyl) tellurium dihalides with NaF and with halogens. In all cases equilibria depending on the stoichiometry are established[34]:

$$(CF_3)_2TeX_2 + 2\,NaF \rightleftharpoons (CF_3)_2TeF_2 + 2\,NaX \quad (X = Cl, Br)$$

$$(CF_3)_2TeX_2 + Cl_2 \rightleftharpoons (CF_3)_2TeCl_2 + \dots \quad (X = F, Br)$$

$$\begin{aligned}(CF_3)_2TeX_2 + Br_2 \rightleftharpoons {} & (CF_3)_2TeBr_2 + CF_3TeBr_3 \\ & + CF_3TeCl_3 + \dots \quad (X = F, Cl)\end{aligned}$$

With elemental iodine only halogenolysis is observed:

$$(CF_3)_2TeX_2 + I_2 \longrightarrow CF_3I + TeI_4 + \dots \quad (X = F, Cl, Br)$$

Analogous with the reaction with ClF, $Te(CF_3)_2$ is oxidized by $ClONO_2$ via the intermediately formed addition product[34]:

$$\begin{array}{llll} Te(CF_3)_2 + ClONO_2 \longrightarrow & (CF_3)_2TeCl(ONO_2) & \rightleftharpoons & (CF_3)_2TeCl_2 + \\ & \downarrow ClONO_2 & & (CF_3)_2Te(ONO_2)_2 \\ & (CF_3)_2Te(ONO_2)_2 + Cl_2 & & \end{array}$$

Further bis(trifluoromethyl) tellurium(IV) derivatives are obtained from ligand exchange reactions of the dihalides with acid anhydrides[34], e. g.:

$$(CF_3)_2TeF_2 + 2\,(CF_3CO)_2O \longrightarrow (CF_3)_2Te(OCOCF_3)_2 + 2\,CF_3COF$$

$$(CF_3)_2TeF_2 + 2\,N_2O_5 \longrightarrow (CF_3)_2Te(ONO_2)_2 + 2\,NO_2F$$

Trimethylsilanes are suitable reagents in fluorine exchange reactions with $(CF_3)_2TeF_2$. From such reactions we prepared e. g. bis(trifluoromethyl) tellurium(IV) fluorosulfonate, isocyanate, amides and alkoxy compounds. In contrast to C_2F_5Te compounds, attempts of a further oxidation to Te(VI) derivatives have not yet been successful. Only when $(CF_3)_2TeF_2$ is oxidized with elemental fluorine we could spectroscopicly detect the formation of very unstable $(CF_3)_2TeF_4$. All attempts to isolate this compound failed.

However, the direct fluorination of $Te(C_6F_5)_2$ led to surprising results. $Te(C_6F_5)_2$ is oxidized step by step to form $(C_6F_5)_2TeF_2$ and $(C_6F_5)_2TeF_4$[35]:

$$\begin{tikzcd} Te(C_6F_5)_2 + F_2 \arrow[r, "-35\,^{\circ}C"] & (C_6F_5)_2TeF_2\ (94\%\ ;\ m.p.\ 166\ ^{\circ}C) \arrow[d, "-35\ ^{\circ}C,\ F_2"] \\ & (C_6F_5)_2TeF_4\ (\sim 90\%\ ;\ m.p.\ 64\ ^{\circ}C) \end{tikzcd}$$

By-products are C_6F_6 and TeF_6. The isolation of highly pure $(C_6F_5)_2TeF_4$ appeared to be difficult. Small excess of F_2 already effects a partial fluorination of the C_6F_5 groups. Thus, further oxidation results in successive fluorination of the aromatic rings to give $(C_6F_7)_2TeF_4$, $(C_6F_9)_2TeF_4$ and finally $(C_6F_{11})_2TeF_4$. All intermediates are identified by their ^{19}F NMR spectra. Bis(perfluorocyclohexyl) tellurium tetrafluoride was isolated as a gelatinous white, highly reactive solid (66.3%; subl. 110 °C).

$$(C_6F_5)_2TeF_4 \longrightarrow (C_6F_7)_2TeF_4 \longrightarrow (C_6F_9)_2TeF_4 \longrightarrow (C_6F_{11})_2TeF_4$$

When storing $(C_6F_{11})_2TeF_4$ at room temperature for some hours, decomposition to TeF_4 and C_6F_{11}-C_6F_{11} occurs. Further fluorination of $(C_6F_{11})_2TeF_4$ at -60 °C yields C_6F_{12} and surprisingly TeF_4. In the presence of F_2, Te(VI) is reduced to Te(IV). We suppose that primarily an intramolecular fluorination takes place and the resulting low valent tellurium difluoride is only fluorinated to Te(IV) at this conditions:

$$(C_6F_{11})_2TeF_4 \xrightarrow{\text{dec.}} C_6F_{11}\text{-}C_6F_{11} + TeF_4$$

$$\begin{tikzcd} (C_6F_{11})_2TeF_4 \arrow[r, "F_2"] & 2\,C_6F_{12} + \text{"}TeF_2\text{"} \arrow[d, "F_2"] \\ & TeF_4 \end{tikzcd}$$

From TeF_4 it is known that it forms the complex anion $[TeF_5]^-$, but not $[TeF_6]^{2-}$, while from $TeCl_4$ and $TeBr_4$ also the hexa-coordinated $[TeCl_6]^{2-}$ and $[TeBr_6]^{2-}$ with octahedral symmetry are known. With halide acceptors tellurium tetrahalides react to the $[TeX_3]^-$ cations.

Therefore, we were interested whether $(CF_3)_2TeX_2$ (X = F, Cl, Br) also behave as amphoters. We investigated the reactions of $(CF_3)_2TeX_2$ with some halide donors and acceptors[36].

$(CF_3)_2TeF_2$ reacts with BF_3, AsF_5, SbF_5 to the thermal unstable compounds $[(CF_3)_2TeF][BF_4]$ and $[(CF_3)_2TeF][EF_6]$ (E = As, Sb), respectively. These compounds decompose already at -10 to -15 °C. No corresponding cations were detected reacting $(CF_3)_2TeX_2$ with BX_3 (X = Cl, Br). We only observed decomposition to CF_3X, $Te(CF_3)_2$ and CF_3TeX_3.

Alkali metal halides, $[(CH_3)_4N]X$ or AgF react with $(CF_3)_2TeX_2$ (X = F, Cl, Br) to the penta-coordinated complex anions $[(CF_3)_2TeX_3]^-$.

In contrast to the binary $TeCl_4$ and $TeBr_4$, no further addition to hexa-coordinated complex anions is observed. The stability of the anions decreases in the order $X = F > Cl > Br$. In CH_3CN solution $[(CF_3)_2TeF_3]^-$ is stable up to +65 °C, $[(CF_3)_2TeCl_3]^-$ decomposes at 0 °C, while $[(CF_3)_2TeBr_3]^-$ is only detectable in the ^{19}F NMR spectra up to -30 °C besides some decomposition products. $M[(CF_3)_2TeX_3]^-$ ($X = F$, Cl) could be isolated as white to pale yellow hydrolysable solids. The thermal stability is significantly enhanced in the solid state compared to the corresponding solutions, e. g. $K[(CF_3)_2TeF_3]$ dec. pt. 215 °C, $K[(CF_3)_2TeCl_3]$ dec. pt. 115 °C.

TETRAKIS(TRIFLUOROMETHYL) TELLURIUM(IV)

While tetraalkyl tellurium[e.g. 37,38], tetrakis(perfluorophenyl) tellurium[39] as well as hexaaryl tellurium[e.g. 40,41] compounds have been described in the literature less is known about perfluoroalkyl tellurium compounds with more than two perfluoroalkyl groups.

Reactions of $TeCl_4$ with polar trifluoromethylation reagents, e. g. $Cd(CF_3)_2$ complexes, only yield bis(trifluoromethyl) tellurium compounds. But when we reacted separately synthezised $(CF_3)_2TeCl_2$ with $Cd(CF_3)_2 \cdot glyme$ in CH_3CN at -10 °C we were able to isolate $Te(CF_3)_4$. The reaction proceeds via $(CF_3)_3TeCl$ as an intermediate[42,43].

$$TeCl_4 + Cd(CF_3)_2 \longrightarrow (CF_3)_2TeCl_2 + CdCl_2$$

$$(CF_3)_2TeCl_2 + Cd(CF_3)_2 \xrightarrow{-10\,^{\circ}C} Te(CF_3)_4 + CdCl_2$$

$Te(CF_3)_4$ is a yellow, easily hydrolysable liquid, m.p. -45 °C, stable at room temperature. From spectroscopic data we must conclude that $Te(CF_3)_4$ forms 1:1 complexes with donor molecules. Only one sharp singlet for the CF_3 groups is detected in the ^{19}F NMR spectra. The values of the chemical shifts and the $^2J(^{125}Te,^{19}F)$ coupling constant depend on the donor number of different bases.

Solutions of $Te(CF_3)_4$ in CH_3CN spontaneously decompose to $Te(CF_3)_2$, CF_3H and CF_3CH_2CN under u.v. irradiation. Thermal decomposition of isolated $Te(CF_3)_4$ at +60 °C results in the formation of $Te(CF_3)_2$, $(CF_3)_2TeF_2$ and the difluorocarben products C_2F_4 and c-C_3F_6. $Te(CF_3)_4$ is a reactive trifluoromethyl group transfer reagent; under polar conditions only two of the four CF_3 groups are replaced. $Te(CF_3)_4$ reacts with alkali metal fluorides to the $[Te(CF_3)_2F_3]^-$ anion as the main product; in small amounts also the very unstable $[Te(CF_3)_4F]^-$ anion is detectable. Further addition of fluoride is not observed.

$Te(CF_3)_4$ forms with Lewis acids, e. g. BF_3, AsF_5, SbF_5, the more stable $[Te(CF_3)_3]^-$ cation. $[Te(CF_3)_3]^-$ $[BF_4]^-$ was isolated as a colourless sublimable solid (m.p. 85 °C, thermally stable at 300 °C). This remarkable thermal stability is comparable to that of the isoelectronic $Sb(CF_3)_3$.

Attempts of further oxidation with e. g. F_2, Cl_2, Br_2, AgF_2 only resulted in decomposition. Using XeF_2 as an oxidizer we obtained NMR spectroscopic evidence of the formation of small amounts of $(CF_3)_4TeF_2$.

In contrast to the high reactivity of $Te(CF_3)_4$ the higher homologous tetrakis(perfluoroalkyl) tellurium compounds are more stable. At room temperature $TeCl_4$ reacts with $Cd(R_f)_2$ complexes (R_f =

C_2F_5, C_3F_7, C_4F_9) to form the yellow, viscous liquids, $Te(R_f)_4$, which are isolated as 1:1 complexes. Hydrolysis occurs only at elevated temperature depending on the solvent, e. g. in $(C_2H_5)_2O$ at 30 °C, in CH_3CN at 50 °C, in diglyme at 80 °C. The $Te(R_f)_4$ complexes are thermally more stable than $Te(CF_3)_4$ but rapidly decompose under u.v. irradiation. In contrast to $Te(CF_3)_4$ we did not observe comparable reactions with fluoride donors or acceptors. Only with a large excess of SbF_5 a reaction takes place to form a not unambigously identified adduct.

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