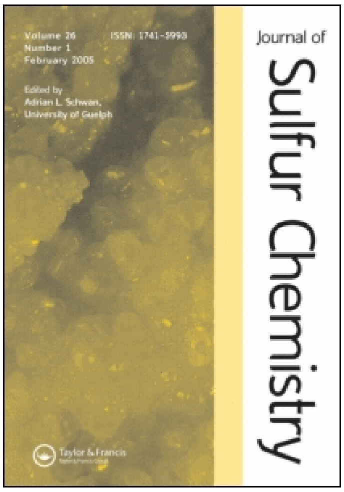

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PERFLUOROALKANE- AND PERFLUOROARENE-CHALKOGEN OXO ACIDS: SYNTHESES, REACTIONS AND STRUCTURES

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Different reactions leading to perfluoroorganyloligosulfanesulfonates and their unusual properties for metathesis are reviewed from 1991. Furthermore recent developments in syntheses of perfluoroorganyl substituted acids of selenium, tellurium and their derivatives allow a full description of this interesting chemistry. The physical properties are reviewed.

Key words: Thiosulfuric acids, sulfur-sulfur bond cleavage, perfluoroalkane- and perfluoroareneselenonic acids, salts, and esters, bis(pentafluorophenyl)tellurium(IV) acid, bis(pentafluorophenyl)tellurium(VI) oxide, pentafluorophenyltellurium(IV) oxo acid.

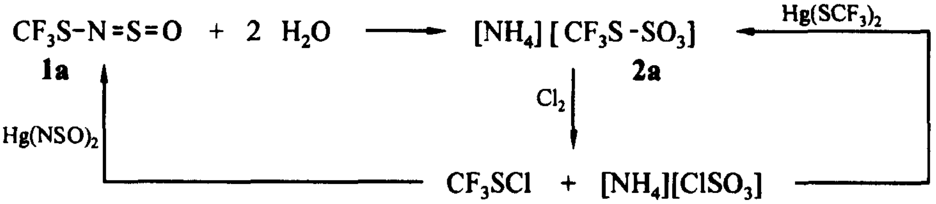
CONTENTS

1. PERFLUOROALKYL- AND PERFLUOROARYLOLIGOSULFANESULFONIC ACIDS

S-Organothiosulfonates of the general formula $RSSO_3R$ were first prepared in 1874 by Bunte.[1] Several publications and patents on partially fluorinated *S*-esters of thiosulfonic acids first appeared more than 91 years later,[2-8] but only one patent deals with perfluorinated *O*-esters of this acid.[9] The intention of this chapter is the description of *S*-perfluoroorganyl substituted oligosulfanemonosulfonates of the type $R_fS_xSO_3R$. The first member of this class of compounds[10] with $R_f = CF_3$ and $x = 1$ was prepared in 1991 and prompted further investigation.

1.1. *Hydrolysis of Perfluoroorganyl(sulfinylamino)oligosulfanes 1*

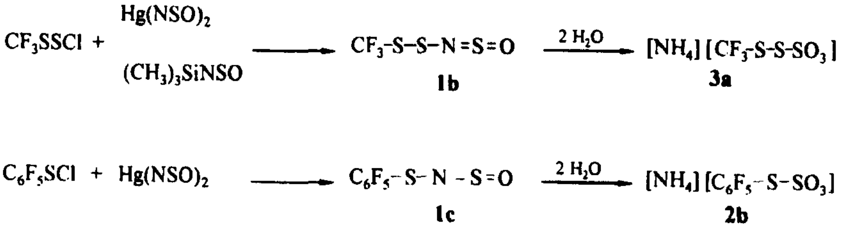
The thiosulfate $[NH_4][CF_3SSO_3]$, **2a**, is synthesized via a stoichiometric reaction of the *N*-sulfinylsulfenamide **1a** with two moles of water in a closed Carius tube. The compound is obtained as a colourless, microcrystalline solid in essentially quantitative yield.



SCHEME 1

Interaction of **2a** with chlorine leads to the well known chlorolysis products CF_3SCl and ammonium chlorosulfate, which can be converted to **1a** and **2a**, respectively, via metathesis with the appropriate mercury salts.[10]

The usefulness of a (controlled) hydrolysis may be demonstrated by the synthesis of the ammonium salts $[NH_4][CF_3SSSO_3]$, **3a**,[11] and $[NH_4][C_6F_5SSO_3]$, **2b**.[12]



SCHEME 2

Starting from *S*-perfluoroorganylsulfanyl chlorides in the first reaction step the *N*-sulfinylimines **1b** and **1c** can be prepared and isolated as slightly yellow liquids. Such reactions are always carried out without solvent, as there are no side reactions and the yields exceed 80%. Subsequent hydrolysis of **1b** and **1c**, respectively, led to the formation of colourless ammonium salts, which could be characterised and represent the first examples of *S*-perfluoroalkylsulfanyl-thiosulfonates **3a** and *S*-perfluoroaryl-thiosulfonates **2b**.

In a more detailed study of the first hydrolysis step, *N*-sulfinyltrifluoromethanesulfenamide **1a** was treated with the Lewis acid arsenic pentafluoride. Colourless crystals of the reaction product, $CF_3SNSO{\cdot}AsF_5$, were obtained by sublimation. The results of a single crystal structure determination[13] are shown below.

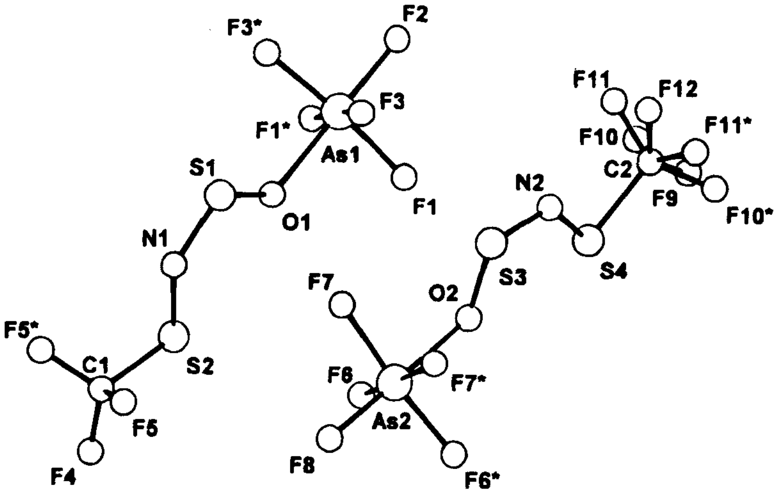
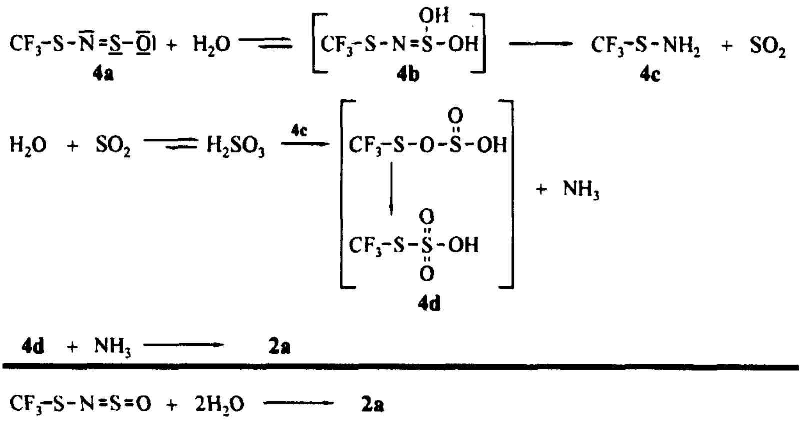


FIGURE 1 Single crystal structure of $CF_3SNSOAsF_5$

The unit cell contains two independent molecules of approximate C_s symmetry. One of the CF_3 groups is disordered. It is noteworthy that the As-O bond, formed between the Lewis acid and base, has an average length of 1.928(6) Å. This corresponds to a single bond and coordination of the nitrogen atom of the NSO cumulene system to AsF_5 is not observed. These results suggest that the main resonance structure of CF_3SNSO is **4a**.

Therefore the initial formation of an unstable iminosulfinic acid **4b** by addition of one mole of water can be assumed.

The acid **4b** decomposes and forms the primary amine **4c**, which is detected as an intermediate by ^{19}F NMR.[11] The S-N bond in **4c** can be cleaved by H_2SO_3, which in turn is formed in the pressure dependent equilibrium between SO_2 and a further mole of water, to lead to the formation of ammonia and a compound with an unstable S(II)-O-S(IV) moiety. Rearrangement to the more stable $S\text{-}SO_3$ moiety results in the formation of **4d**. The last step is the neutralization of free *S*-trifluoromethylthiosulfuric acid **4d** with ammonia, to form the ammonium salt **2a**. Therefore the hydrolysis pathway of CF_3SNSO to the sole product **2a** is readily explained by the stoichiometric reaction of one mole of the *N*-sulfinylamide with two moles of water in a Carius tube.



SCHEME 3

1.2. *Syntheses via Metathesis Reactions*

Covalent derivatives of *S*-trifluoromethylthiosulfuric acid can be synthesized readily from bis(trifluoromethylthio)mercury and covalent derivatives of chlorosulfonic acid in yields exceeding 80%.

$$Hg(SCF_3)_2 + Cl\text{-}SO_2R \longrightarrow \underset{\mathbf{5}}{CF_3\text{-}S\text{-}SO_2R} + HgCl_2$$

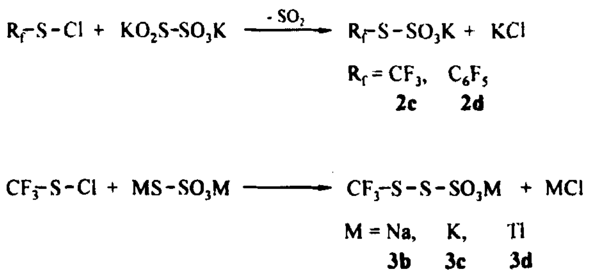
$$R = \underset{\mathbf{5a}}{NH_2},\ \underset{\mathbf{5b}}{N(CH_3)_2},\ \underset{\mathbf{5c}}{OSi(CH_3)_3}$$

SCHEME 4

The use of carbon tetrachloride as nonpolar solvent is advantageous, as the educts and reaction products, except mercury(II) chloride, are quite soluble, which will shift the equilibria from left to right. The primary amide $CF_3SSO_2NH_2$, **5a**, is a colourless solid; however, the colourless liquids $CF_3SSO_2N(CH_3)_2$, **5b**, and $CF_3SSO_3Si(CH_3)_3$, **5c**, are more reactive and more sensitive to hydrolysis due to their basic donor substituents.[11]

Sulfenyl chlorides of the type R_fSCl react with compounds containing sulfur in an oxidation state below six as shown.

Thus, reactions with disulfites result in cleavage of the S-S bonds with formation of ionic salts of the type $K[R_fSSO_3]$, i.e. **2c** and **2d**. Noticeably the reactions forming the ionic *S*-trifluoromethyldisulfanesulfonates **3b**, **3c** and **3d** are highly selective, since the only nucleophilic center in the inorganic thiosulfates is the thiol sulfur atom and no products due to side reactions are detected.



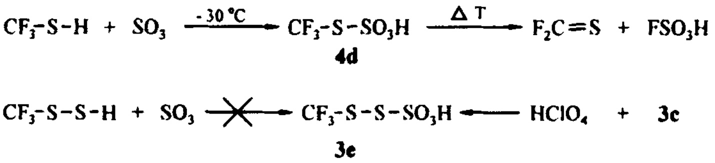
$$R_f\text{-S-Cl} + KO_2S\text{-}SO_3K \xrightarrow{-SO_2} R_f\text{-S-}SO_3K + KCl$$
$$R_f = CF_3,\ C_6F_5 \quad \mathbf{2c}\ \mathbf{2d}$$

$$CF_3\text{-S-Cl} + MS\text{-}SO_3M \longrightarrow CF_3\text{-S-S-}SO_3M + MCl$$
$$M = Na,\ K,\ Tl \quad \mathbf{3b}\ \mathbf{3c}\ \mathbf{3d}$$

SCHEME 5

1.3. *Trifluoromethyloligosulfanesulfonic Acids*

The first member of the series $CF_3S_xSO_3H$, (**4d**, x = 1) is obtained by insertion of SO_3 into the S-H bond of CF_3SH. This preparation is carried out at –30°C, with $CFCl_3$ as solvent, because at room temperature **4d** decomposes within 8 hours completely to thiocarbonyl difluoride and fluorosulfonic acid.



$$CF_3\text{-S-H} + SO_3 \xrightarrow{-30\,^\circ C} \underset{\mathbf{4d}}{CF_3\text{-S-}SO_3H} \xrightarrow{\Delta T} F_2C{=}S + FSO_3H$$

$$CF_3\text{-S-S-H} + SO_3 \xcancel{\longleftarrow} \underset{\mathbf{3e}}{CF_3\text{-S-S-}SO_3H} \longleftarrow HClO_4 + \mathbf{3c}$$

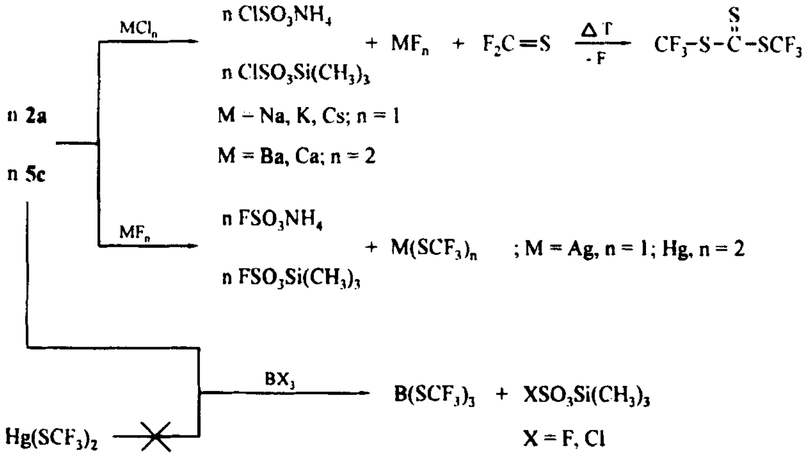
SCHEME 6

S-Trifluoromethylthiosulfuric acid CF_3SSO_3H, **4d**, is extremely sensitive to hydrolysis. In moist air a white fog, which smells of the thiol CF_3SH, forms. The hydrolysis is accompanied by the formation of sulfuric acid. The acidity of **4d** was estimated by use of ^{29}Si NMR. The chemical shift δ (^{29}Si) of the trimethylsilyl ester **5c** correlates with the ^{29}Si shifts of various silyl esters where the acidity of the parent acid is known.[11] The acidity in water is found to be comparable to that of trifluoromethanesulfonic and perchloric acid.

Due to a redox reaction between CF_3SSH and SO_3, the second member of the series $CF_3S_xSO_3H$ (x = 2) cannot be prepared by an insertion reaction, and the formation of $CF_3S_4CF_3$ predominates. The reaction of the potassium salt **3c** with perchloric acid is employed as alternative route to the acid CF_3SSSO_3H, **3c**. The method of its preparation suggests that CF_3SSSO_3H, **3c**, is much less sensitive to electrophilic attack than CF_3SSO_3H, **4d**.[12]

1.4. *Reactions of S-Trifluoromethylthiosulfates* 2

Typical examples for the reactions of *S*-trifluoromethylthiosulfates are the reactions of the ammonium salt $[NH_4][CF_3SSO_3]$, **2a**, and the more reactive trimethylsilyl ester $CF_3SSO_2OSi(CH_3)_3$, **5c**.



SCHEME 7

Reactions with metal chlorides and fluorides lead to quantitative cleavage of the sulfur-sulfur bond. The products of their reactions with alkali and alkaline earth metal chlorides are chlorosulfonate derivatives and the corresponding trifluoromethanethiolates, which decompose to fluorides and thiocarbonyl difluoride. Fluoride catalysed trimerisation of $F_2C{=}S$ produces a red coloured reaction mixture, the colour being due to $(CF_3S)_2C{=}S$. Analogous reactions with silver(I) and mercury(II) fluoride lead to the well known stable thiolates $M(SCF_3)_n$ (M = Ag, n = 1; Hg, n = 2) and derivatives of fluorosulfonic acid.

These results are consistent with a negatively polarised sulfur atom of the SCF_3 group. The title compounds can be used as nucleophiles in the transfer of CF_3S groups. Such reactions are usually carried out with $Hg(SCF_3)_2$. Metathesis of this compound with boron trifluoride or trichloride fails. In contrast to this, **5c** reacts quantitatively with boron trifluoride or trichloride at −30 °C to tris(trifluoromethylthio)borane $B(SCF_3)_3$.

In summary *S*-trifluoromethylthiosulfates can be used as synthons for a wide range of metatheses, which had not been studied previously.

2. PERFLUOROORGANO ACIDS OF SELENIUM AND TELLURIUM

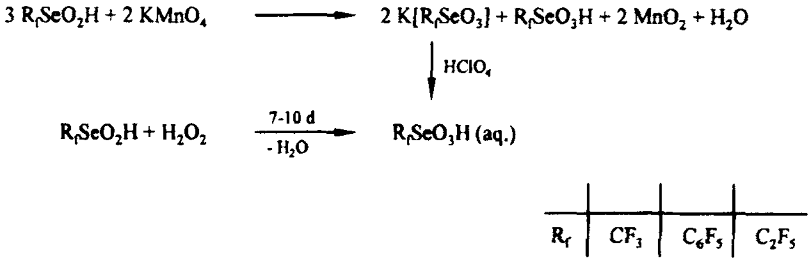
The chemistry of substituted oxoacids of Se(VI) and Te(VI) is not as extensively studied as that of the corresponding sulfur(VI) acids, where a large number of organo- and perfluoroorganosulfonic acids are known. Some of them are of industrial importance. A different situation is found for the homologous selenium(VI) and tellurium(VI) oxo acids.

2.1. *Syntheses of Perfluoroalkane- and Perfluoroareneselenonic Acids*

The first selenonic acid, $C_6H_5SeO_2OH$, was synthesised in 1906 by the oxidation of $(C_6H_5)_2Se_2$ with chlorine in aqueous solution.[14] A generally applicable method for the preparation of aliphatic and aromatic selenonic acids was published in 1919. Oxidation of seleninic acids with aqueous permanganate gave the corresponding selenonic acids.[15]

The first perfluoroorganic acid of selenium was obtained by treatment of $(CF_3)_2Se_2$ with conc. HNO_3 to give trifluoromethaneseleninic acid, CF_3SeO_2H.[16]

After unsuccessful attempts to oxidise CF_3SeO_2H in aqueous solution at 0 °C to CF_3SeO_3H with 40% $HClO_3$, 100% H_2O_2 or F_2, it was found that the salts of the corresponding selenonic acid can be prepared by reaction of trifluoromethaneseleninic acid with saturated aqueous $KMnO_4$. The free trifluoromethaneselenonic acid is obtained by treatment of the potassium salt with concentrated $HClO_4$.[17]



SCHEME 8

Pentafluorobenzeneselenonic acid and pentafluoroethaneselenonic acid can be synthesised in an analogous manner. Surprisingly, the reaction of $C_2F_5SeO_2H$ with $KMnO_4$ produces up to 30% trifluoroacetic acid. At pH 3.5, the yield of this by-product is reduced to about 3%.[18,19,20,21]

An alternative method to oxidise Se(IV) to Se(VI) in the syntheses of perfluoroorganoselenonic acids involves the use of concentrated H_2O_2 in stoichiometric amounts (an excess will attack the C-Se bond). This reaction, which can be followed by ^{19}F NMR, takes about 7 to 10 days. Formation of CF_3CO_2H as by-product in the case of $R_f = C_2F_5$ cannot be totally avoided.

Evaporation of aqueous solutions of the free acids gives hydrates with varying amounts of water. The acid $C_6F_5SeO_3H$ crystallises as a dihydrate. The pure acid is obtained by dehydration at 80 °C *in vacuo*. Conversion into its anhydride is achieved by dehydration at 200 °C *in vacuo*.

$$2\ C_6F_5SeO_3H \xrightarrow[-\ H_2O]{200\ ^\circ C\ /\ 10^{-3}\ Torr} [C_6F_5SeO_2]_2O$$

SCHEME 9

Solutions of the acid CF_3SeO_3H can only be concentrated up to a total acid content of 90%. The composition is then close to that of a 1:1 compound, $CF_3SeO_3H{\cdot}H_2O$, which can be considered as an oxonium salt, $[H_3O][CF_3SeO_3]$. Attempts at further concentration result in spontaneous decomposition with the formation of selenium and further unidentified products. In order to obtain $[CF_3SeO_2]_2O$ a solution of the selenium(IV) acid, CF_3SeO_2H, was treated at 20 °C with HOF in acetonitrile in a molar ratio 1:3.[22] The trifluoromethaneselenonic acid is identified by NMR spectroscopy together with another substance, probably a Se(VI) derivative. Evaporation of the solution to dryness produces the Se(IV) anhydride $[CF_3Se(O)]_2O$. The formation of a peroxy acid as probable intermediate is suggested.

2.2. *Derivatives of Perfluoroalkane- and Perfluoroareneselenonic Acids*

Salts of perfluoroorganoselenonic acids can be readily obtained either by neutralisation with the corresponding hydroxides or by reaction of the acid with nitrates. Except for the silver salts, which are only slightly soluble, the salts all dissolve in water.

$$R_fSeO_3H + Ag^+ \longrightarrow 2\,Ag[R_fSeO_3] + H^+$$

$$+\,MOH \longrightarrow M[R_fSeO_3] + H_2O$$

R_f \ M	Ag	Li	Na	NH_4	0.5 Ba
CF_3	**6a**	-	-	**6b**	-
C_6F_5	**7a**	**7b**	**7c**	**7d**	**7e**
C_2F_5	**8a**	-	-	**8b**	-

SCHEME 10

While halogenations fail it is possible to synthesise alkyl and silyl esters from the silver salts and alkyl and silyl iodides, respectively:

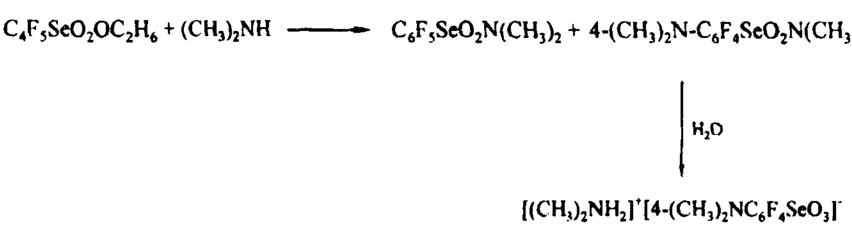
$$Ag[R_fSeO_3] + RI \longrightarrow R_fSeO_2OR + AgI$$

$R_f = CF_3$, $R = C_2H_5$; $R_f = C_6F_5$, $R = C_2H_5, n\text{-}C_3H_7, (CH_3)_3Si$; $R_f = C_2F_5$, $R = C_2H_5$

SCHEME 11

Surprisingly, the reaction of **7a** with CH_3I produces both the expected methyl ester, but also the ethyl ester, probably formed in a subsequent reaction between the methyl ester and excess CH_3I. The products cannot be separated and only a mixture of the two esters is isolated. The pure esters are obtained from **7a** and C_2H_5I and $n\text{-}C_3H_7I$, respectively. At 20 °C all esters are colourless liquids soluble in polar organic solvents.

At a molar ratio of 1:1 $C_6F_5SeO_2OC_2H_5$ reacts with $(CH_3)_2NH$ to the corresponding amide, $C_6F_5SeO_2N(CH_3)_2$, and the 4-substituted derivative, $4\text{-}(CH_3)_2NC_6F_4SeO_2N(CH_3)_2$.



$$C_4F_5SeO_2OC_2H_6 + (CH_3)_2NH \longrightarrow C_6F_5SeO_2N(CH_3)_2 + 4\text{-}(CH_3)_2N\text{-}C_6F_4SeO_2N(CH_3)_2$$

$$\Big\downarrow H_2O$$

$$[(CH_3)_2NH_2]^+[4\text{-}(CH_3)_2NC_6F_4SeO_3]^-$$

SCHEME 12

When two moles of $(CH_3)_2NH$ are used the latter is the only product. It is sensitive to moisture and hydrolyses quantitatively to $[(CH_3)_2NH_2][4\text{-}(CH_3)_2NC_6F_4SeO_3]$.

The salt $[(C_6H_5)_4As][C_2F_5SeO_3]$ can be produced in 90% yield from $Ag[C_2F_5SeO_3]$ and $[(C_6H_5)_4As]Cl$ in CH_3CN at 35 °C. A structure determination by single crystal X-ray diffraction shows an SeO_3 moiety with three equivalent Se-O distances of 1.612(4), 1.612(4) and 1.617(4) Å. The peroxy acids $R_fSe(O)OOH$ cannot be detected.[23,24]

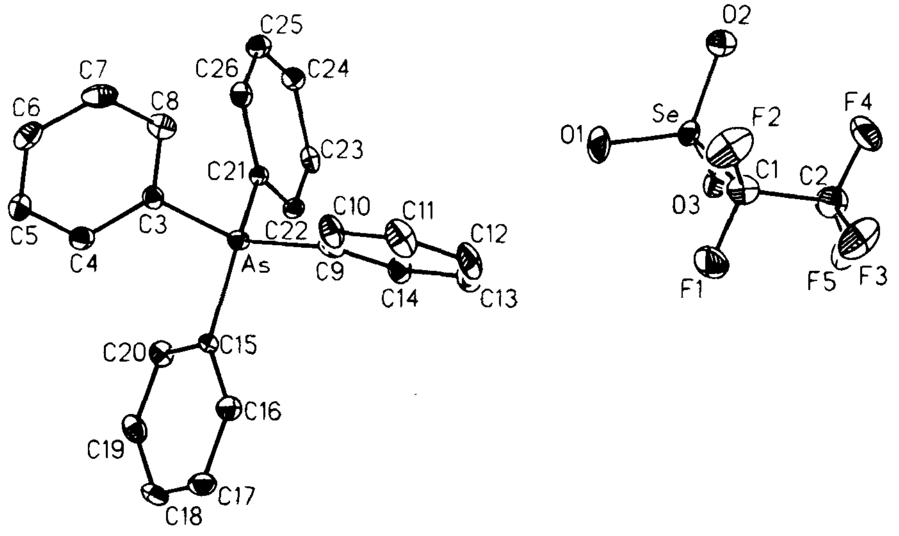


FIGURE 2 Single crystal structure of $[(C_6H_5)_4As][C_2F_5SeO_3]$

2.3. *Physical Properties of Perfluoroalkane- and Perfluoroareneselenonic Acids*

Perfluoroorganoselenonic acids are strong acids in water.[25,26] Estimated pK_a values show an increase in acidity upon going from R to R_f and from Se(IV) to Se(VI). Results of a back titration of a 1 M aqueous solution of KX ($X = Cl, NO_3, C_2F_5SeO_3$) and K_2SeO_4 with 60% $HClO_4$ indicate that the acidity of $C_2F_5SeO_3H$ is between that of HCl and H_2SeO_4. Consequently in water it cannot be considered as a super acid, as is $C_2F_5SO_3H$.

Attempts to measure the redox potentials of R_fSeO_2H and R_fSeO_3H by cyclic voltammetry were only partly successful. When power is applied, solutions of 10^{-3} M Se(VI) acids decompose immediately with the deposition of selenium. For Se(IV) only a reduction peak is observed at a potential identical to that of H_2SeO_3 ($E^{red} = -0.64$ V vs Ag/AgCl $\equiv E^{red} = -0.765$ vs SHE). The process is irreversible and the Nernst equation cannot be applied to estimate the redox potential.

2.4. *Syntheses of Perfluoroorganyl Substituted Oxo Acids of Tellurium*

The first arenetellurinic acid, $C_6H_5Te(O)OH$, was prepared in 1915 from $(C_6H_5)_2Te_2$ and conc. HNO_3. The corresponding 1-butanetellurinic acid was obtained from $(C_4H_9)_2Te$ and H_2O_2 in 1938.[27,28] Alkaline hydrolysis of diaryl ditellurides in the presence of oxygen and activation by phase transfer catalysts produced primarily the tellurinate anion $ArTe(O)O^-$, which upon acidification was converted to the corresponding tellurinic anhydride, $(ArTeO)_2O$.[29]

First indications of the possible existence of a perfluoroorganyltellurium(IV) acid were reported in 1992, when unstable $Te(CF_3)_4$ hydrolysed to $(CF_3)_3TeOH$ which decomposed further to the already known $(CF_3)_2TeO$: the acid $(CF_3)_3TeOH$ was not isolated, but characterized by its ^{19}F NMR spectrum.[30,31]

$$\mathrm{Te(CF_3)_4 + H_2O \xrightarrow[-\,CF_3H]{CH_3CN} <(CF_3)_3TeOH> \xrightarrow[-\,CF_3H]{0\,^{\circ}C} (CF_3)_2TeO}$$

SCHEME 13

Oxidation of $(C_6F_5)_2Te$ with conc. HNO_3 at 20 °C starts with the spontaneous evolution of nitrogen oxides. The reaction is finished after about 3 h, when a colourless amorphous powder of reasonable thermal stability could be produced, which is characterised as bis(pentafluorophenyl)tellurium(IV) nitrate. Detailed infrared spectroscopic investigations show that the structure of $(C_6F_5)_2Te(OH)NO_3$ is covalent. The NO_3 group is bonded through oxygen to the tellurium atom. On heating the compound to 50 °C *in vacuo* for several hours, no decomposition is detected, in contrast to the instability of $(CF_3)_2Te(ONO_2)_2$ which yields, as the final product, $(CF_3)_2TeO$. The product is slightly soluble in $CHCl_3$, and dissolves in CH_3CN or acetone with adduct formation, is insoluble in CH_3OH, C_2H_5OH, THF, SO_2ClF, $POCl_3$, CCl_4 and decomposes in DMSO, DMF or HMPA.

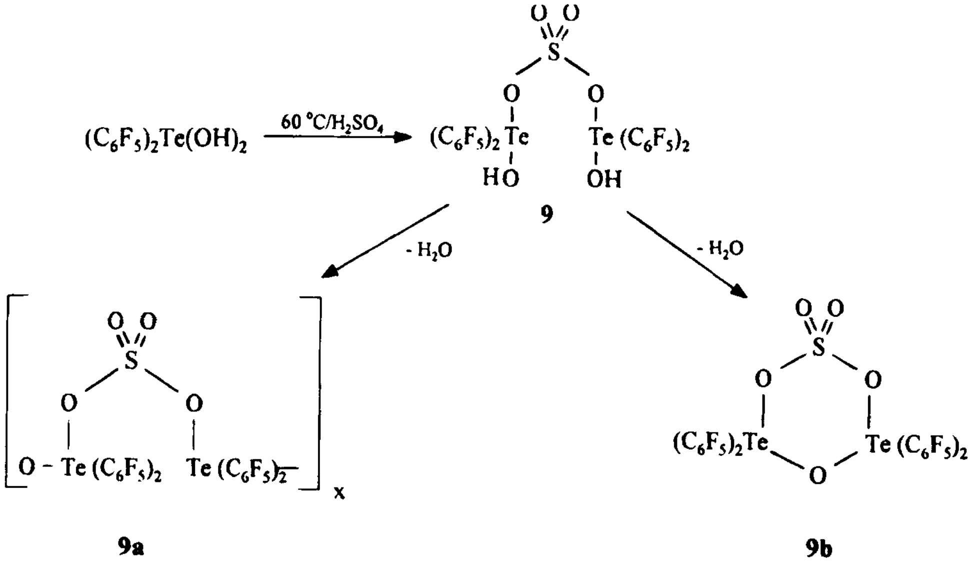
$$\mathrm{(C_6F_5)_2Te + 3\,HNO_3 \longrightarrow (C_6F_5)_2Te(OH)ONO_2 + 2\,NO_2 + H_2O}$$

$$\mathrm{(C_6F_5)_2Te(OH)ONO_2 + H_2O \longrightarrow (C_6F_5)_2Te(OH)_2 + HNO_3}$$

$$\mathrm{(C_6F_5)_2Te(OH)_2 + H^+ \xrightarrow[-\,H_2O]{100\,^{\circ}C} [(C_6F_5)_2Te(OH)]^+ \xrightarrow{20\,^{\circ}C/ClO_4^-} [(C_6F_5)_2Te(OH)][ClO_4]}$$

SCHEME 14

Compared to C_6H_5, it seems that C_6F_5 is a stronger electron withdrawing group, which in turn makes the tellurium atom in $(C_6F_5)_2Te(OH)ONO_2$ a stronger electrophile than that of the corresponding acid derivative $C_6H_5Te(O)NO_3$. Hydrolysis in the first case in water and for $(C_6F_5)_2Te(OH)ONO_2$ in basic solution (stronger nucleophile) converts the starting materials to bis(pentafluorophenyl)tellurium(IV) acid, $(C_6F_5)_2Te(OH)_2$. The free acid dissolves slowly in hot 60% aqueous $HClO_4$. On cooling to 20 °C for several hours thin, long needles of $[(C_6F_5)_2Te(OH)][ClO_4]$ precipitate. A similar reaction takes place with conc. H_2SO_4 at 60 °C. Product **9** is obtained as an amorphous powder. It is not clear whether the substance is the expected sulfate, its cyclic, **9b**, or noncyclic, **9a**, polycondensate or a mixture of these possible forms.



SCHEME 15

Attempts to synthesise salts by neutralisation of the acid with dilute aqueous bases (KOH, RbOH, CsOH) at 20 °C failed, only polytellurates being formed. Obviously the Te-C bond is unstable towards strong nucleophiles like OH^-.

Acidic aqueous H_2O_2 (35%) oxidises $(C_6F_5)_2Te(OH)_2$ at 40 °C over a period of 48 hours to $(C_6F_5)_2TeO_2$, the anhydride of the corresponding orthotellurium(VI) acid. The substance is totally insoluble in H_2O and organic solvents. In CF_3SO_3H at 20 °C (in an inert atmosphere) the anhydride reacts to form bis(pentafluorophenyl)tellurium(VI) tetrakis(trifluoromethylsulfonate) which is readily soluble in CH_3CN. In the presence of water, partial hydrolysis of the CH_3CN solution takes place after several hours to form $(C_6F_5)_2Te(OSO_2CF_3)_2(OH)_2$.

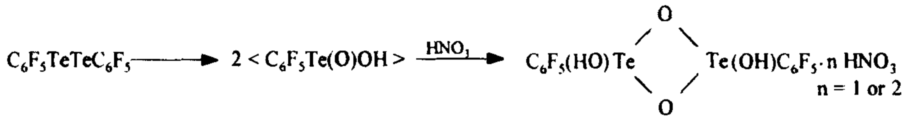
$$(C_6F_5)_2Te(OH)_2 + H_2O_2 \xrightarrow{H^+} (C_6F_5)_2TeO_2 + 2\,H_2O$$

$$(C_6F_5)_2TeO_2 + 4\,CF_3SO_3H \xrightarrow[-2\,H_2O]{20\,°C} (C_6F_5)_2Te(OSO_2CF_3)_4$$

$$(C_6F_5)_2Te(OSO_2CF_3)_4 + 2\,H_2O \xrightarrow{CH_3CN} (C_6F_5)_2Te(OSO_2CF_3)_2(OH)_2 + 2\,CF_3SO_3H$$

SCHEME 16

In order to obtain monosubstituted tellurium oxo acids, $(C_6F_5)_2Te_2$ was used as starting material. With conc. HNO_3 at 20 °C and after one hour a colourless solid, **7**, formed, insoluble in most common organic and inorganic solvents. Its characterisation is based mainly on elemental analysis. The formula $[(C_6F_5Te(O)OH]_x$ is suggested, but the material contains some HNO_3. IR and Raman data indicate the conversion of a Te-Te to a Te-O-Te moiety. Since double bonds are very uncommon in tellurium chemistry, the product should be oligomeric, possibly dimeric and containing a four-membered ring.



7

SCHEME 17

Additional evidence for the proposed structure comes from the reaction of **7** with $(CH_3)_2SO$. Attempts to dissolve the product in this solvent give initially a clear solution, but after a few minutes a colourless substance precipitates and C_6HF_5 can be detected in the solution. The insoluble solid is identified as polymeric $TeO_2 \cdot HNO_3$ which is known to contain a four-membered ring unit.[32]

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