

Perfluoro-organochalcogenyl acids in high oxidation states [☆]

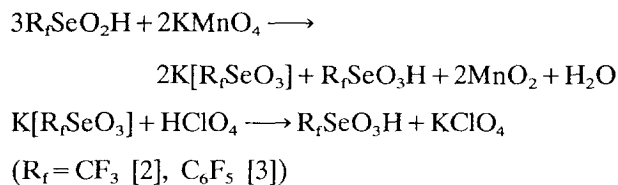
A. Haas ^{*}, S. Herkt

Lehrstuhl für Anorganische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany

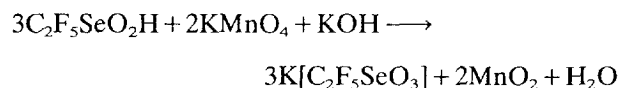
Keywords: Perfluoro-organochalcogenyl acids; High oxidation states; Sulphur; Selenium; Tellurium; Single-crystal X-ray diffraction study

The chemistry of substituted oxyacids of the chalcogens, with S, Se and Te in oxidation state VI, is well known as far as sulphur is concerned. Various organo- and perfluoro-organosulfonic acids are available and some have achieved industrial importance. However, a completely different picture exists as far as the sulfur homologues selenium and tellurium are concerned.

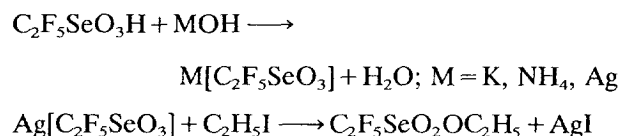
The first perfluoro-organoselenonic acids were synthesized by oxidation of $R_f\text{SeO}_2\text{H}$ with KMnO_4 in aqueous solution. By treating $\text{K}[R_f\text{SeO}_3]$ with 74% HClO_4 , the free acids were obtained according to:



Surprisingly, the oxidation of $\text{C}_2\text{F}_5\text{SeO}_2\text{H}$ with KMnO_4 gave up to 30% of $\text{K}[\text{CF}_3\text{CO}_2]$ besides $\text{K}[\text{C}_2\text{F}_5\text{SeO}_3]$. When this process was carried out at a pH value of 3.5 by adding stoichiometric amounts of KOH , the formation of $\text{K}[\text{CF}_3\text{CO}_2]$ could be reduced to about 3%.



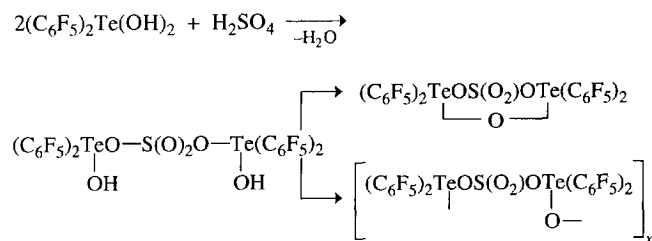
Salts may be prepared by neutralization. Esterification is accomplished by treating $\text{Ag}[\text{C}_2\text{F}_5\text{SeO}_3]$ with $\text{C}_2\text{H}_5\text{I}$ according to:



The acidity of $\text{C}_2\text{F}_5\text{SeO}_3\text{H}$ in H_2O lies between that of HCl , HNO_3 and H_2SeO_4 . For this reason, it cannot be considered a super acid.

A structure determination by single-crystal X-ray diffraction of $[(\text{C}_6\text{H}_5)_4\text{As}][\text{C}_2\text{F}_5\text{SeO}_3]$, prepared from $[(\text{C}_6\text{H}_5)_4\text{As}]\text{Cl}$ and $\text{Ag}[\text{C}_2\text{F}_5\text{SeO}_3]$ in CH_3CN at 35 °C showed unambiguously the presence of a selenium(VI) moiety with three equivalent oxygens bound to selenium. The values of $D(\text{Se}-\text{O})$ were equal to 1.612 (4) Å to within error limits.

Oxidation of $(\text{C}_6\text{F}_5)_2\text{Te}$ with conc. HNO_3 at 20 °C provides, after 3 h, a colourless amorphous powder of composition $(\text{C}_6\text{F}_5)_2\text{Te}(\text{OH})\text{NO}_3$. This is slightly soluble in CHCl_3 and dissolves in CH_3CN or acetone with adduct formation. On heating for several hours in vacuo to 50 °C, no decomposition was detected. Hydrolysis takes place to give $(\text{C}_6\text{F}_5)_2\text{Te}(\text{OH})_2$ quantitatively, this being the first stable perfluoro-organotellurium acid. The acid dissolves in hot 60% aqueous HClO_4 which on cooling to 20 °C (several hours) gives thin, long needles. The product obtained is the perchlorate $(\text{C}_6\text{F}_5)_2\text{Te}(\text{OH})\text{ClO}_4$. A similar reaction took place with conc. H_2SO_4 at 60 °C, but the compound obtained was an amorphous powder. It is not clear whether the substance is the expected sulfate or its cyclic, respectively non-cyclic polycondensate formed according to:



Attempts to synthesize salts by neutralization of the acid with dilute bases such as KOH , RbOH or CsOH at 20 °C failed and only polytellurates were formed.

[☆] See Ref. [1].

^{*} Corresponding author.

Obviously the Te–C bond is not resistant towards hydroxylic nucleophiles.

An acidic aqueous 35% H₂O₂ solution oxidizes (C₆F₅)₂Te(OH)₂ at 40 °C (48 h) to yield (C₆F₅)₂TeO₂, the anhydride of the corresponding orthotellurium(VI) acid. The substance is totally insoluble in H₂O and common organic solvents. It is soluble in CF₃SO₂OH at 20 °C (inert atmosphere) to form (C₆F₅)₂Te(OSO₂CF₃)₄, which dissolves readily in CH₃CN. In the presence of H₂O, partial hydrolysis to (C₆F₅)₂Te(OH)₂(OSO₂CF₃)₂ is observed.

Monosubstituted tellurium oxoacids are formed from (C₆F₅)₂Te₂ and conc. HNO₃ at 20 °C (1 h) yielding [C₆F₅Te(O)OH]_k as a colourless solid, which is insoluble in most common organic and inorganic solvents. Evidence for the proposed structure comes from its reaction with (CH₃)₂SO. Attempts to dissolve the product gave a clear solution at first but after a few minutes a colourless substance precipitated and in solution C₆F₅H could be detected by ¹⁹F and ¹³C NMR spectroscopy. The insoluble solid was identified as polymeric TeO₂·HNO₃.

Summarizing the results obtained to date, the following conclusions can be tentatively drawn regarding the chemical properties of perfluoro-organooxo acids of sulphur, selenium and tellurium in high oxidation states.

1 (a) Sulphur and selenium form molecular oxyacids of the general formula R_fXO_nH with X = S, Se and n = 2, 3.

- (b) Tellurium does not form monomeric acids of the type R_fTeO_nH with n = 2, 3. The only acid of composition C₆F₅TeO₂H is oligo- or polymeric and a solvate containing HNO₃.
- 2 (a) No acids of formula (R_f)₂E(OH)₂ have been detected to date (e.g. E = S, Se).
- (b) With tellurium, the acid (C₆F₅)₂Te(OH)₂ and the anhydride (C₆F₅)₂TeO₂ were synthesized and characterized.
- 3 (a) The acidity of perfluoro-organochalcogeno oxoacids decreases in the order S > Se > Te and at least for S and Se with decreasing oxidation states from VI to IV.
- (b) They are stronger acids than the corresponding organo derivatives.
- (c) No salts were synthesized from R_fTe oxoacids in contrast to the salt formation observed for S and Se.
- 4 (a) The oxidizing power increases with increasing oxidation states from S to Se. As yet no definite conclusions can be reached for the corresponding tellurium derivatives.

References

- [1] A. Haas and H.-U. Weiler, *Chem. Ber.*, 118 (1985) 943.
 [2] A. Haas and K. Schinkel, *Chem. Ber.*, 123 (1990) 685.
 [3] A. Haas and S. Herkt, *Chem. Ber.*, in press.