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Perfluoroethanesulfonyl Fluoride: Preparation from Sultone

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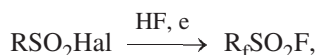
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Abstract—A procedure was developed for preparing perfluoroethanesulfonyl fluoride by synthesis of hexafluoropropane-2- β -sultone from sulfuric anhydride and perfluoropropene, followed by hydrolysis of the sultone to α -tetrafluoroethanesulfonyl fluoride and fluorination of the latter with elemental fluorine.

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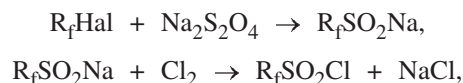
Perfluoroalkanesulfonyl halides (PFASHs), including sulfonyl fluorides, are starting compounds for preparing perfluoroalkanesulfonic acids and their salts. They are also used as sources of perfluoroalkanesulfonyl groups in the synthesis of surfactants, dyes, antioxidants, UV stabilizers, and materials for chemical power cells [1–6]. Among PFASHs, of particular interest are lower homologs with 1–3 carbon atoms. However, application of PFASHs is limited by their high cost, caused by the lack of an efficient synthesis process. There are a number of procedures for preparing PFASHs, each having certain features and shortcomings. The best studied process is electrochemical fluorination (ECF), i.e., electrolysis of solutions of alkanesulfonyl halides in hydrogen fluoride [7, 8]:



where Hal is F or Cl, R is alkyl, and R_f is perfluoroalkyl.

In Russia, the method is implemented at the Angarsk Electrochemical Plant for the production of trifluoromethanesulfonyl fluoride from methanesulfonyl chloride; the yield is 80–85%. Methanesulfonyl chloride, like other lower alkanesulfonyl chlorides, is not produced in Russia. Commercial electrochemical synthesis of perfluoroethanesulfonyl fluoride (PFESF) from ethanesulfonyl fluoride appeared to be unfeasible because of the low yield, which did not exceed 45%. The electrolysis is accompanied by formation of a large amount of impurities with boiling points close to that of PFESF; furthermore, a part of PFESF is mixed with hydrogen fluoride, and its significant fraction (up to 30%) remains dissolved in the electrolyte. Interme-

diate conversion of ethanesulfonyl chloride into ethanesulfonyl fluoride by the reaction with HF in the presence of a chromium–magnesium catalyst [9] allowed the PFESF yield to be increased to 70%, but its isolation appeared to be difficult. In electrolysis of higher alkanesulfonyl chlorides, the PFASH yields are as low as 25–30%. Another route to PFASHs is the reaction of perfluoroalkyl iodides or bromides with sodium dithionite, followed by chlorination of the resulting sodium perfluoroalkanesulfinate [10–12]:

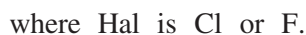


where R_f is perfluoroalkyl, and Hal is Br or I.

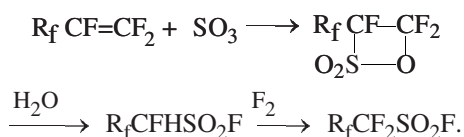
The reaction was performed in a water–acetonitrile mixture. The yield of perfluoroalkylsulfonyl chlorides reached 80%. We reproduced this procedure with perfluoroethyl iodide and obtained perfluoroethanesulfonyl chloride in 76% yield. Despite reasonable yield of PFASH, this procedure has significant drawbacks:

- (1) use of expensive perfluoroalkyl iodides and bromides, which are in short supply, as starting compounds;
- (2) use of sodium dithionite, which is not produced in Russia, and instability of this salt in storage, which gives rise to additional problems;
- (3) strong corrosion of apparatus and pipelines, caused by chlorination of sodium perfluoroalkanesulfinate in aqueous solutions;
- (4) overall complexity of the process: It involves steps of extraction, filtration, and regeneration of solvents. Implementation of the process requires a

Another procedure suggested for preparing PFASHs is based on the reaction of perfluoroolefins with sulfuryl fluoride or sulfuryl fluorochloride in the presence of cesium fluoride [13, 14]:

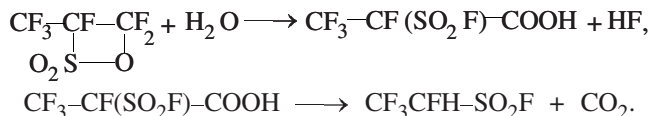


The drawbacks of the above-considered procedures for preparing PFASHs make it necessary to search for a simple procedure for their synthesis involving chemicals commercially produced in Russia and to develop an efficient technology based on this procedure. Among possible routes to PFASHs, we chose conversion of sultones. In accordance with [15–17], polyfluorinated alkanesulfonyl fluorides are formed by hydrolysis of perfluorinated sultones which, in turn, are prepared by the reaction of sulfuric anhydride with perfluoroolefins. According to data reported by Knuynyants [15, 16] and results of our experiments, the yield of hexafluoropropane-2- β -sultone is as high as 96–98%. The impurities (0.5–2%) are the linear isomer $\text{CF}_3\text{--CF}(\text{SO}_2\text{F})\text{--COF}$, six- and eight-membered sultones, and perfluoroallyl sulfate $\text{CF}_2=\text{CF--CF}_2\text{O}\cdot\text{SO}_2\text{F}$. Sultones are hydrolyzed to α -hydroperfluoroalkanesulfonyl fluorides (HPFSFs), which, as we expected, can be fluorinated to perfluoroalkanesulfonyl fluorides:

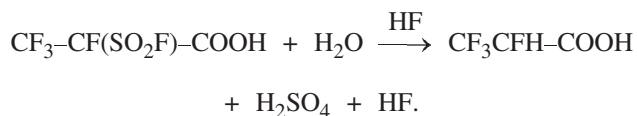


The optimal temperature of sultone synthesis is 105°C. Above this temperature, the sultone starts to decompose, and its yield decreases. At temperatures below 100°C, the reaction becomes slower. At 50°C, the yield is 53%.

Hydrolysis of hexafluoropropane-2- β -sultone involves two successive reactions: formation of (fluorosulfonyl)perfluoropropionic acid and its spontaneous decarboxylation with the formation of α -hydrotetrafluoroethanesulfonyl fluoride (TFESF):



The formation of hydrogen fluoride in the course of hydrolysis leads to the formation of tetrafluoropropionic acid:



The optimal hydrolysis temperature is 0–2°C. At this temperature, the yield of TFESF is 90%. TFESF contained up to 1% water. The content of other impurities did not exceed 0.03 wt %. After drying, the product was used for fluorination without additional purification.

Fluorination of polyfluorinated paraffins, ethers, tertiary amines, and their heterocyclic analogs by various procedures, including that with elemental fluorine, is a fairly well studied process, and high yields of the target products can be attained [18]. Fluorination of compounds containing an S–C bond is

vessel packed with copper chips and cooled to 0°C was charged with 18.5 g of TFESF, and fluorine was fed at a rate of 0.5–0.7 ml s⁻¹ for 1 h (the procedure was performed in a steel box). After 24 h, the reaction mixture was condensed in a 12Cr18Ni10Ti stainless steel trap cooled with liquid nitrogen. After warming, it was neutralized with aqueous NaOH, dried over CaA zeolite, and collected in a trap cooled to -30°C. The product (yield 20 g) contained 95% PFESF and 5% impurities (CF₃SO₂F, SO₂F₂, C₂F₆, CF₄, SF₆).

Fluorination under dynamic conditions. A solution containing 92 g of TFESF and 10 g of HF was fed at a rate of 0.8–1.0 g min⁻¹ from a batcher to a vaporizer (nickel tube 38 mm in diameter and 500 mm long, heated to 80–100°C). Fluorine was also fed to this tube at a rate of 120–130 ml min⁻¹. Then the mixture of the components came into a reactor (nickel tube 38 mm in diameter and 900 mm long, packed with copper chips and heated to 130–140°C). The reaction products were collected in a 12Cr18Ni10Ti stainless steel trap cooled to -120°C. After the reaction completion, the condensate was worked up as described above. The product (yield 90 g) contained 96.5% PFESF and 3.5% impurities (CF₃SO₂F, SO₂F₂, C₂F₆, CF₄, SF₆).

CONCLUSIONS

(1) A procedure was developed for preparing perfluoroethanesulfonyl fluoride by fluorination of tetrafluoroethanesulfonyl fluoride.

(2) The steps of perfluoroethanesulfonyl fluoride synthesis were optimized, and its pilot production was set up at the Galogen Open Joint-Stock Company.

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