Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE-CONTAINING POLYMERS, PERFLUOROALKANESULFONIC ACIDS

Perfluoroalkanesulfonic acids and their derivatives are of commercial significance because of their unusual acid strength, chemical stability, and the surface activity of the higher members of the series (eight carbons and larger).

1. Preparation

The perfluoroalkane sulfonic acids were first reported in 1954. Trifluoromethanesulfonic acid was obtained by the oxidation of bis(trifluoromethyl thio) mercury with aqueous hydrogen peroxide (1). The preparation of a series of perfluoroalkanesulfonic acids derived from electrochemical fluorination (ECF) of alkane sulfonyl halides was also disclosed in the same year (2). The synthetic operations employed when the perfluoroalkanesulfonic acid is derived from electrochemical fluorination, which is the best method of preparation, are shown in equations 1–3.

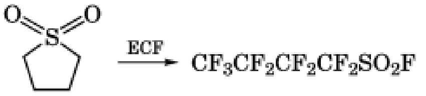
$$R_hSO_2F + HF \longrightarrow R_fSO_2F + H_2 \qquad (1)$$

where R_h is an alkyl group and R_f is a perfluoroalkyl group

$$R_fSO_2F + KOH \longrightarrow R_fSO_3K + HF \qquad (2)$$

$$R_fSO_3K + H_2SO_4 \longrightarrow R_fSO_3H + KHSO_4 \qquad (3)$$

Perfluorosulfonyl fluorides can also be prepared by the electrochemical fluorination of saturated or unsaturated cyclic sulfones (3–5). Perfluorobutanesulfonyl fluoride can be prepared in 40–48% yield from sulfolane (eq. **4**) (6).



(4)

Yields of sulfonyl fluorides prepared by ECF vary depending on the particular structure. Chain degradation becomes more important as the chain length increases (6). Yields can vary from 96% for perfluoromethanesulfonyl fluoride (7) to 43–50% for perfluorooctanesulfonyl fluoride (8).

Trifluoromethanesulfonic acid can be prepared via trifluoromethanesulfenyl chloride as shown in equations 5–7 (9).

$$CF_3S-SCF_3+Cl_2 \longrightarrow 2\ CF_3SCl \qquad (5)$$

$$CF_3SCl+2\ HOCl \longrightarrow CF_3SO_2Cl+2\ HCl \qquad (6)$$

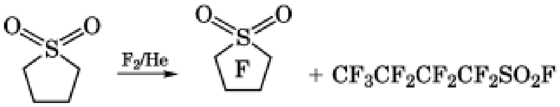
$$CF_3SO_2Cl+NaOH \longrightarrow CF_3SO_3Na+HCl \qquad (7)$$

Other preparations of trifluoromethanesulfonic acid include oxidation of methyltrifluoromethyl sulfide under a variety of conditions (10, 11). Perfluorosulfonyl fluorides have also been prepared by reaction of fluoroolefins with sulfuryl fluoride (12, 13). Chinese chemists have published numerous papers on the conversion of telomer-based alkyl iodides to sulfonyl fluorides (14, 15) (eqs. 8 and 9):

$$2\ R_f I+Na_2S_2O_4+NaHCO_3 \longrightarrow 2\ R_f SO_2Na \qquad (8)$$

$$R_f SO_2Na+Cl_2 \longrightarrow R_f SO_2Cl+NaCl \qquad (9)$$

Perfluorosulfonyl fluorides have also been prepared by direct fluorination, although in general yields are lower than preparation by ECF. Perfluoromethanesulfonyl fluoride has been produced in 15% yield from direct fluorination of dimethyl sulfone (16). Perfluoro-2-propanesulfonyl fluoride was prepared in 29% yield from propanesulfonyl fluoride (17). Direct fluorination of tetramethylene sulfone leads to the intact perfluorinated sulfone in 28% yield and the ring-opened product (perfluorobutanesulfonyl fluoride) in 10% yield (eq. **10**) (17).



(10)

Currently, the commercially important methods of preparations of perfluorinated sulfonic acid derivatives are electrochemical fluorination and sulfur trioxide addition to tetrafluoroethylene with subsequent ring opening.

The boiling points of a series of perfluoroalkanesulfonic acids are listed in Table 1 (2).

2. Trifluoromethanesulfonic Acid

The first member of the series, CF_3SO_3H, has been extensively studied. Trifluoromethanesulfonic acid [1493-13-6] is a stable, hydroscopic liquid which fumes in air. Addition of an equimolar amount of water to the acid results in a stable, distillable monohydrate, mp 34°C, bp 96°C at 0.13 kPa (1 mm Hg) (18). Measurement of conductivity of strong acids in acetic acid has shown the acid to be one of the strongest protic acids known, similar to fluorosulfonic and perchloric acid (19).

Table 1. Boiling Points of Perfluoroalkanesulfonic Acids

Compound	CAS Registry Number	Bp, °C/kPa[a]	Bp, °C[b]
CF_3SO_3H	[1493-13-6]	60/0.4	166
$C_2F_5SO_3H$	[354-88-1]	81/2.9	175[c]
$C_4F_9SO_3H$	[59933-66-3]	76–84/0.017	200[c]
$C_5F_{11}SO_3H$	[3872-25-1]	110/0.67[d]	212[c], [e]
$C_6F_{13}SO_3H$	[355-46-4]	95/0.47	225[c]
$C_8F_{17}SO_3H$	[1763-23-1]	133/0.8	249
4-CF_3(cyclo-C_6F_{10})SO_3H	[374-62-9][f]	120/0.4	241
4-C_2F_5(cyclo-C_6F_{10})SO_3H	[335-24-0][f]		254

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] At $101.3\ \text{kPa} = 1\ \text{atm}$.

[c] Estimated.

[d] The hydrate, $C_5F_{11}SO_3H{\cdot}H_2O$.

[e] $C_5F_{11}SO_3H$ anhydrous.

[f] Potassium salt.

Table 2. Comparative Electrical Conductivity[a] of Lithium Salts

Concentration, *M*	CF_3SO_3Li	$LiClO_4$	$LiAsF_6$
0.5	24.4	29.9	26.3
0.1	5.81	7.4	6.94
0.05	3.12	3.83	3.57
0.01	0.70	0.83	0.79

[a] In water at 25°C, $\text{ohm}^{-1}\text{cm}^{-1} \times 10^{-3}$.

Trifluoromethanesulfonic acid is miscible in all proportions with water and is soluble in many polar organic solvents such as dimethylformamide, dimethylsulfoxide, and acetonitrile. In addition, it is soluble in alcohols, ketones, ethers, and esters, but these generally are not suitably inert solvents. The acid reacts with ethyl ether to give a colorless, liquid oxonium complex, which on further heating gives the ethyl ester and ethylene. Reaction with ethanol gives the ester, but in addition dehydration and ether formation occurs.

Alkyl esters of trifluoromethanesulfonic acid, commonly called triflates, have been prepared from the silver salt and an alkyl iodide, or by reaction of the anhydride with an alcohol (18, 20, 21). Triflates of the 1,1-dihydroperfluoroalkanols, $CF_3SO_2OCH_2R_f$, can be prepared by the reaction of perfluoromethanesulfonyl fluoride with the dihydroalcohol in the presence of triethylamine (22, 23). Triflates are important intermediates in synthetic chemistry. They are among the best leaving groups known, so they are commonly employed in anionic displacement reactions.

The metallic salts of trifluoromethanesulfonic acid can be prepared by reaction of the acid with the corresponding hydroxide or carbonate or by reaction of sulfonyl fluoride with the corresponding hydroxide. The salts are hydroscopic but can be dehydrated at 100°C under vacuum. The sodium salt has a melting point of 248°C and decomposes at 425°C. The lithium salt of trifluoromethanesulfonic acid [33454-82-9], CF_3SO_3Li, commonly called lithium triflate, is used as a battery electrolyte in primary lithium batteries because solutions of it exhibit high electrical conductivity, and because of the compound's low toxicity and excellent chemical stability. It melts at 423°C and decomposes at 430°C. It is quite soluble in polar organic solvents and water. Table 2 shows the electrical conductivities of lithium triflate in comparison with other lithium electrolytes which are much more toxic (24).

Due to the strong ionic nature of lithium trifluoromethanesulfonate, it can increase the conductivity of coating formulations, and thereby enhance the dissipation of static electricity in nonconducting substrates (see Antistatic agents) (25).

Trifluoromethanesulfonic acid anhydride, bp 84°C, is prepared by refluxing the acid over an excess of phosphorous pentoxide (18, 26). The anhydride reacts instantaneously with ammonia or amines to form trifluoromethanesulfonamides. The anhydride reacts with most polar organic solvents. It polymermizes THF to give a living polyether having cationic activity at each chain end (27).

Several excellent review articles (28–31) cover the chemistry of the acid and its derivatives in great detail. Trifluoromethanesulfonic acid is available from the 3M Co. as Fluorochemical Acid FC-24; the lithium salt is available as Fluorochemical Specialties FC-122, FC-123, and FC-124 (32).

3. Higher Perfluoroalkanesulfonic Acids

The longer perfluoroalkanesulfonic acids are hydroscopic oily liquids. Distillation of the acid from a mixture of its salt and sulfuric acid gives a hydrated mixture with melting points above 100°C. These acids show the same general solubilities as trifluoromethanesulfonic acid, but are insoluble in benzene, heptane, carbon tetrachloride, and perfluorinated liquids. All of the higher perfluoroalkanesulfonic acids have been prepared by electrochemical fluorination (20).

The longer-chain acids and their salts, particularly $C_8F_{17}SO_3H$ and higher, are surface-active agents in aqueous media. They reduce the surface tension of water to levels not possible with hydrocarbon surfactants. The surfactant $C_8F_{17}SO_2N(C_2H_5)CH_2COOK$ [2991-51-7] lowers the surface tension of water to 17 mN/m(=dyn/cm) at 0.2 weight percent (33) and exhibits outstanding thermal and chemical stabilities. The potassium salt of perfluorooctanesulfonic acid [2795-39-3], $C_8F_{17}SO_3K$, or perfluoroethylcyclohexanesulfonic acid [335-24-0], C_2F_5-cyclo-(C_6F_{10})-SO_3K, can form a stable foam in hostile media such as chromium trioxide and sulfuric acid where conventional hydrocarbon and silicone surfactants would be destroyed (34). The ability of these materials to foam concentrated sulfuric acid is utilized to prevent sulfuric acid from aerosoling into the air in industrial situations where chrome plating is done. Instead of forming an aerosol, the sulfuric acid forms a foam blanket on top of the plating bath. The foam derived from $C_8F_{17}SO_3K$ is generally more stable and dense than that derived from C_2F_5-cyclo-(C_6F_{10})-SO_3K. As a result these fluorochemical surfactants are often used in combination to produce desired wetting and foaming activity.

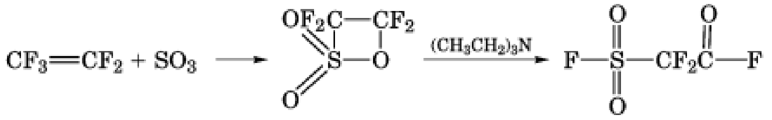
Generally, derivatives of the longer-chain perfluoroalkanesulfonic acids have a number of unique surface-active properties and have formed a basis for a number of commercial products. Derivatives of *N*-alkyl perfluorooctanesulfonamidoethanol, $C_8F_{17}SO_2N(R)CH_2CH_2OH$, and polymers of *N*-alkyl perfluorooctanesulfonamidoethyl methacrylate, $C_8F_{17}SO_2N(R)CH_2CH_2OCOC(CH_3){=}CH_2$, impart soil, oil, and water repellency to treated fabrics and paper; this forms the basis for 3M's Scotchguard and Scotchban products (35). Polymers of *N*-alkyl perfluorooctanesulfonamidoethyl acrylates, $C_8F_{17}SO_2N(R)CH_2CH_2OCOC(R'){=}CH_2$, with certain hydrocarbon acrylates and methacrylates have also been found to be surface-active agents in organic solvents and water. These polymers have applications in the areas of secondary crude oil recovery and wetting, leveling, and flow control agents (36, 37).

Higher perfluoroalkanesulfonates are slightly more reactive than triflates toward nucleophilic displacements. The rate constants for acetolysis of methyl nonafluorobutanesulfonate [6401-03-2], methyl trifluoromethanesulfonate [333-27-7], and methyl toluenesulfonate [80-48-8] are 1.49×10^{-4}, 7.13×10^{-5}, and 3.1×10^{-9} s^{-1}, respectively. This means that the relative reactivities for nonafluorobutanesulfonate, trifluoromethanesulfonate, and toluenesulfonate are 48,000/22,900/1 (38).

4. Difunctional Perfluoroalkanesulfonic Acids

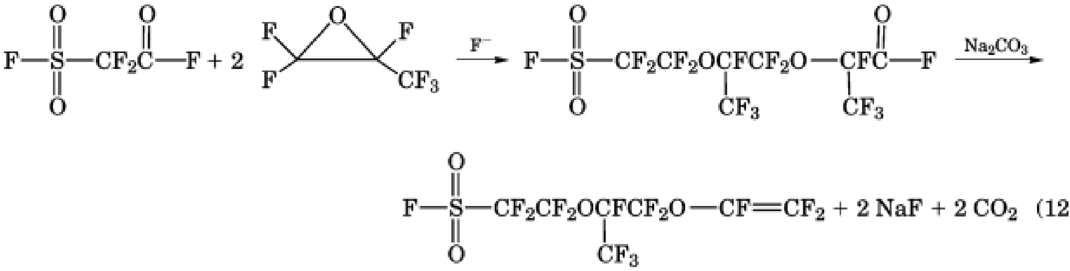
Alpha, omega-perfluoroalkanedisulfonic acids were first prepared by aqueous alkali permanganate oxidation of the bis-sulfone, $RSO_2(CF_2CF_2)_nSO_2R$ (39). Disulfonyl fluorides of the formula $FSO_2(CF_2)_nSO_2F$ have also been prepared by electrochemical fluorination where $n = 1$ to 5. These disulfonyl fluorides have been converted to the cyclic anhydrides by basic hydrolysis of the disulfonyl fluoride, acidification, and dehydration with phosphorous pentoxide (40). The alpha, omega-perfluoroalkanedisulfonic acids can also be prepared by the action of sodium dithionate on the diiodides to form the disulfinate salt, followed by chlorination and hydrolysis to give the disulfonic acids (14, 15).

Carbonyl sulfonyl fluorides of the formula $FCO(CF_2)_nSO_2F$ have been prepared by electrochemical fluorination of hydrocarbon sultones (41, 42). More commonly in a technology pioneered by Du Pont, perfluoroalkanecarbonyl sulfonyl fluorides are prepared by addition of SO_3 to tetrafluoroethylene followed by isomerization with a tertiary amine such as triethylamine (43).



(11)

Fluorosulfonyldifluoracetyl fluoride [677-67-8] is an important industrial intermediate used in the production of Du Pont's Nafion ion-exchange membrane. Nafion is an ion-exchange membrane used under the extreme conditions in electrolytic cells, especially for the electrolysis of sodium chloride to produce chlorine and caustic soda. Other commercial fluorinated ion-exchange resins utilize perfluorinated carboxylate groups instead of sulfonate groups in the monomer in order to make the polymer conductive. Shown in equation **12** are the synthetic operations used to convert fluorosulfonyldifluoracetyl fluoride to its polymerizable form.



(12)

The vinyl ether in the latter part of the equation is copolymerized with tetrafluoroethylene, and then the sulfonyl fluoride group is hydrolyzed under basic conditions in order to produce the ion-exchange membrane (44–46).

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