33) Boiling point (acid form) (200°C at 101 kPa)

Contains No CBI

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PERFLUOROALKANE SULFONIC ACIDS

The perfluoroalkane sulfonic acids were first reported in 1954. Trifluoromethanesulfonic acid was obtained by oxidation of bis(trifluoromethylthio)mercury with aqueous hydrogen peroxide (1) (see also Sulfonic acids). The preparation of a series of perfluoroalkane sulfonic acids by electrochemical fluorination (ECF) of alkane sulfonyl halides was also disclosed in the same year (2).

$$RSO_2F \xrightarrow[ECF]{HF} R_fSO_2F \xrightarrow[\text{aq KOH}]{} R_fSO_3K \xrightarrow{H_2SO_4} R_fSO_3H$$

CF_3SO_3H may also be prepared from trifluoromethanesulfenyl chloride (3).

$$CF_3SSCF_3 \xrightarrow{Cl_2} CF_3SCl \xrightarrow[H_2O]{Cl_2} CF_3SO_2Cl \xrightarrow[\text{aq NaOH}]{} CF_3SO_3Na$$

[421-83-0] [2926-30-9]

or by the oxidation of methyl trifluoromethyl sulfide under a variety of conditions (4–5).

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

Trifluoromethanesulfonic Acid

The first member of the series, CF_3SO_3H, has been studied extensively. Two excellent review articles (6–7) cover the chemistry of the acid and its derivatives in great detail.

Trifluoromethanesulfonic acid is available as Fluorochemical Acid FC-24 (3M Co.). The technical brochure (8) is an excellent source for applications, safety, and handling data of the acid.

Properties. Trifluoromethanesulfonic acid is a stable, hygroscopic liquid which fumes in air. An equimolar amount of water with the acid results in a stable, distillable monohydrate, mp 34°C, bp 96°C at 0.13 kPa (1 mm Hg) (9). Measurement of conductivity of strong acids in acetic acid has shown the acid to be one of the strongest simple protic acids known, similar to fluorosulfonic and perchloric acid (10). Trifluoromethanesulfonic acid is miscible in all proportions in water, and is soluble in many polar organic solvents such as dimethylformamide, dimethyl sulfoxide, and acetonitrile. In addition, it is soluble in alcohols, ketones, ether, and esters, but these generally are not suitably inert solvents. The acid with diethyl ether gives a colorless, liquid oxonium complex, which with further heating, gives the ethyl ester and ethylene. Reaction with ethanol gives the ester, but in addition, dehydration and ether formation occurs.

Table 1. Boiling Points of a Series of Perfluoro Alkane Sulfonic Acids.

Compound	CAS Reg. No.	Boiling point[a] °C/kPa	°C/101 kPa
CF_3SO_3H	[1493-13-6]	60/0.4	166
$C_2F_5SO_3H$	[354-88-1]	81/2.9	175[b]
n-$C_4F_9SO_3H$	[59933-66-3]	76-84/0.13	200[b]
n-$C_5F_{11}SO_3H$	[3872-25-1]	110/0.67[c]	212[b,d]
n-$C_6F_{13}SO_3H$	[355-46-4]	95/0.47	225[b]
n-$C_8F_{17}SO_3H$	[1763-23-1]	133/0.8	249
CF_3-F-SO_3H[e]	[72441-89-5]	120/0.4	241
C_2F_5-F-SO_3H[e]	[41242-13-1]		254

[a] To convert kPa to mm Hg, multiply by 7.5.
[b] Estimated boiling point.
[c] n-$C_5F_{11}SO_3H.H_2O$.
[d] n-$C_5F_{11}SO_3H$.
[e] F = *cyclo*-C_6F_{12}.

The strongly electron-attracting $CF_3SO_3^-$ group makes the esters excellent alkylating agents. Methyl trifluoromethanesulfonate [333-27-7] is more than 10^4 times as reactive as methyl toluenesulfonate in acetolysis (11). Trifluoromethyl trifluoromethane sulfonate [3582-05-6] was obtained by the reaction of trifluoromethanesulfonic acid with fluorosulfuric acid (12). The trifluoromethylating ability of the triflate (see below) is limited, benzene at 100°C giving only small amounts of benzotrifluoride.

Derivatives. Alkyl esters of trifluoromethanesulfonic acid, commonly called triflates have been prepared primarily from the silver salt [51098-28-3] and an alkyl iodide, or by reaction of the anhydride with alcohol (9,13).

The metallic salts of trifluoromethanesulfonic acid, also called triflates, are prepared by reaction of the acid with the corresponding hydroxide or carbonate. The salts are hygroscopic 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 rare earth salts are also obtained from the acid and rare earth metal oxides (14). Organic trifluoromethanesulfonate salts are quantitatively prepared from the acid and amines (9). Triflate salts show promise as electrolytes for nonaqueous electrochemical cells (15), as catalysts for epoxy resins (16), and latent catalysts for cationically polymerizable monomers (17–18).

Trifluoromethanesulfonic acid anhydride [358-23-6], bp 84°C, is prepared by refluxing the acid over an excess of phosphorus pentoxide (19). It reacts instantaneously with ammonia, aqueous ammonium hydroxide, or amines, to form trifluoromethanesulfonamides. The anhydride is generally a more effective esterification promotor than trifluoroacetic acid anhydride. A number of methods have appeared that allow the introduction of the $CF_3SO_2^-$ group on carbon; the synthetic utility of these derivatives in organic chemistry has been reviewed (20).

Higher Perfluoroalkane Sulfonic Acids

The longer chain perfluoroalkane sulfonic acids are very hygroscopic oily liquids. Distillation of the acid from a mixture of its salt and H_2SO_4 gives hydrated mixtures with melting points above 100°C. The acids show the same polar solvent solubilities as trifluoromethanesulfonic acid but are quite insoluble in benzene, heptane, carbon tetrachloride, and the perfluorinated liquids. Many of the higher perfluoroalkane sulfonic acids have been prepared by electrochemical fluorination as previously described (13). α,ω-Perfluoroalkane disulfonic acids can be prepared by aqueous alkali permanganate oxidation of the bis-sulfone, $R_fSO_2(CF_2CF_2)_nSO_2R$ (21).

The longer chain acids, particularly $C_8F_{17}SO_3H$ and higher, are surface-active agents in aqueous media. Derivatives of the acids have unique surface-active properties and have formed the basis for a number of commercial fluorochemical surfactants (22). The chemical and thermal stability of the perfluorosulfonate salts as well as their surface activity has led to their use in strong acid and base environments. Very low surface tensions in aqueous media, less than 20 mN/m (= dyn/cm), are obtained with most fluorochemical surfactants derived from the perfluoro sulfonic acids. This has led to their use as wetting and leveling agents (see also Surfactants).

Safety and Storage

Extreme caution should be used when handling the perfluoroalkane sulfonic acids. Eye irritation studies with albino rabbits suggest extreme irritation and permanent eye damage could occur following eye contact, even if the eyes are immediately flushed with water. Acute inhalation toxicity studies (albino rats) indicate that high vapor of mist concentration can cause significant respiratory irritation. All contact of the acids and alkyl esters with the skin should be avoided. Normal procedures for treatment of strong acid burns should be used.

Contact of the perfluoroalkane sulfonic acids with cork, rubber, cellulosics, and plasticized materials will cause discoloration and deterioration of those materials. Samples are best stored in glass ampuls or glass bottles with Kel-F or Teflon plastic screw-cap linings.

Trifluoromethanesulfonic acid in contact with stainless steel, iron or aluminum typically causes a weight loss of about 20 mg/(m^2-d). Use of glass equipment where possible is recommended.

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PERFLUOROALKYLSULFUR FLUORIDES

Compounds containing fluorine bound to both carbon and sulfur with no other elements present are relatively rare and little known substances. Less than fifty examples of these materials are known and none of them have any current commercial utility. In general, they are difficult and costly to prepare. Their properties range from thermally stable and chemically inert to extremely unstable.

The only member of this group worthy of mention is the parent compound trifluoromethylsulfur pentafluoride [*373-80-8*], CF_3SF_5, which is a good gaseous dielectric material (1), and this use has been mentioned in two patents (2–3). A bibliography on CF_3SF_5 is available in ref. 4.

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