J. Chem. Eng. Data 1981, 26, 344-346

Synthesis of Three Partially Fluorinated Alkanesulfonic Acids as Potential Fuel-Cell Electrolytes

Chaiyun Bunyagidj,* Hanna Piotrowska, and Mary H. Aldridge

Department of Chemistry, The American University, Washington, D.C. 20016

The simple and effective syntheses of $CH_2FCH_2SO_3H$, $CF_3CH_2SO_3H$, and $CHF_2CF_2CH_2SO_3H$ have been achieved with 18.8%, 34.1%, and 33.7% overall yields. The low molecular weight partially fluorinated alkanesulfonic acids containing α-methylene groups can be prepared from the *p*-toluenesulfonates of the corresponding alcohols, via a reaction with benzyl mercaptan, followed by an oxidative chlorination of the resulting sulfides, with subsequent hydrolysis of the sulfonyl chloride formed: R_fCH_2OH (TsCl) $\rightarrow$ R_fCH_2OTs ($C_6H_5CH_2SNa$ + DMF) $\rightarrow$ $R_fCH_2SCH_2C_6H_5$ (Cl_2 + H_2O) $\rightarrow$ $R_fCH_2SO_2Cl$ (H_2O + Δ) $\rightarrow$ $R_fCH_2SO_3H$. The reaction of partially fluorinated alkyl halides with sodium sulfite (Strecker's method) proved to be inefficient (very low yields) and unreliable. The sulfonate salts formed are difficult to recover and purify: $R_fCH_2X + Na_2SO_3 \rightarrow R_fCH_2SO_3Na \rightarrow R_fCH_2SO_3H$.

Introduction

Our objective was to prepare some strong acids for evaluation as potential fuel-cell electrolytes. The major acid, other than H_3PO_4, currently under investigation is TFMSA ($CF_3SO_3H{\cdot}H_2O$). TFMSA has been found to be superior to H_3PO_4 from the standpoint of electrode kinetics, but certain undesirable characteristics (volatility, wetting of Teflon) led to this search for a better fuel-cell electrolyte. Barrick (*1*, *2*) and Coffman (*3*) prepared $CHF_2CF_2SO_3H$ in a 54% yield by addition of sodium sulfite to fluoroolefin. Koshar et al. (*4*) synthesized $CF_3CHFCF_2SO_3H$, $C_3H_7CHFCF_2SO_3H$, and $C_5H_{11}CHFCF_2SO_3H$ in good yields in a similar way. Haszeldine (*5*) used similar methods to prepare $CFCl_2CF_2CHFCF_2SO_3H$ and other chlorofluoroalkanesulfonic acids. Hazeldine and Kidd (*6*) oxidized $(CF_3S)_2Hg$ with 35% H_2O_2 to produce CF_3SO_3H. The oxidation of mercaptans, sulfides, disulfides, and sulfones by $KMnO_4$ (*7*), CrO_3 (*7*), Br_2 water (*8*, *9*), H_2O_2 (*10*), HNO_3 (*11*), and alkalis (*12*) yielded sulfonic acids as reported.

Results and Discussions

After this considerable literature search, we decided upon employing the following two approaches.

Exchange of Halogen for Sulfonic Group in Partially Fluorinated Alkyl Halides (Strecker's Method). The reactions of the following halides were investigated: CF_3CH_2I, CF_3CH_2Br, CH_2FCH_2Br, $CHF_2CF_2CH_2Br$, and $C_2F_5CH_2I$. Since only CF_3CH_2I and $C_2F_5CH_2I$ were commercially available, the other compounds were prepared from the corresponding alcohols via their *p*-toluenesulfonyl derivatives. One of the alcohols, CH_2FCH_2OH was prepared from CH_2ClCH_2OH by the method described by Hoffmann (*13*). The tosylates were prepared according to the method described by Tiers, Brown, and Reid (*14*) for CF_3CH_2OTs. The tosylates were converted into their corresponding bromides, by reacting with anhydrous KBr in diethylene glycol (*14*). For CH_2FCH_2Br, another method of synthesis was evaluated, it being the reaction of CH_2BrCH_2OTs and anhydrous KF in diethylene glycol as described by Edgell and Parts (*15*). However, the yield of CH_2FCH_2Br prepared from CH_2BrCH_2OTs was much lower.

Table I. Yields (%) of Crude Sulfonate Salts

halide	reaction in water	reaction in 50% ethanol	reaction in Parr pressure reactor
CF_3CH_2I	no reaction	5	5
$CF_3CF_2CH_2I$	no reaction	traces	5
CF_3CH_2Br			10
$CHF_2CF_2CH_2Br$	5	5	15
CH_2FCH_2Br	75	82	

Three procedures were evaluated for conversion of the above-mentioned partially fluorinated alkyl halides into the corresponding sulfonates. The results are in Table I. Only CH_2FCH_2Br can be used successfully as the starting material for the preparative synthesis of $CH_2FCH_2SO_3H$ by this method. CF_3CH_2I and $C_2F_5CH_2I$ did not react satifactorily with sodium sulfite. Very small amounts of sulfonic acid salt, probably containing sodium iodide in the form of double salts, were obtained. CF_3CH_2Br could be used only in Parr pressure reaction because of its low boiling point (25 °C) and seemed to react slightly better than the corresponding iodide. $CHF_2CF_2CH_2Br$ gave better results and a sample of pure $CHF_2CF_2CH_2SO_3H$ could be prepared from the salt.

The results indicate that Strecker's method is complicated and inefficient for synthesis of partially fluorinated alkanesulfonic acids. Yields are rather erratic, and recovery and purification of the sulfonate salts are very difficult.

Introduction of Sulfur into a Partially Fluorinated Alkyl Moiety with Subsequent Oxidation to a Sulfonic Acid. Moore (*16*) described a very convenient method for preparation of CH_2FSO_2Cl and CHF_2SO_2Cl from CH_2FCl and CHF_2Cl, respectively. In our work, an attempt was made to adapt this procedure to the preparation of other partially fluorinated alkanesulfonic acids.

In the first experiment, CH_2FCH_2Br and $CHF_2CF_2CH_2Br$ were reacted with the sodium salt of benzyl mercaptan, yielding the corresponding sulfides. We found that the bromides in this case may be substituted by the tosylates of the corresponding alcohols. The good results obtained with the tosylates simplified the synthesis because the bromides are usually prepared from the tosylates. The $CF_3CH_2SCH_2C_6H_5$ was prepared only from the tosylate.

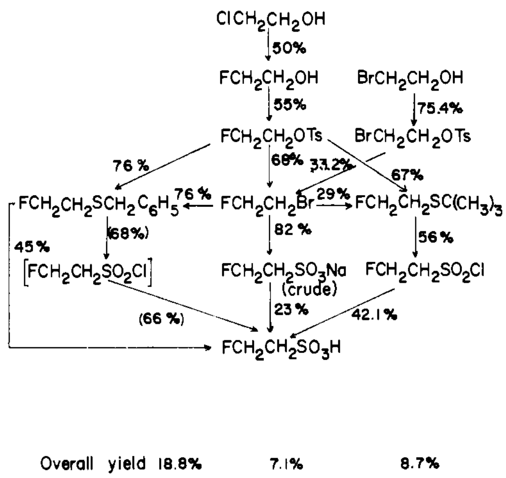
The oxidative chlorination of the sulfides was very exothermic and had to be very carefully controlled. The reaction product, containing sulfonyl chloride and equimolar amounts of benzyl chloride, was extracted with methylene chloride, dried, and vacuum distilled. The hydrolysis of $CF_3CH_2SO_2Cl$ was accomplished by refluxing with water. The hydrolysis of the mixutre of $CH_2FCH_2SO_2Cl$ and $CHF_2CF_2CH_2SO_2Cl$ with $C_6H_5CH_2Cl$ was also accomplished by refluxing with water. The aqueous solutions of the sulfonic acids were extracted with small amounts of ether to remove the benzyl alcohol and unreacted benzyl chloride, evaporated, and vacuum distilled.

An attempt was made to replace benzyl with *tert*-butyl in the sulfides. The reaction of CH_2FCH_2OTs, CF_3CH_2OTs, and $CHF_2CF_2CH_2OTs$ with *tert*-butyl mercaptan in DMF proceeded smoothly but gave lower yields even when 100% excess of the mercaptan was used. Oxidative chlorination of the sulfides gave

0021-9568/81/1726-0344$01.25/0

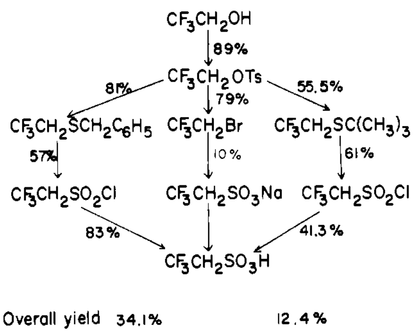
Scheme I

Preparation of 2-Fluoroethanesulfonic Acid



Scheme II

Preparation of 2,2,2-Trifluoroethanesulfonic Acid



even poorer results. Not only were the yields lower but the products were highly contaminated with unidentified mixtures which could not be separated by fractional distillation. Although pure sulfonic acids could be obtained from these sulfonyl chlorides, the yields were again much lower.

The results described above are summarized in Schemes I-III for each individual sulfonic acid.

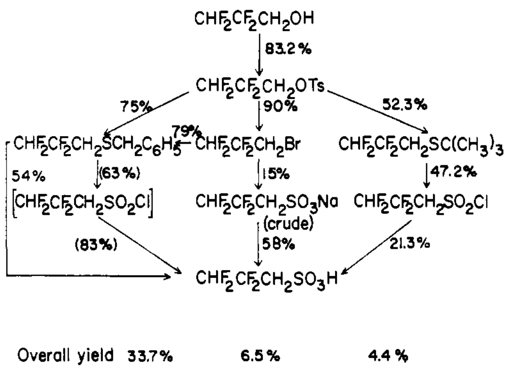
Experimental Section

Partially Fluorinated Alkyl p-Toluenesulfonates. All sulfonates, CH_2FCH_2OTs (*15*), CF_3CH_2OTs (*15*), and $CHF_2CF_2CH_2OTs$, were prepared in a similar method. A mixture of 66 g (0.5 mol) of $CHF_2CF_2CH_2OH$, 100.8 g (0.53 mol) of TsCl, and 150 mL of H_2O was heated to 50 °C. A solution of 23 g (0.53 mol) of NaOH in 95 mL of H_2O was added, stirring being done at a rate to keep the reaction mixture below 60 °C. The stirring was continued until the solution became neutral; it was then cooled and extracted with ether. The ethereal extract was washed twice with concentrated NH_4OH and twice with H_2O and dried over anhydrous Na_2SO_4. The solvent was removed, and the vacuum-distilled residue gave 118.9 g (83.2%) of a colorless liquid: bp 117-120 °C (0.5 mm); NMR (CD_3COCD_3) showed ArH at 7.65 ppm (quartet, $J = 8$ Hz), CHF_2 at 6.25 ppm (split triplet, $J_{HFgem} = 52$ Hz, $J_{HFvic} = 5$ Hz), CH_2 at 4.56 ppm (triplet, $J_{HF} = 13$ Hz), and CH_3 at 2.42 ppm (singlet).

Partially Fluorinated Alkyl Bromides. Two bromides, CH_2FCH_2Br (*17*) and CF_3CH_2Br (*18*), were prepared according to the literature. CHF_2CF_2Br was synthesized from reacting 100 g (0.35 mol) of $CHF_2CF_2CH_2OTs$ with 63 g (0.62 mol) of anhydrous KBr in 150 mL of diethylene glycol at 160-170 °C. At 150 °C evolution started while the mixture was stirred continuously. After the reaction product was washed several times with water and dried over Drierite, fractional distillation gave 64.8 g (95%) of a colorless liquid: bp 68-69 °C; NMR (CD_3COCD_3) showed CHF_2 at 6.16 ppm (split triplt, $J_{HFgem} = 53$ Hz, $J_{HFvic} = 4$ Hz) and CH_2 at 3.78 ppm (triplet, $J_{HF} = 15$ Hz).

Scheme III

Preparation of 2,2,3,3-Tetrafluoropropanesulfonic Acid



Reaction of Partially Fluorinated Alkyl Halides with Sodium Sulfite. A. In Water. A solution of 20 g (0.16 mol) of Na_2SO_3 in 100 mL of H_2O was placed in a three-necked flask fitted with an efficient reflux condenser and a dropping funnel. The halide (0.15 mol) was added slowly with stirring over a period of 2 h at 50-60 °C. The reaction mixture was refluxed gently with stirring for 48 h. After cooling, the unreacted halide (if present) was separated, the aqueous layer evaporated to dryness, and the residue extracted with hot EtOH. Evaporation of solvent gave the crude sodium salt of the corresponding sulfonic acid.

B. In 50% Ethanol. A mixture of 7 g (0.05 mol) of Na_2SO_3, 80 mL of 50% EtOH, and 0.05 mol of the halide was refluxed with stirring for 48 h. It was cooled and filtered, the filtrate evaporated to dryness, and the solid residue treated as above.

C. In Parr Pressure Reactor. A solution of 40 g (0.32 mol) of Na_2SO_3 dissolved in 200 mL of H_2O, and 0.30 mol of the halide, were placed in a 1-L Parr pressure reactor and slowly heated while being stirred. Usually at ~90 °C an exothermic reaction started, and the temperature rose to ~125 °C. After the exothermic process subsided, the reactor was heated at 100 °C for 12-16 h. The reaction mixture was cooled, the unreacted halide (if present) separated, the aqueous solution evaporated to dryness, and the solid residue treated as above.

The results are in Table I. The approximate yields are based on the amounts of crude sulfonate salts isolated. The IR spectra of all salt samples showed distinct absorption at 1160 and 1060 cm^{-1}, which is characteristic of sulfonic acid salts. The salts obtained from alkyl iodides were contaminated with sodium iodide.

Convertion into Free Acids. A 10% aqueous solution of the sodium alkanesulfonate was passed through an ion-exchange column packed with IR-120 resin. The collected aqueous solution of the acid was evaporated, and the residue vacuum distilled. Samples of the following acids were prepared: $CH_2FCH_2SO_3H$, yield 23%, bp 150-151 °C (1.7 mm) M_r 127 (calcd 128); $CHF_2CF_2CH_2SO_3H$, yield 58%, bp 90-91 °C (0.4 mm), M_r 191 (calcd 196).

Reaction of Partially Fluorinated Alkyl Bromides and Tosylates with Benzyl Mercaptan. All sulfides were prepared by the same method. A mixture of 16 g (0.20 mol) of 50% NaOH and 60 mL of DMF was flushed well with N_2, and 24.8 g (0.20 mol) of $C_6H_5CH_2SH$ was added. When homogeneous, the warm solution was treated with 0.17 mol of R_fCH_2OTs or R_fCH_2Br to maintain the internal temperature and was quenched in 250 mL of H_2O. The product was extracted with CH_2Cl_2, and the organic layer was washed with dilute NaOH, washed again with H_2O, and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the residue vacuum distilled.

The following compounds were prepared.

(1) $CH_2FCH_2SCH_2C_6H_5$ was prepared from CH_2FCH_2Br (yield 77%) and from CH_2FCH_2OTs (yield 76%): bp 84–85 °C (1.5 mm); NMR (neat) showed ArH at 7.18 ppm (singlet), CH_2 at 3.60 ppm (singlet), and CH_2FCH_2 at 4.67, 3.90, 2.67, and 2.33 ppm (triplets).

(2) $CF_3CH_2SCH_2C_6H_5$ was prepared from CF_3CH_2OTs (yield 81%): bp 45–46 °C (0.20 mm); NMR (neat) showed ArH at 7.14 ppm (singlet), CH_2 at 3.16 ppm (singlet), and CF_3CH_2 at 2.68 ppm (quartet, J_{HF} = 10 Hz).

(3) $CHF_2CF_2CH_2SCH_2C_6H_5$ was prepared from $CHF_2CF_2CH_2Br$ (yield 79%) and from $CHF_2CF_2CH_2OTs$ (yield 75%): bp 69–71 °C (0.15 mm) NMR (neat) showed ArH at 7.18 ppm (singlet), CHF_2 at 5.78 ppm (split triplet, J_{HFgem} = 53 Hz, J_{HFvic} = 5 Hz), CH_2 at 3.67 ppm (singlet), and CF_2CH_2 at 2.72 ppm (triplet, J_{HF} = 16 Hz).

Reaction of Partially Fluorinated Alkyl Tosylates with tert-Butyl Mercaptan. In the same fashion the following sulfides were prepared from the reaction of 0.34 mol of 50% NaOH in 125 mL of DMF, 30.7 g (0.34 mol) of $(CH_3)_3CSH$, and 0.17 mol of the tosylates (CH_2FCH_2OTs, CF_3CH_2OTs, and $CHF_2CF_2CH_2OTs$). The following compounds were prepared.

(1) $CH_2FCH_2SC(CH_3)_3$: yield 65% bp 73–77 °C (95 mm); NMR (neat) showed CH_2FCH_2 at 4.82, 4.03, 2.92, and 2.63 ppm (triplets) and $(CH_3)_3C$ at 1.32 ppm (singlet).

(2) $CF_3CH_2SC(CH_3)_3$: yield 55%; bp 70–72 °C (100 mm); NMR (neat) showed CF_3CH_2 at 3.10 ppm (quartet, J_{HF} = 11 Hz) and $(CH_3)_3C$ at 1.30 ppm (singlet).

(3) $CHF_2CF_2CH_2SC(CH_3)_3$: yield 45%; bp 63–65 °C (100 mm); NMR (neat) showed CHF_2 at 5.92 ppm (split triplet, J_{HF} = 53 Hz), CF_2CH_2 at 3.05 ppm (triplet, J_{HF} = 16 Hz), and $(CH_3)_3C$ at 1.30 ppm (singlet).

Partially Fluorinated Alkanesulfonyl Chlorides. All sulfides were oxidized in a similar manner. A mixture of 0.12 mol of sulfide and 50 mL of H_2O was chilled in a dry ice–acetone bath. At 0 °C, with ice beginning to form on the walls, Cl_2 was added above the mixture, controlling the temperature to within −5 to 0 °C. Cl_2 was introduced until saturation was obtained. The lower layer was mixed with 10 mL of CH_2Cl_2, separated, and chilled while drying over anhyrous $MgSO_4$. CH_2Cl_2 was removed, and the residue distilled under reduced pressure. The following compounds were prepared.

(1) $CH_2FCH_2SO_2Cl$: (a) from $CH_2FCH_2SCH_2C_6H_5$, the product was obtained as a mixture with $C_6H_5CH_2Cl$; yield 68% (estimated by NMR); bp 80–83 °C (25 mm); (b) from $CH_2FCH_2SC(CH_3)_3$; yield 56%; bp 76–78 °C (16 mm (*19*)); NMR (neat) showed four triplets at 5.47, 4.67, 4.38, and 3.98 ppm.

(2) $CF_3CH_2SO_2Cl$: (a) from $CF_3CH_2SCH_2C_6H_5$; yield 57%; bp 65–67 °C (45 mm); (b) from $CF_3CH_2SC(CH_3)_3$; yield 61%; bp 57–60 °C (40 mm (*20*)); NMR (neat) showed at quartet at 4.37 ppm (J_{HF} = 9 Hz).

(3) $CHF_2CF_2CH_2SO_2Cl$: (a) From $CHF_2CF_2CH_2SCH_2C_6H_5$, the product was obtained as a mixture with $C_6H_5CH_2Cl$; yield 63% (estimated by NMR); bp 70–75 °C (15 mm); (b) from $CHF_2CF_2CH_2SC(CH_3)_3$; yield 47%; bp 70–71 °C (12 mm); NMR (neat) showed a split triplet at 5.97 ppm (J_{HFgem} = 53 Hz, J_{HFvic} = 5 Hz).

All sulfonyl chlorides obtained from *tert*-butyl sulfides contained unidentified mixtures which could not be removed by fractional distillation.

Partially Fluorinated Alkanesulfonic Acids. All of the sulfonic acids were prepared in the same way by refluxing 0.5 mol of sulfonyl chloride or sulfonyl chloride mixture with benzyl chloride and 20 mL of H_2O for 10 h. After cooling, the solution was extracted twice with 10 mL of ether, the aqueous layer was evaporated, and the residue was vacuum distilled. The following acids were prepared.

(1) $CH_2FCH_2SO_3H$: yield 66%; bp 122–124 °C (0.1 mm); M_r 127 (calcd 128); NMR (D_2O) showed CH_2FCH_2 at 5.22, 4.44, 3.54, and 3.12 ppm. Anal. Calcd for $C_8H_{12}O_3NFS$: C, 43.44; H, 5.43; F, 8.60; S, 14.48. Found: C, 44.67; H, 5.29; F, 5.26; S, 14.14.

(2) $CF_3CH_2SO_3H$: yield 83%; bp 90–93 °C (0.1 mm); M_r 167 (calcd 164); NMR (D_2O) showed CF_3CH_2 at 3.87 ppm (quartet, J_{HF} = 10 Hz). Anal. Calcd for $C_8H_{10}O_3NF_3S$: C, 37.35; H, 3.89; F, 22.18; S, 12.45. Found: C, 37.13; H, 3.74; F, 22.05; S, 12.16.

(3) $CHF_2CF_2CH_2SO_3H$: yield 83%; bp 106–107 °C (0.1 mm); M_r 200 (calcd 196); NMR (D_2O) showed CHF_2 at 6.01 ppm (split triplet, J_{HFgem} = 53 Hz, J_{HFvic} = 5 Hz) and CF_2CH_2 at 3.53 ppm (triplet, J_{HF} = 16 Hz). Anal. Calcd for $C_9H_{11}O_3NF_4S$: C, 37.37; H, 3.81; F, 26.30; S, 11.07. Found: C, 37.54; H, 3.88; F, 26.12; S 10.96.

Literature Cited

(1) Barrick, P. L. U.S. Patent 2 403 207, 1946.
(2) Barrick, P. L. British Patent 579 897, 1946.
(3) Coffman, D. D.; Raasch, M. S.; Rigby, G. W.; Barrick, P. L.; Hanford, W. E. *J. Org. Chem.* **1949**, *14*, 747.
(4) Koshar, R. J.; Trott, P. W.; LaZerte, J. D. *J. Am. Chem. Soc.* **1953**, *75*, 4595.
(5) Haszeldine, R. N. *J. Chem. Soc.* **1955**, 4291.
(6) Haszeldine, R. N.; Kidd, J. M. *J. Chem. Soc.* **1954**, 4228.
(7) Collin, G.; Hilditch, T. P.; Marsh; McLeod *J. Soc. Chem. Ind., London* **1933**, *52*, 272T.
(8) Clarke, H. T. *Org. Synth.* **1940**, *20*, 23.
(9) Young, H. A. *J. Chem. Soc.* **1937**, *59*, 811.
(10) Boacker *Recl. Trav. Chim. Pays-Bas* **1935**, *54*, 205.
(11) Murray *J. Chem. Soc.* **1933**, 739.
(12) Wallace, T. J.; Schriesheim, A. *Tetrahedron* **1965**, *21*, 2271.
(13) Hoffman, F. W. *J. Am. Chem. Soc.* **1946**, *70*, 2596.
(14) Tiers, G. V. D.; Brown, H. A.; Reid, T. S. *J. Chem. Soc.* **1953**, *75*, 5978.
(15) Edgell, W. F.; Parts, L. *J. Am. Chem. Soc.* **1955**, *77*, 4899.
(16) Moore, G. G. I. *J. Org. Chem.* **1979**, *44*, 1708.
(17) Henne, A. L.; Renoll, M. W. *J. Am. Chem. Soc.* **1936**, *58*, 889.
(18) Henne, A. L.; Ruh, R. P. *J. Am. Chem. Soc.* **1948**, *70*, 1025.
(19) Saunders, B. C.; Stacey, G. J.; Wilding, I. G. E. *J. Chem. Soc.* **1949**, *773*.
(20) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

Received for review November 24, 1980. Accepted April 16, 1981. We gratefully acknowledge the support of this research by the U.S. Army Mobility Equipment Research and Development Command at Fort Belvoir, VA, under Contract No. DAAK-77-C-0047 with The American University. The work was authorized under DA Project/Task Area/Work Unit No. 1L161102-AH51 PA 053 EF.