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AN ABSTRACT OF THE THESIS OF Robert J. Willenbring for the Master of Arts in Chemistry presented June 4, 1987.

Title: Synthesis and Characterization of Some SF_5 - Containing Sulfonic Acids

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

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Pentafluorosulfur(VI) bromide (SF_5Br) adds to olefins of the form $\text{CX}_2=\text{CX}_2$, where $\text{X} = \text{H}$ or F , with the pentafluorosulfur group usually adding to the carbon with more hydrogens attached to it. This series of compounds was used in an attempt to prepare the corresponding sulfonic acid hydrates of the general formula $\text{SF}_5\text{CX}_2\text{CX}_2\text{SO}_3\text{H} \cdot n\text{H}_2\text{O}$, in order to have these compounds tested as possible fuel cell electrolytes. The reaction scheme involved reflux of the SF_5Br adduct with

an equimolar amount of sodium sulfite in 50% ethanol for two days, followed by acidification of the recovered solid material using HCl or H₂SO₄.

Upon removal of the solvent, sublimation of the solid residue gave the acids SF₅CH₂CH₂SO₃H and SF₅CHFCF₂SO₃H·H₂O, while SF₅CH₂CF₂SO₃H·H₂O was recovered as the major component of a binary mixture. The sodium salts corresponding to these three acids were also made by neutralization of the acids with sodium hydroxide. For the other two members of the series, SF₅CH₂CHFSO₃H was identified as a minor component of its product mixture, while SF₅CF₂CF₂SO₃H was not recovered at all, possibly due to a redox reaction in which SF₅CF₂COOH, sulfur, and bromine were formed. The acids could not be isolated from these last two product mixtures.

The addition of Pentafluorosulfur(VI) bromide to CF₂=CFBr was used to prepare a new adduct SF₅CF₂CFBr₂ and telomer SF₅(CF₂CFBr)₁₀Br. Also, addition of SF₅Br to CF₂=CF₂ under mild conditions was found to produce good yields of the monomeric adduct SF₅CF₂CF₂Br, where previously the reaction had produced a telomer.

The compound SF₅CHFCF₂SO₃H·H₂O is currently undergoing preliminary testing as a fuel cell electrolyte.

Infrared, ¹H and ¹⁹F NMR, and mass spectra as well as elemental analyses are presented in order to support the proposed structures of these compounds.

SYNTHESIS AND CHARACTERIZATION OF SOME
SF₅- CONTAINING SULFONIC ACIDS

by

ROBERT J. WILLENBRING

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF ARTS

in

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Portland State University

1987

TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH:

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CHAPTER I

INTRODUCTION

FUEL CELLS

A fuel cell is a device in which the chemical energy of a fuel is converted to electrical energy without first being converted into heat. Ideally, the cell is a static system, in that it remains invariant while oxidant and fuel are supplied and electricity and other products are removed. The fuel is oxidized, just as in a normal combustion process, but by separating the oxidation and reduction reactions the electrons can be forced to flow through a wire and do work (see Figure 1). While fuel cells are

Figure 1. A typical acid electrolyte fuel cell.

conceptually simple, they have proved a difficult concept to realize, due to problems in maintaining an invariant structure and in enhancing the reaction kinetics in order to generate high current densities.^{1,2,3}

In a typical acid electrolyte fuel cell, the gaseous fuel is fed through a porous electrode made of platinum bonded to Teflon. The platinum serves both as electrode and catalyst for the reaction, while the Teflon is an inert support material. Oxidation occurs at the phase boundary between the fuel gas, the electrode, and the electrolyte solution, and fuel which doesn't react before leaving the electrode either bubbles out of the solution or diffuses to the cathode and reacts directly with oxygen.

The electrons from the anode reaction travel through an external circuit to the cathode, while the hydrogen ions are transported there by the electrolyte. The cathode is another gas diffusion electrode, where again the reaction between oxygen, hydrogen ions, and electrons must take place in the three phase boundary between electrode, gas, and electrolyte. Most acid electrolyte fuel cells are operated at a high enough temperature that water, the sole product if hydrogen is used as fuel, can be removed as steam, to prevent dilution of the electrolyte.

There are several methods which can be employed in order to generate a higher current density in a fuel cell.

Increasing the size of the electrodes (they are usually shaped like flat plates, so their size is given by their area), increases the surface available for reaction, which increases the output. While this is easy to do, the platinum electrodes are a major part of the cost of a cell, so this isn't a cost effective solution.

Most fuel cells are run at elevated temperatures, to improve their reaction kinetics. Phosphoric acid fuel cells operate at about 200°C, while sulfonic acid cells typically operate at 120°C to 150°C. The temperature is determined more by the stability of the cell materials than anything else; cells are usually run at the highest temperature they can survive.

These two solutions involve changing physical parameters, while the remaining two involve changing the components of the cell. Catalysis of the reactions will increase the reaction rate and allow for higher currents to be produced. The platinum electrode acts as a catalyst for the anode reaction, so much of the research is directed at finding a suitable catalyst for the cathode reaction, and at finding an inexpensive replacement for the platinum.

FUEL CELL ELECTROLYTES

The current density of a fuel cell may also be increased by altering the electrolyte. Concentrated

phosphoric acid is the electrolyte used in first generation fuel cells, but its failings as an electrolyte have spurred much of the current research into improved catalysts and a replacement electrolyte. Some of the characteristics which an ideal electrolyte should possess are:⁴

1) High ionic conductivity and acid strength. High conductivity and acid strength reflect fast proton transport through the solution, which makes it possible to operate the cell at lower temperatures and still maintain a reasonable reaction rate.

2) Low vapor pressure. The electrolyte must remain in the cell while water and other reaction products are removed, usually by evaporation. Also, the vapor pressure of water over the electrolyte must be balanced with the rate of formation of water, so the concentration of the electrolyte remains constant. For phosphoric acid, a concentrated solution is required to accomplish this, while for sulfonic acids a dilute solution is sufficient.⁵

3) Electrochemical and thermal stability. The electrolyte must not decompose or react with any of the cell materials. Aside from the loss of electrolyte, the products of such reactions may interfere with the cell operation in other ways. The electrolyte also cannot act as an electron carrier (i.e. it must not be oxidized or reduced under cell conditions) in addition to an ion carrier, as this will allow the electrons to circumvent the external circuit.

4) Chemical inertness. It must not react with the materials of the cell. Of particular importance are adsorption on or reaction with the platinum electrodes by either the electrolyte or its anion.⁶ While phosphoric acid doesn't affect the operation of the electrode, under cell operating conditions it can be reduced to other phosphorus oxides which do.⁷

5) Favorable surface activity. The electrolyte should not wet Teflon, which is used as a binder and seal in the electrodes, and it should not foam excessively when gases are bubbled through it. If the Teflon becomes wetted, capillary action floods the electrode with electrolyte and the gas flow becomes blocked.⁸

6) High oxygen and hydrogen solubility. The gases must react while they are still in contact with the electrodes, so if the gases can go into solution this increases the effective surface area of the electrode.

In addition, an electrolyte which will support use of hydrocarbon fuels is desirable. Phosphoric acid is suitable for purified reformat fuels, where the steam from the cell operation is used in the reforming process, and the carbon monoxide is removed by a shift reaction,⁹ but the fuel processing is then a major energy drain on the cell output.

Both perfluoroalkane carboxylic acids and perfluoroalkane sulfonic acids meet the requirements for acidity, solubility, and stability needed to be effective as an

electrolyte. The organic end of the molecule in both cases allows for flexibility in tailoring the molecule to fit the needed characteristics, but in general, the perfluoroalkane carboxylic acids are too volatile for use in a fuel cell. The first system studied as a potential replacement for phosphoric acid was trifluoromethanesulfonic acid (TFMSA). The success of this acid demonstrated that the search for a better electrolyte was a viable alternative to the search for improved electrocatalysts in improving fuel cell performance.¹⁰

In looking at sulfonic acids as possible fuel cell electrolytes, the length of the organic tail is significant. Shorter chain length sulfonic acids have relatively high vapor pressures, but increasing the chain length to more than four makes them extremely surface active.¹¹ This creates problems both with wetting of the Teflon electrode binding and with foaming in the cell as the gases bubble out. Introduction of functional groups that decrease the vapor pressure without affecting the surface activity is one possible solution, and this is the route looked at in this thesis.

SULFONIC ACIDS AS FUEL CELL ELECTROLYTES

In a direct comparison with phosphoric acid using synthetic reformat fuel mixtures, trifluoromethanesulfonic

acid showed four times the performance level overall as measured by current density under different operating conditions.¹² One of the main factors limiting the efficiency of phosphoric acid is the overpotential for oxygen reduction on platinum. This causes oxygen reduction to be two orders of magnitude slower for phosphoric acid than for aqueous TFMSA.¹³

The cathode reaction in a fuel cell is first order in both oxygen concentration and proton activity.¹⁴ TFMSA is one of the strongest protic acids known, as it will protonate sulfuric acid,¹⁵ and it is a much stronger acid than phosphoric acid. Also, the concentrated phosphoric acid solutions that must be used in fuel cells have low oxygen solubility. TFMSA shows higher oxygen solubility, due mainly to the ability to use dilute solutions and still maintain high ionic conductivity while preventing wetting of Teflon.

The high conductivity of the TFMSA fuel cell allows it to operate effectively at the lower temperatures where TFMSA is stable, around 60°C. Though higher temperatures will cause decomposition of TFMSA, these cells are usually run at about 120°C, in order to prevent poisoning of the platinum electrode by carbon monoxide, one of the components of reformat fuels.¹⁶

The success of TFMSA has spurred interest in other sulfonic acids as potential fuel cell electrolytes. Most of

the research is centered on short chain sulfonic acids, and usually methane or ethane derivatives. Methanesulfonic acid, methanedi- and tri-sulfonic acids and their perchloro-analogues,¹⁷ ethanedisulfonic acid and tetrafluoroethane-disulfonic acid¹⁸ among others have been made and tested as potential fuel cell electrolytes. While none of them have been entirely successful, they show enough promise to indicate that these or similar compounds will eventually replace phosphoric acid as the leading acid fuel cell electrolyte.

This chapter has provided a general overview of fuel cells and their electrolytes. In the next chapter, the equipment, reagents, and methods used in the synthesis and characterization of several sulfonic acids will be described. Chapters III and IV contain the experimental results, and Chapter V contains a summary of the results and suggestions for further work.

CHAPTER 2

EXPERIMENTAL

VACUUM SYSTEM

Gases and volatile liquids were manipulated in a single manifold vacuum line constructed of 25 mm inside diameter Pyrex glass tubing to which four Eck and Krebs 2 mm high vacuum stopcocks with Pyrex Standard Taper 10/30 ground glass outer joints were attached. Pressure was measured using a Frederick Televac vacuum guage and thermocouple or a mercury manometer. The line was evacuated through a liquid N₂ trap by a Welch Duo-Seal vacuum pump. A Consolidated Vacuum Corporation two-stage oil diffusion pump was also attached, though it was only used to calibrate the vacuum guage. With the rotary and diffusion pumps both operating, the Televac was set to read 0.0 μ . Normal operating pressures were less than 5 μ unless otherwise noted. All joints and stopcocks were lubricated with either Apiezon M or Fluorolube GR-290 grease. Vacuum guage connections were sealed with Halocarbon wax.

High pressure reactions were carried out in a stainless steel Hoke vessel equipped with a Whitey stainless steel valve and a brass Standard Taper 10/30 inner joint. Metal vessels with volumes of 75 mL, 150 mL, and 300 mL were used.

Low pressure gas reactions were carried out in a 1, 2, or 3 liter Pyrex glass vessel equipped with a cold finger for condensing materials into them, and a Kontes stopcock with a Standard Taper 10/30 inner joint. Other reactions were carried out in Pyrex Standard Taper glassware using Fluorolube GR-290 grease to seal the joints.

INSTRUMENTATION

NMR spectra were obtained on a Varian EM-390 Spectrometer operating at 90.00 MHz for ^1H and 84.67 MHz for ^{19}F . TMS and Freon-11 external standards were used. A Nicolet 20 DX FTIR spectrometer operating at 2.0 cm^{-1} resolution was used to obtain the IR spectra. Gas IR spectra were taken using an 8.5 cm path length cell with KBr or KRS-5 windows. Solid and liquid IR spectra were taken on KBr or KRS-5 disks. Mass spectra were measured on a VG 7070 HS mass spectrometer operated at 70 eV. Perfluorokerosene was used as an internal standard. $\text{SF}_5\text{CF}_2\text{CFBr}_2$ was purified using an Aerograph Autoprep A-700 gas chromatograph equipped with a $10' \times 3/8"$ column packed with 20% Carbowax adsorbed on Chromosorb W. Melting points were determined on a Mel-Temp melting point apparatus. Melting and boiling points were uncorrected.

REAGENTS

All reactants were reagent grade and were used as purchased unless noted otherwise. Chemicals were obtained from Aldrich Chem. Co. (benzoyl peroxide, sodium sulfite (98+%), sodium bisulfite, tris-thiomethylmethane (99%), and 1,1,1-trifluoro-2-iodoethane (99%)), J.T. Baker Chem. Co. (bromine, sulfuric acid (95.6%), sodium hydroxide, and sodium borate), Mallinckrodt Chem. Works (iodine), Matheson (hydrogen chloride, tech. grade), Peninsular Chem. Research (vinyl fluoride, 1,1-difluoroethene, trifluoroethene, tetrafluoroethene, and bromotrifluoroethene) and Air Products and Chemicals (ethylene). Water was deionized using a Crystalab CL-5 water demineralizer. SF_5Br was prepared and handled by literature methods.¹⁹

CHAPTER III

SYNTHESIS OF SF_5 - CONTAINING SULFONIC ACIDS

DISCUSSION

In the introduction it was stated that in order for an alkanesulfonic acid to be effective as a fuel cell electrolyte, it should have a short chain length to prevent wetting of Teflon, and it should have a low vapor pressure. It should also not contain a terminal CH_3 - group and possibly not contain any C-H bonds, as adsorption on platinum may block the catalyst.²⁰ While increasing the chain length would decrease the vapor pressure, the problem with surface activity made other methods, such as the use of hydrates instead of anhydrous acids and the introduction of bulky functional groups, better for achieving a lower vapor pressure.

Compounds of the general form $\text{SF}_5\text{CX}_2\text{CX}_2\text{Br}$ where X= H or F were chosen as starting materials, as they would generate sulfonic acids of the form $\text{SF}_5\text{CX}_2\text{CX}_2\text{SO}_3\text{H}$, which should meet the criteria outlined above. All but the perfluorinated adduct $\text{SF}_5\text{CF}_2\text{CF}_2\text{Br}$ had been reported, and they could easily be synthesized by the addition of SF_5Br to the appropriate olefin.²¹ The tetrafluoroethylene adduct had been isolated in small amounts as a by-product in the synthesis of the

corresponding telomer,²² and as it was thought that telomer formation would predominate in this reaction, $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$ was prepared by a different method²³ for use as a starting material. It was later found that by running the reaction under suitably mild conditions, the bromide monomer was produced in good yields. Since synthesis of the iodide was a messy multistep process, it was hastily abandoned in favor of the SF_5Br adduct.

Three general schemes have been used in the synthesis of fluorinated sulfonic acids from the corresponding halide.²⁴ The oldest is the Strecker reaction, in which an alkyl halide is reacted with hot aqueous alkali metal sulfite, giving a sulfonic acid salt. Acidification of the salt gives the sulfonic acid. This reaction is considered unreliable, inefficient, and complicated,^{25,26} because of the inability to isolate the sulfonate salt, which is formed with other salts having similar solubility characteristics.

The second method involves metal bisulfite addition to fluoroolefins, which can be made by dehydrohalogenation of the bromide or iodide. The salt is then treated with 100% H_2SO_4 and the sulfonic acid is distilled out of the mixture. This method was used to prepare $\text{SF}_5\text{CFHCF}_2\text{SO}_3\text{M}$ where $\text{M} = \text{H}$ or Na ²⁷ (see Figure 2).

Figure 2. Synthetic scheme for $\text{SF}_5\text{CFHCF}_2\text{SO}_3\text{H}$.

The yield for this scheme was 6.7% based on the olefin. While dehydrohalogenation of the other adducts should give olefins which could then be converted into the acids using this method, the yield for this process was rather low, and perfluoroalkanesulfonic acids cannot be made by this route.

Finally, conversion of the alkyl halide into a thioether followed by oxidation generated the sulfonic acid directly. Benzyl mercaptan and an appropriate alkyl chloride were used as starting materials,²⁸ but the odor associated with the mercaptan was sufficient cause to abandon this scheme.

The reaction of the alkyl halide with Na_2SO_3 in 50% ethanol was found to give a good yield of the sulfonate salt for all but the perfluorinated adduct. Here the salt still seemed to be formed, but in much lower yields. The salts were extracted from the reaction mixture using hot 100% ethanol. It was soon learned that due to the solubility of the other reaction products in this solvent, a clean separation was not being achieved, so the extractions were abandoned.

Instead, the sulfonic acids were formed by treating the entire recovered solid with acid. Treating the crude salts with 100% H_2SO_4 generated large amounts of colorless gas along with some bromine, and usually resulted in significant amounts of charring as the mixture was distilled to isolate the anhydrous acid.

Acidification using $\text{HCl}/\text{H}_2\text{O}^{29}$ was adopted to avoid these problems, as this method served both to turn the salt into the acid and to isolate it from the other salts in the mixture (see Figure 3). In this method the sulfonic acid remains in solution, while the other salts precipitate and

Figure 3. Reaction scheme for conversion of $\text{SF}_5\text{CX}_2\text{CX}_2\text{Br}$ to $\text{SF}_5\text{CX}_2\text{CX}_2\text{SO}_3\text{H}$.

were removed by filtration. Evaporation of the saturated HCl followed by repeated sublimation of the solid material resulted in the pure acid hydrates of $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ and $\text{SF}_5\text{CHFCH}_2\text{SO}_3\text{H}$ in good yields.

For the other members of the series, mixed products resulted. With $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H}$, repeated sublimation gave a product that was about 80% sulfonic acid and 20% some other compound, based on the integration of the SF_5^- peaks in the ^{19}F NMR spectrum. The impurity exhibited an additional fluorine resonance at -105.5 ppm ($J_{\text{HF}} = 27.1$ Hz (doublet),

$J_{F-SF_4} = 21.2$ Hz (pentet), $J_{F-SF} = 3.7$ Hz (doublet)), and a 1H resonance at 7.15 ppm ($J_{H-SF_4} = 7.9$ Hz (pentet), $J_{HF} = 27.1$ Hz (doublet)). The SF_5^- pattern was a doublet at 69.0 ppm and a nine-line pattern at 77.5 ppm, with $J_{SF-SF_4} = 147$ Hz. The NMR data were consistent with a partial structure of $SF_5-CHX-CFYZ$, where X, Y, and Z were neither H nor F.

While this reaction is generally thought to proceed through a nucleophilic substitution mechanism, with the lone pair on the sulfur displacing the C-Br bond,³⁰ a free radical mechanism has been postulated for similar reactions³¹ (see Figure 4). Investigation of the effect of free radical

Figure 4. Free radical mechanism.

inhibitors should help to distinguish between these mechanisms.

The mixed products and the lability of the fluorines alpha to the acid group can be explained by a carbene mechanism,³² shown for the difluoroethane adduct in Figure 5. The product of step 3, which has lost a fluorine from the alpha carbon, can go on to form the other products seen in

this reaction. The F^- generated in step 2 explains the etching of the glassware used in these reactions, and the

Figure 5. Carbene mechanism.

metal corrosion noted when these reactions have been run in pressure vessels.³³

With $SF_5CH_2CHFSO_3H$, the situation is less clear. The elemental analysis for the product generated indicates either substantial impurities are present or a different product is formed. While ^{19}F and 1H NMR contain resonances which are consistent with the sulfonic acid structure, many other peaks are present, and further study is needed before definitive statements can be made.

The synthesis of the perfluorinated sulfonic acid $SF_5CF_2CF_2SO_3H$ was attempted through both the iodide and the bromide. These systems showed several differences from the other adducts. First, the yield of the salt was much lower; assuming that the solid residue from the reaction of $SF_5CF_2CF_2Br$ and Na_2SO_3 was entirely Na_2SO_3 , $NaBr$, and $SF_5CF_2CF_2SO_3Na$, the yield for these reactions ranged from 10-15%, while the other adducts gave calculated yields of 45-85%. Second, when the salt mixture was acidified, the solid

precipitate for this reaction was yellow. All of the other reactions gave a colorless precipitate. Finally, concentration of the acidified mixture resulted in a black, viscous liquid instead of the white solid isolated in the other reactions. Attempts to isolate a product from this liquid by distillation proved fruitless, while vacuum sublimation gave a small quantity of a yellow, water-insoluble solid. It is possible that a redox reaction occurred, in which the carboxylic acid $\text{SF}_5\text{CF}_2\text{COOH}$, either Br_2 or I_2 , and sulfur were formed.³⁴ This would account for the difficulty in isolating a product, and explain the yellow color of the precipitate and the solid material that sublimed out of the mixture.

The remainder of this chapter contains a summary of the procedure for the reactions discussed above, as well as tabulations and more extensive discussions of the elemental analyses, ^{19}F and ^1H NMR spectra, IR spectra, and mass spectroscopy.

EXPERIMENTAL

Synthesis of $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$

Reaction using sodium sulfite with a borax buffer. A 150 mL metal vessel to which 3.8 g of $\text{SF}_5\text{CH}_2\text{CH}_2\text{Br}$ (16 mmol), 1.8 g (0.5 mmol) of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, and 2.90 g (23.0 mmol) of Na_2SO_3 were added was closed and shaken. After 10.9 g of H_2O was added the vessel was sealed, cooled to -196°C , and

volatile materials were removed under vacuum. The vessel was placed in an oil bath at 105–110°C for 3 hours, with shaking every 15 minutes. The contents of the vessel were transferred to a beaker and the water was removed by heating. The solid residue was extracted with 40 to 60 mL ethanol several times. The ethanol was removed, and an IR spectrum of the solid material was taken. The spectrum showed the SF_5^- group was no longer present, so the procedure was discontinued.

Reaction using sodium bisulfite. A 75 mL metal vessel to which 4.8 g (20 mmol) of $\text{SF}_5\text{CH}_2\text{CH}_2\text{Br}$, 2.3 g of NaHSO_3 , and 10.2 g of water were added was closed and shaken. The vessel was cooled to -196°C, and volatile materials were removed under vacuum. The vessel was placed in an oil bath at 120°C for a total of 11 hours, with shaking every 15 minutes. When the material was removed from the reaction vessel, only unreacted $\text{SF}_5\text{CH}_2\text{CH}_2\text{Br}$ (4.6 g) was recovered.

Reaction using sodium sulfite in 50% ethanol. A 250 mL round bottomed flask to which 9.65 g (41.1 mmol) of $\text{SF}_5\text{CH}_2\text{CH}_2\text{Br}$, 5.29 g (42.0 mmol) of Na_2SO_3 , and 140 mL 50% ethanol were added, was attached to a Fredrick condenser. The mixture was refluxed with stirring for 50 hr. The solvent was removed, the residue was extracted twice with 50 to 60 mL ethanol, and the extracts were dried on a vacuum line. The yield was 5.62 g (21.8 mmol) crude sulfonate salt, m.p. 270°C (dec).

Acid distillation using 100% H_2SO_4 . A 25 mL round bottom flask to which 0.5 g of 100% H_2SO_4 (an additional 1.70 g were added later) and 4.0 g (15 mmol) of the crude salt were added was attached to a semimicrodistillation apparatus. After degassing, the mixture was distilled under vacuum. A few drops of product were collected in two fractions, one at 120°C and the other at 140°C (150–200 μ). Significant charring occurred to the products upon standing, so they were discarded.

Acidification using H_2SO_4 . A 50 mL round bottom flask containing 4.8 g (19 mmol) of crude salt, 12.1 g water and 0.94 g of 30% H_2SO_4 was heated with stirring until the temperature reached 55°C, after which it was allowed to cool. The solvent was removed, and the solid material was extracted with $\text{CF}_2\text{ClCFCl}_2$ and ether. The IR spectrum showed no SF_5^- group in the extract or the residue.

Acidification using HCl . A 200 mL 3-neck flask containing 19.1 g of crude salt (estimated 10.1 g of the sulfonic acid salt, 9.0 g of other salts) dissolved in about 100 mL H_2O was equipped with a reflux condenser, HCl gas bubbler, and a Teflon stirring bar. HCl was bubbled in until the solution was yellow and a white precipitate had formed. The mixture was filtered using a gooch crucible, and the volume of the liquid was reduced by heating on a hot plate. The solution was transferred to a 50 mL roundbottom flask, and the remaining solvent was removed under vacuum.

The solid material was sublimed under vacuum (100°C at $<10\ \mu$), yielding 4.3 g (18 mmol) of the sulfonic acid as a colorless crystalline solid.

Acid neutralization with NaOH. A NaOH solution was prepared and standardized using KHP. The normality was found to be 0.0999 N. Two solutions of $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ in water were prepared and titrated using the NaOH solution. The equivalent weight was found to be 231 g/eq. (calculated 236 g/eq. for the anhydrous acid). Activated charcoal was added to the solutions, and they were filtered while hot. Removal of the water, first by heating on a hot plate, then by drying under vacuum, gave the sodium salt $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$, m.p. $268\text{--}270^{\circ}\text{C}$ (dec).

Synthesis of $\text{SF}_5\text{CH}_2\text{CHF}\text{SO}_3\text{H}$

Reaction using sodium sulfite in 50% ethanol. A 250 mL roundbottom flask containing 15.89 g (62.81 mmol) of $\text{SF}_5\text{CH}_2\text{CHFBr}$, 120 mL of 50% ethanol and 8.23 g (65.3 mmol) of Na_2SO_3 was equipped with a reflux condenser and a Teflon stir bar. The mixture was refluxed while being stirred for 69 hours. The solvent was removed by heating on a hot plate, then final drying was done under vacuum. A colorless solid (13.57 g) was recovered, and the weight gain indicated that the salt was formed. No attempt was made to isolate the salt.

Acidification using HCl The crude salt was placed in a 200 mL 3-neck flask and 80 ml of water was added. The solution was stirred until the solid had dissolved, then a reflux condenser was attached and HCl was bubbled into the solution. Too much water was added in an attempt to dissolve some material that proved to be insoluble, so the volume of the solution was reduced to 60 mL, the solid material was filtered off, and the acidification was restarted. After formation of a precipitate occurred, the mixture was filtered. The solvent was removed, and the solid residue was sublimed. The yield was 1.31 g (5.16 mmol, 8.2% yield, from the bromide) damp colorless crystals, but the NMR spectrum indicated a mixture of products was present.

Synthesis of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H}$

Reaction using sodium sulfite in 50% ethanol. A 100 mL roundbottom flask to which 3.81 g (14.1 mmol) of $\text{SF}_5\text{CH}_2\text{CF}_2\text{Br}$, 1.92 g (15.2 mmol) of Na_2SO_3 , and 50 mL of 50% ethanol were added, was equipped with a reflux condenser and a Teflon stir bar. The solution was refluxed for 44 hours, then it was filtered. The solvent was removed by heating on a hot plate. The solid material was extracted with 100% ethanol. Evaporation of the ethanol yielded crude salt. The percentage yield was estimated to be 85%, based on the

weight gain. A later reaction used 23.22 g (85.68 mmol) adduct, and yielded 20.67 g crude salt, m.p. 239°C (dec).

Acid distillation with 100% H_2SO_4 . A 25 mL roundbottom flask in which 12.11 g (41.2 mmol) of the crude sodium salt and 5.0 g (51 mmol) of 100% sulfuric acid were mixed was attached to a vacuum distillation apparatus. Distillation was started but the mixture bumped so the reaction was halted and the apparatus was cleaned out. An additional 4.3 g H_2SO_4 was added and the mixture was distilled. The pressure was maintained, with some difficulty, at about 400 μ . When the temperature reached 75°C, a white gas began to evolve from the pot and move through the apparatus. The first distillate collected was found to be H_2SO_4 .

Second run: A 100 mL roundbottom flask containing 12.95 g (44.0 mmol) crude salt and 12.77 g (130.3 mmol) H_2SO_4 was attached to a semimicrodistillation apparatus. After degassing, the mixture was distilled under vacuum. A clear colorless liquid (3.18 g) was collected at 60°C, 300 μ . The liquid was redistilled, and a few drops of clear liquid were collected at 30-35°C, 200-400 μ . This liquid showed a singlet in the ^{19}F NMR spectrum which may indicate an $-\text{SO}_2\text{F}$ group, but did not show any resonances for an SF_5^- group.

Acidification using HCl . The sulfonic acid salt (13.16 g, 44.8 mmol) was dissolved in a small quantity of water. Addition of 10.0 mL of 12 molar HCl did not produce a precipitate as expected. More HCl was added, in stages,

bringing the total volume to 40 mL, but no precipitation was observed. The volume was reduced to 20-25 mL by heating on a hot plate, and the solution was put in a 50 mL 3-neck flask. The flask was equipped with a reflux condenser and an HCl gas bubbler. After excess HCl was added, a yellow liquid and white precipitate were noted. The mixture was filtered, and the solvent was removed first by heating on a hot plate then by drying under vacuum. The residue was sublimed (100°C, <20 μ) and 8.13 g acid hydrate (28.0 mmol, 62.6% yield) was collected.

Acid neutralization using NaOH. Two samples of the acid (1.0807 g and 0.8260 g) were dissolved in water and titrated using a previously standardized NaOH solution (0.0999 N). The equivalent weight was found to be 280 g/eq. which corresponds to a formula of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H} \cdot 1/2\text{H}_2\text{O}$. Activated charcoal was added and the solution was filtered. The water was removed by heating on a hot plate, then by drying on a vacuum line, to recover the sodium salt.

Synthesis of $\text{SF}_5\text{CHF}_2\text{CF}_2\text{SO}_3\text{H}$

Reaction using sodium sulfite in 50% ethanol. A 250 mL roundbottom flask containing 23.44 g (81.11 mmol) of $\text{SF}_5\text{CHF}_2\text{CF}_2\text{Br}$, 10.29 g (81.67 mmol) of Na_2SO_3 , and 145 mL of 50% ethanol was equipped with a Fredrick condenser, and the mixture was refluxed for 48 hours. The mixture was cooled, and the solvent was removed by heating on a hot plate, with

final drying done under vacuum. A colorless solid (27.07 g) was recovered. The solid was extracted with 100% ethanol, and the extract was dried, yielding 19.76 g (63.33 mmol) crude $\text{SF}_5\text{CHFCF}_2\text{SO}_2\text{Na}$.

Acidification using 100% H_2SO_4 . $\text{SF}_5\text{CHFCF}_2\text{Br}$ (24.07 g, 83.29 mmol) was dissolved in 76 mL of 95% ethanol in a 3-neck flask, while 10.51 g (83.41 mmol) of Na_2SO_3 was dissolved in 57 mL of water and was placed in a dropping funnel. After the solution was heated to reflux, the Na_2SO_3 solution was added over several hours. The mixture was refluxed for 48 hours after the addition was complete. After the solvent was removed, the solid was mixed with 40 mL of 100% H_2SO_4 . After degassing, the mixture was refluxed under vacuum, with the pressure maintained between 100 and 200 μ , and the oil bath at 120°C. A white crystalline solid collected in the condenser. The solid was collected and sublimed (60°C, 5 μ). The yield was 11.09 g of the sulfonic acid monohydrate (36 mmol, 43%), m.p. 68-70°C, dec 195°C.

Acidification using HCl. A 200 mL 3-neck flask containing 19.68 g (63.08 mmol) of crude $\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{Na}$ dissolved in 100 mL of water was equipped with a gas inlet and reflux condenser. HCl was bubbled in until a precipitate formed and the solution was pale yellow-green. The solution was filtered, and the solvent was removed by heating on a hot plate, until the material was an orange slushy solid. Final drying was done under vacuum. The

solid was sublimed (100°C , $<40\ \mu$) and 7.14 g of the sulfonic acid monohydrate (23.2 mmol, 36.8%) was collected.

Acid neutralization using NaOH. Two samples of the acid hydrate (0.7676 g and 0.4299 g) were dissolved in water. Titration with 0.0999 N NaOH required 25.74 mL and 14.48 mL respectively. This gave an equivalent weight of 298 g/eq. (calculated for the acid: 290 g/eq. and for the monohydrate 308 g/eq.). The solutions were cleaned with activated charcoal, filtered, and dried to recover the sodium salt.

Attempted synthesis of $\text{SF}_5\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$ using iodide adduct

Reaction using sodium sulfite in H_2O -dioxane. The iodide adduct³⁵ (15.33 g, 43.3 mmol) was added to 9.0 mL of water, 3.0 mL of dioxane, 0.2 g of benzoyl peroxide, and 5.63 g (44.7 mmol) of Na_2SO_3 in a nitrogen-flushed flask equipped with a reflux condenser and nitrogen bubbler. The mixture was heated to 80°C for 18.5 hours, then cooled to room temperature. The solvent was removed under vacuum. The solid residue was extracted with hot ethyl acetate, but the IR spectrum indicated that both the extract and residue lacked the SF_5 - group.

Reaction using sodium sulfite in 50% ethanol. A 250 mL roundbottom flask containing 14.59 g (41.21 mmol) of $\text{SF}_5\text{CF}_2\text{CF}_2\text{I}$, 75 mL of 50% ethanol, and 5.36 g (42.5 mmol) of Na_2SO_3 was equipped with a Fredrick condenser. The solution

was refluxed for 66 hours (changing from bright yellow to orange-brown to black). The mixture was cooled, and the solvent and other volatile materials were removed. The flask was filled with N_2 and sealed. The IR spectrum indicated the presence of an SF_5^- group in the solid, along with other peaks which were consistent with the structure $SF_5CF_2CF_2SO_3Na$.

Acidification using HCl. The dirty grey-brown powder from the previous reaction was dissolved in 60 mL water in a 200 mL 3-neck flask. An HCl bubbler was attached, and HCl was added. After precipitate formation, the solution was filtered and the clear colorless solution was put on a hot plate to remove solvent. As the solution became concentrated it turned light green. The slushy solid was transferred to a 35 mL roundbottom flask and the remaining solvent was removed under vacuum. Some orange solid collected in the trap. A colorless solid (12.81 g) was collected and was re-acidified (15 mL water, HCl bubbler). The precipitate was filtered and the solvent was removed under vacuum. As the volume decreased, the solution darkened and eventually became a brown-black viscous mass. Attempts to sublime a product out of this mixture were unsuccessful.

Attempted synthesis of $\text{SF}_5\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$ using bromide adduct

Synthesis of $\text{SF}_5\text{CF}_2\text{CF}_2\text{Br}$. A 150 mL metal vessel containing 35.99 g (173.9 mmol) of SF_5Br and 94 mmol of CF_2CF_2 (3.94 atm in 0.57 L) was put in an oven at 70°C for 44 hours. The contents of the vessel were transferred to a 50 mL roundbottom flask and allowed to warm to room temperature. The liquid was distilled, and the product was collected at $60\text{--}62^\circ\text{C}$. The yield was 20.21 g (65.83 mmol, 70%) of $\text{SF}_5\text{CF}_2\text{CF}_2\text{Br}$.

Reaction with sodium sulfite in 50% ethanol. A 250 mL roundbottom flask containing 20.21 g (65.80 mmol) of $\text{SF}_5\text{CF}_2\text{CF}_2\text{Br}$, 72 mL of 50% ethanol, and 10.82 g (85.9 mmol) of Na_2SO_3 was equipped with a Fredrick condenser and a Teflon stir bar. The mixture was refluxed with stirring for 43 hours, then transferred to a beaker and heated on a hot plate to remove the solvent. The damp solid was put on a vacuum line to remove the last bit of solvent. A colorless solid (12.71 g) was recovered.

Acidification attempts. In a 500 mL roundbottom flask 29.09 g (94.76 mmol) of $\text{SF}_5\text{CF}_2\text{CF}_2\text{Br}$ was added to 220 mL of 50% ethanol. After 12.05 g (95.6 mmol) of Na_2SO_3 was added, the mixture was refluxed for 60 hours. The solvent was removed by heating, and the damp solid was dissolved in 60 mL of water in a 3-neck flask for acidification. The flask was equipped with a reflux condenser and an HCl bubbler. HCl was added until a precipitate formed, and the mixture

was filtered. The liquid was evaporated, and the residue was dried under vacuum. A dark, viscous liquid formed. Sublimation of the product mixture was attempted, and it resulted in a small amount of yellow solid which was insoluble in water. The residue was mixed with 80 mL of 100% sulfuric acid. After degassing, the mixture was distilled under vacuum. The solution gave puffs of white smoke, but no products.

Acidification using HCl. A 200 mL 3-neck flask containing 12.71 g of crude salt dissolved in 80 mL of water was equipped with an HCl bubbler and a reflux condenser. HCl was bubbled in as the solution was stirred. The solution became rust-colored, then reddish purple. When a precipitate formed, the solution was peach-red. When HCl started bubbling vigorously from the solution, the precipitate was yellow/tan and the solution was yellow. The mixture was cooled, filtered, and the volume was reduced by heating on a hot plate. When the volume was about 20 mL, the solution was transferred to a vacuum line. Once again, reduction of the volume gave an intractable liquid.

ELEMENTAL ANALYSIS

The elemental analyses of $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$, $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$, $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$, $\text{SF}_5\text{CHFCH}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$, and $\text{SF}_5\text{CHFCH}_2\text{SO}_3\text{Na}$ are tabulated below. Agreement between

calculated and found values is good. The differences can be explained by the presence of a mixture of hydrates, though the integral hydrates used match the found data well. Most of the fluorine analyses are slightly low, and since the proposed carbene mechanism includes loss of a fluoride, it is possible that minor impurities from this side reaction are still present.

TABLE I
ELEMENTAL ANALYSIS OF SULFONIC ACIDS

$\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$		Calc.	Found
	C	10.17	10.26
	H	2.12	2.32
	F	40.3	39.8
	S	27.12	27.44
$\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$			
	C	9.30	9.38
	H	1.55	1.51
	F	36.8	36.5
	S	24.80	24.48
$\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$			
	C	8.28	8.37
	H	1.72	1.87
	F	45.9	45.3
	S	22.07	22.25

TABLE I, cont.

$\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$			
	C	8.16	8.28
	H	0.68	0.71
	F	45.2	44.8
	S	21.77	21.58
$\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$			
	C	7.79	7.87
	H	1.30	1.30
	F	49.4	48.9
	S	20.78	20.85
$\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{Na}$			
	C	7.69	7.82
	H	0.34	0.38
	F	48.7	48.8
	S	20.51	20.64

INFRARED SPECTRA

Infrared spectral data for $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$, $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$, $\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, and $\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{Na}$ are compiled in Tables II through VII, and the spectra are reproduced in the appendix. The most prominent feature of these spectra are the SF_5^- symmetric and antisymmetric stretches in the region from 830 to 885 cm^{-1} .³⁶

These peaks were used to track these compounds as they were being synthesized and purified. In a few cases these peaks were not easily distinguished, so the SF_5^- deformation modes at about 600 cm^{-1} were used to confirm the presence of this group. The other major peaks are consistent with the assigned structures, with the SO_3 symmetric and antisymmetric stretching modes in the region from 1050 to 1100 cm^{-1} and 1180 to 1280 cm^{-1} respectively, and the CF stretching modes appearing at slightly higher frequencies, between 1100 and 1300 cm^{-1} . Because of this overlap, unambiguous assignment of the peaks in this region is difficult. The SO_3 scissor and wag vibrational modes are visible at 550 to 570 cm^{-1} . The presence of electronegative groups has shifted many of

TABLE II
IR DATA FOR $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ (cm^{-1})

peak	description*	peak	description
3400	str, br	1005	str
2943	str, br	885	v str
1720	str, br	851	v str
1291	med	614	med
1171	v str	576	str
1069	med	454	med

*str= strong, med= medium, br= broad, v= very

the vibrations to higher frequencies, with the CH stretching frequencies appearing between 2950 and 3050 cm^{-1} . The OH stretching and bending modes are also shifted, with the stretch appearing close to 3400 cm^{-1} and the bend between 1650 and 1750 cm^{-1} .³⁷

TABLE III
IR DATA FOR $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ (cm^{-1})

peak	description	peak	description
3040	weak	993	med
2987	v weak	917	med
1443	weak	833	v str
1429	weak	809	med
1258	med	612	med
1226	v str	574	str
1193	v str	565	med
1072	str	550	weak
1055	weak	531	med

TABLE IV
IR DATA FOR $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ (cm^{-1})

peak	description	peak	description
3490	med, br	991	str
3038	weak	909	med
2988	v weak	896	med
1653	med	855	str
1420	med	834	v str
1296	med	800	med
1285	med	675	med
1266	str	632	med
1229	v str	605	med
1096	str	567	med
1054	med	553	med

TABLE V
IR DATA FOR $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$ (cm^{-1})

peak	description	peak	description
3116	weak	915	med
3038	weak	898	med
2987	weak	856	v str
1656	med	834	v str
1420	str	800	med
1337	weak	675	med
1267	v str	634	med
1229	v str	613	mec
1096	str	567	med
1049	weak	552	med
990	str	528	weak

TABLE VI
IR DATA FOR $\text{SF}_5\text{CHF}_2\text{CF}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (cm^{-1})

peak	description	peak	description
3150	str, br	999	str
3013	v weak	859	v str
2919	v weak	812	med
2851	v weak	727	weak
1730	str, br	645	str
1356	weak	598	str
1269	str	568	str
1231	v str	522	med
1132	str	479	med
1094	med	408	med

TABLE VII
IR DATA FOR $\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{Na}$ (cm^{-1})

peak	description	peak	description
3674	str	1098	str
3480	str, br	1008	v str
3007	weak	919	str
1653	med	859	v str
1635	med	809	str
1355	weak	728	weak
1285	v str	651	str
1270	v str	610	str
1247	v str	599	str
1154	str	571	str
1131	str	531	med

NMR SPECTRA

The NMR chemical shifts, relative peak areas, and coupling constants for $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$, $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$, $\text{SF}_5\text{CFHCF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$, and $\text{SF}_5\text{CFHCF}_2\text{SO}_3\text{Na}$ are presented in Tables VIII through XIII and the spectra are reproduced in the appendix. In some cases, the coupling constants were not calculated, either because the splitting was not visible or second-order effects made them too difficult to determine.

TABLE VIII
NMR DATA FOR $F^a-SF_4^b-CH_2^c-CH_2^d-SO_3H^e$

Chemical shifts (ppm from $CFCl_3$ or TMS) and relative areas				
a	b	c	d	e
82.5	65.4	4.34	3.94	12.1
1.0	4.1	2.0	2.0	1.0
Coupling constant: $J_{ab} = 145$ Hz.				

The SF_5^- group appears as an AB_4 pattern in all of these compounds, with the axial $-SF$ appearing as a nine-line pattern and the equatorial $-SF_4^-$ as a broad doublet with fine structure. Line 6 was used as the band center for the axial fluorine, while the midpoint of the integration was chosen as the peak position for the equatorial fluorines. The coupling constant was measured between the centers of the doublet peaks, the center was determined as the midpoint of the rise in the integration curve.

Fluorine chemical shifts reported for these compounds are consistent to those found in similar compounds,^{38,39} with axial SF resonances ranging from 84 to 71 ppm, equatorial SF resonances from 53 to 72 ppm, CF at -167 to -173 ppm, and CF_2 from -108 to -125 ppm. The proton chemical shifts are shifted downfield as expected, due to the electronegativity of the neighboring fluorines,⁴⁰ with CH_2 resonances ranging

TABLE IX
NMR DATA FOR $F^a-SF_4^b-CH_2^c-CH_2^d-SO_3-Na$

Chemical shifts (ppm from $CFCl_3$ or TMS) and relative areas			
a	b	c	d
84.1	65.6	4.58	3.96
1.0	4.2	1.0	1.0
Coupling constants: $J_{ab} = 144$ Hz, $J_{bc} = 7.8$ Hz.			

from 4 to 5 ppm, and CH resonances at 6.4 to 6.8 ppm. The acid peaks for these compounds are far downfield, ranging from 12.1 ppm in $SF_5CH_2CH_2SO_3H$ to 13.7 ppm in the other two acids. Both acid hydrates exhibit a second peak for the water at 9.2 ppm. An NMR spectrum of $SF_5CHFCF_2SO_3H \cdot H_2O$ taken after several weeks showed a single peak of relative area three at 10.52 ppm instead of separate acid and water peaks. This would be assigned to water bound to the acid group as H_3O^+ , rather than as H_2O .

Due to both the size and the electronegativity of the SF_5^- and $-SO_3^-$ groups, the expected conformation of these compounds has these two groups anti to each other. This makes the NMR spectra more complex than they would otherwise be, as a spin will experience different environments depending on which side of the molecule it is on. The 1H spin system for $SF_5CH_2CH_2SO_3H$ is therefore $AA'BB'$, rather than A_2B_2 .⁴¹ In $SF_5CH_2CF_2SO_3H$ two different vicinal J_{HF} s are seen,

TABLE X
NMR DATA FOR $F^a-SF_4^b-CH_2^c-CF_2^d-SO_3-H^e \cdot H_2O^f$

Chemical shifts (ppm from $CFCl_3$ or TMS) and relative areas					
a	b	c	d	e	f
79.0	72.5	4.78	-110.3	13.7	9.2
1.0	4.0	2.0	1.9	1.0	2.0

Coupling constants (Hz)				
	a	b	c	d
a	-	n.a.	n.a.	2.3
b	133	-	n.a.	n.a.
c	n.a.	7.7	-	17.4, 15.9
d	2.2	11.8	17.8, 16.1	-

one for the gauche interaction and one for the anti coupling. In $SF_5CHFCF_2SO_3H$ the presence of the chiral carbon further complicates matters, as the neighboring fluorines will interact with the spins on the chiral center differently.⁴² Coupling constants for vicinal H-F groups can vary from near zero to 50 Hz, and this coupling varies with the dihedral angle.⁴³ This relationship can be used to assign coupling constants, for example in $SF_5CHFCF_2SO_3H$, $^3J_{HF}$ ⁴⁴ is near zero for one of the fluorines in the CF_2 group, and about 20 Hz for the other. $^3J_{HF}$ is typically near zero for dihedral angles ranging from 65° to 110° , so the anti

TABLE XI
NMR DATA FOR $\text{F}^{\text{a}}\text{-SF}_4^{\text{b}}\text{-CH}_2^{\text{c}}\text{-CF}_2^{\text{d}}\text{-SO}_3\text{-Na}$

Chemical shifts (ppm from CFCl_3 or TMS) and relative areas			
a	b	c	d
80.0	73.2	5.10	-108.6
1.0	3.9	-	1.9

Coupling constants (Hz)				
	a	b	c	d
a	-	n.a.	n.a.	n.a.
b	144	-	n.a.	n.a.
c	n.a.	n.a.	-	n.a.
d	2.1	11.9	15.2, 17.8	-

fluorine is the one that is observed coupling with the proton and the gauche fluorine has the coupling constant near zero.

TABLE XII
NMR DATA FOR $F^a-SF_4^b-CF^cH^d-CF^eF^f-SO_3H^g \cdot H_2O^h$

Chemical shifts (ppm from $CFCl_3$ or TMS) and relative areas							
a	b	c	d	e	f	g	h
71.1	53.0	-167.3	6.39	-113.9	-124.9	13.68	9.2
1.0	4.2	1.1	1.0	1.0	1.0	1.0	2.0

Coupling constants (Hz)						
	a	b	c	d	e	f
a	-	n.a.	n.a.	n.a.	n.a.	n.a.
b	144	-	n.a.	n.a.	n.a.	n.a.
c	2.6	n.a.	-	43.2	11.9	16.9
d	n.a.	5.1	41.4	-	n.a.	20.7
e	1.4	15.7	12.7	n.a.	-	265
f	1.6	11.9	16.9	20.3	262	-

TABLE XIII
NMR DATA FOR $F^a-SF_4^b-CF^cH^d-CF^eF^f-SO_3Na$

Chemical shifts (ppm from $CFCl_3$ or TMS) and relative areas.					
a	b	c	d	e	f
71.2	53.7	-172.7	6.79	-112.5	-123.5
1.0	4.0	1.0	-	1.1	1.0

Coupling constants (Hz)						
	a	b	c	d	e	f
a	-	n.a.	n.a.	n.a.	n.a.	n.a.
b	147	-	n.a.	n.a.	n.a.	n.a.
c	2.6	n.a.	-	40.6	12.7	16.9
d	n.a.	4.9	41.5	-	n.a.	20.8
e	1.7	15.2	11.8	n.a.	-	266
f	1.7	11.8	17.3	20.3	266	-

MASS SPECTRA

The mass spectra of $SF_5CH_2CH_2SO_3H$, $SF_5CH_2CF_2SO_3H \cdot H_2O$, and $SF_5CHF CF_2SO_3H \cdot H_2O$ are reported in Tables XIV through XVI.

The data are similar for the three compounds, especially in the lower molecular weight fragments. Fragments at M/e values of 127 (SF_5^+), 89 (SF_3^+), 70 (SF_2^+), and 51 (SF^+) provide strong evidence for the presence of the SF_5^- group in

all three acids. The SF_3^+ fragment is the base peak for all three, and none of the three show a molecular ion. The remainder of the fragmentation patterns are consistent with the structures assigned to these compounds.

TABLE XIV
MASS SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$

M/e	Rel. Int.	Type	M/e	Rel.Int.	Type
43.0	11.7	C_2F^+	69.9	6.8	SF_2^+
44.0	3.8	CS^+	79.9	6.3	SO_3^+
45.0	99.5	HCS^+	80.9	17.5	SO_3H^+
46.0	3.3	H_2CS^+	81.9	4.9	CSF_2^+
47.0	72.0	$\text{C}_2\text{H}_4\text{F}^+$	88.9	100.0	SF_3^+
47.9	9.0	SO^+	90.0	4.5	$^{34}\text{SF}_3^+$
51.0	2.7	SF^+	108.9	16.7	$\text{C}_2\text{H}_4\text{SO}_3\text{H}^+$
63.9	9.6	SO_2^+	110.9	3.6	$\text{FSCH}_2\text{CH}_2\text{S}^+$
64.9	63.3	$\text{SO}_2\text{H}^+, \text{H}_2\text{CSF}^+$	126.8	17.0	SF_5^+
66.9	6.8	$\text{SOF}^+, \text{SOH}_3\text{O}^+$	134.8	8.5	$\text{SF}_4\text{C}_2\text{H}_3^+$

TABLE XV
MASS SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
41.0	3.1	C_2OH^+	69.9	8.2	SF_2^+
44.0	8.0	CS^+	79.9	8.4	SO_3^+
45.0	14.6	HCS^+	80.9	16.1	$\text{CH}_2\text{CF}_2\text{OH}^+$
47.9	11.3	SO^+	82.9	92.5	HCSF_2^+
51.0	4.4	SF^+	88.9	100.0	SF_3^+
57.0	4.2	SC_2H^+	90.9	4.1	$^{34}\text{SF}_3^+$
61.0	21.5	HCCFOH^+	126.8	30.1	SF_5^+
63.0	6.5	CSF^+	148.9	10.2	$\text{SF}_5\text{CHCOH}^+$
63.9	50.9	HCSF^+	168.8	3.1	$\text{SF}_5\text{CH}_2\text{CFOH}^+$
64.9	28.2	H_2CSF^+	190.8	94.3	$\text{SF}_5\text{CH}_2\text{CF}_2^+$
66.9	2.9	$\text{SOF}^+, \text{SOH}_3\text{O}^+$	192.8	4.1	$^{34}\text{SF}_5\text{CH}_2\text{CF}_2^+$

TABLE XVI
MASS SPECTRUM OF $\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
43.9	5.2	CS+	69.8	5.5	SF ₂ +
44.9	6.9	HCS+	78.8	8.9	C ₂ F ₂ OH+
47.9	7.4	SO+	79.8	4.5	SO ₃ +
48.9	12.0	SOH+	80.8	14.0	C ₂ F ₃ +, HSO ₃ +
50.9	43.9	SF+	81.8	18.4	CFHCF ₂ +
60.9	6.6	CHCFOH+	82.8	29.1	HCSF ₂ +
62.9	6.2	CHCF ₂ +	88.8	100.0	SF ₃ +
63.8	18.6	SO ₂ +, HFCS+	100.8	25.5	SF ₃ C+
64.8	36.5	HSO ₂ +	126.7	17.4	SF ₅ +
66.8	2.9	SOF+, SOH ₃ O+	190.6	21.8	SF ₅ CHCF ₂ H+

Mass spectral data for $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$, $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$, and $\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{Na}$ are given in Tables XVII to XIX. All three spectra were run using fast atom bombardment in a glycerol matrix, which is the preferred method for ionic, multi-functional molecules.⁴⁵ As with the acids, the three sets of fragmentation patterns are similar, especially at low M/e. All three show many peaks with M/e greater than the calculated molecular weight, including prominent peaks at M+Na+ and 2M+Na+, which are typical for the method being used.⁴⁶ There are also additional peaks at M/e = 43, 57, and 75 which are from the glycerol.^{47,48} Unidentified peaks may

be the result of combinations of salt and glycerol fragments. The peaks indicating the SF_5^- group are not as apparent, as only the SF_3^+ fragment has an appreciable intensity.

TABLE XVII
MASS SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
42.9	9.2	$\text{C}_2\text{H}_3\text{O}^+$	148.6	4.8	$\text{SF}_3\text{CH}_2\text{CH}_2\text{S}^+$
43.9	3.0	CS^+	152.7	7.2	$\text{SF}_5\text{C}_2\text{H}_2^+$
44.9	9.2	HCS^+	154.7	4.4	$\text{SF}_5\text{C}_2\text{H}_4^+$
56.9	8.4	$\text{C}_3\text{H}_5\text{O}^+$	170.8	3.3	$\text{CFHCHSO}_3\text{Na}_2^+$
60.8	4.3	HCSO^+	280.5	75.1	$\text{M}+\text{Na}^+$
62.8	10.2	CSF^+	282.5	7.7	$^{34}\text{S}-\text{M}+\text{Na}^+$
64.8	48.5	CH_2SF^+	322.4	3.5	?
74.8	4.0	$\text{C}_3\text{H}_7\text{O}_2^+$	372.5	6.5	?
88.7	6.6	SF_3^+	383.4	4.1	?
104.7	4.1	HC_2SO_3^+	537.4	18.9	$2\text{M}+\text{Na}^+$
114.7	100.0	CSO_3Na^+	539.52	3.6	?
125.6	12.0	Na_2SO_3^+	579.8	2.6	?
136.7	24.8	$\text{SF}_4\text{C}_2\text{H}_3^+$	798.5	3.2	?

TABLE XVIII
MASS SPECTRUM OF $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
42.9	15.5	$\text{C}_2\text{H}_3\text{O}^+$	136.8	26.7	$\text{SF}_4\text{C}_2\text{H}_3^+$
44.9	10.8	HCS^+	148.7	11.7	$\text{HCCFSO}_3\text{Na}^+$
56.9	17.4	$\text{C}_2\text{H}_5\text{O}^+$	164.7	4.3	$\text{CF}_2\text{HSO}_3\text{Na}^+$
60.9	5.9	HCSO^+	170.8	5.6	SF_5CHCF^+
62.8	17.3	CSF^+	190.7	11.6	$\text{SF}_5\text{CH}_2\text{CF}_2^+$
64.8	100.0	H_2CSF^+	214.8	10.6	$\text{CF}_2\text{HCF}_2\text{SO}_3\text{Na}^+$
74.8	5.8	$\text{C}_3\text{H}_7\text{O}_2^+$	296.6	5.9	317-HF+
88.7	16.6	SF_3^+	316.5	66.2	M+Na+
104.7	6.3	C_2SO_3^+	318.5	6.2	$^{34}\text{S}^+$
106.7	86.8	HC_2SO_3^+	358.5	2.6	?
114.8	68.8	CSO_3Na^+	418.2	2.5	$-\text{SF}_4, 2\text{HF}, \text{SO}_2$
125.7	21.0	Na_2SO_3^+	610.0	3.8	2M+Na+

TABLE XIX
MASS SPECTRUM OF $\text{SF}_5\text{CHF}_2\text{SO}_3\text{Na}$

M/e	Rel. Int.	Type	M/e	Rel. Int.	Type
40.9	2.5	C_2OH^+	114.8	100.0	CSO_3Na^+
42.9	12.3	$\text{C}_2\text{H}_3\text{O}^+$	115.8	7.2	CFHCF_2S^+
43.9	4.4	CS^+	125.7	10.4	Na_2SO_3^+
44.9	18.7	HCS^+	136.8	19.1	$\text{SF}_4\text{C}_2\text{H}_3$
56.9	16.0	$\text{C}_3\text{H}_5\text{O}^+$	156.8	3.9	$\text{CF}_2\text{SO}_2 \cdot \text{C}_3\text{H}_7\text{O}_2^+$
60.9	6.6	HCSO^+	170.8	6.4	$\text{CH}_2\text{CFSO}_3\text{Na}_2^+$
64.8	19.6	H_2CSF^+	188.8	3.7	SF_5CFCF^+
74.8	12.8	$\text{C}_3\text{H}_7\text{O}_2^+$	206.8	13.6	$\text{CF}_2\text{CF}_2\text{SO}_3\text{Na}_2^+$
88.7	5.6	SF_3^+	212.8	2.9	?
92.8	17.6	CFCFS^+	217.7	4.8	$\text{Na}_2\text{SO}_3 \cdot \text{C}_3\text{H}_8\text{O}_3^+$
96.8	4.0	H_2CSO_2^+	334.5	46.3	$\text{M}+\text{Na}^+$
104.7	2.5	C_2SO_3^+	425.0	16.1	?
113.8	3.8	CF_2SO_2^+	645.9	5.3	$2\text{M}+\text{Na}^+$

CHAPTER 4

OTHER REACTIONS

DISCUSSION

This chapter includes reactions that are not a part of the main project. The first of these is the attempted synthesis of $(\text{CF}_3\text{SO}_2)_2\text{CHSO}_3\text{H}$ by SO_3 insertion into the sodium salt $(\text{CF}_3\text{SO}_2)_2\text{CHNa}$.⁴⁹ While the salt synthesis went well, the SO_3 insertion did not, as not only was there no weight gain as expected, but the weight was down slightly, indicating decomposition had occurred.

Sulfonation of the iodide $\text{CF}_3\text{CH}_2\text{I}$ was tried by both the Strecker reaction and sodium sulfite in 50% ethanol. In neither case was there any evidence that a reaction had occurred, possibly because the inductive effect of the CF_3 -group stabilized the C-I bond.

A route to $\text{C}(\text{SCH}_3)_4$ was known,⁵⁰ so the oxidation of $(\text{CH}_3\text{S})_3\text{CH}$, which is commercially available, was attempted to see if the tris sulfonyl chloride would result.⁵¹ Unfortunately, methanesulfonyl chloride was recovered instead.

A new SF_5Br adduct and telomer were synthesized by addition of SF_5Br to $\text{CF}_2=\text{CFBr}$. The procedure was similar to that used for the tri- and tetra- fluoroethylene adducts.

The remainder of this chapter contains the procedure for the reactions mentioned here, as well as the elemental analysis, IR spectra, NMR spectra, and mass spectra for these new compounds.

EXPERIMENTAL

Synthesis of $(\text{CF}_3\text{SO}_2)_2\text{CHNa}$

$(\text{CF}_3\text{SO}_2)_2\text{CH}_2$ (4.00 g, 14.7 mmol) was dissolved in 20 mL of methanol. The solution was neutralized with Na_2CO_3 until bubbling ceased. A total of 0.92 g (8.7 mmol) sodium carbonate was used. The solution was filtered, the solvent was evaporated, and the damp solid was dried on a vacuum line. The crude salt (4.2 g) was recovered, m.p. 255-258°C (dec).

Attempted Synthesis of $(\text{CF}_3\text{SO}_2)_2\text{CHSO}_3\text{Na}$

The Na salt (3.9 g, 13.3 mmol) was transferred to a 100 mL glass reaction vessel. Sulfur trioxide (3.28 g, 41.1 mmol) was added, and the mixture was heated to 85-90°C for a total of 8 hours, after which the unreacted SO_3 was pumped off. Weight gain indicated that the reaction was not complete, so more SO_3 was added (1.40 g additional) and the mixture was reheated to 90°C for 2 days. The vessel was cooled to -196°C, and volatile materials were removed under vacuum. There was no net weight gain, so the reaction was abandoned.

Reaction of $\text{CF}_3\text{CH}_2\text{I}$ with Na_2SO_3

A 150 mL metal reaction vessel containing 12.5 g (99.2 mmol) of Na_2SO_3 , 22.5 g (107 mmol) of $\text{CF}_3\text{CH}_2\text{I}$ and 60 mL of water was put in an oil bath at 125°C for 24 hours with frequent shaking. When the vessel was opened, the reactants were recovered unchanged.

Reaction of $(\text{CH}_3\text{S})_3\text{CH}$ with $\text{Cl}_2/\text{H}_2\text{O}$

Water (40 mL) and $(\text{CH}_3\text{S})_3\text{CH}$ (4.9 g, 31.8 mmol) were added to a 100 mL flask equipped with a thermometer, dry ice/acetone reflux condenser, and a gas inlet tube for Cl_2 . Chlorine was added slowly, until further addition of Cl_2 caused no further reaction. Methylene chloride was added, the layers were separated, and the organic layer was dried with MgSO_4 then distilled under reduced pressure (20 torr). A clear yellow liquid (3.78 g) was collected at $72\text{--}73^\circ\text{C}$, 21 torr. This was found to be $\text{CH}_3\text{SO}_2\text{Cl}$, from the IR spectrum.

Reaction of SF_5Br with $\text{CF}_2=\text{CFBr}$

A 150 mL metal vessel containing 26.45 g (127.8 mmol) of SF_5Br and 45 mmol $\text{CF}_2=\text{CFBr}$ ($V = 1.57\text{ L}$, $P = 1.89\text{ atm}$) was warmed in hot water. The vessel was placed in an oven at 67°C for 51 hours. The contents of the vessel were transferred to a 50 mL roundbottom flask, and allowed to warm to room temperature. Distillation of the mixture yielded $\text{SF}_5\text{CF}_2\text{CFBr}_2$ mixed with other minor components. Preparative gas chromatography of the distillate yielded

22.94 g (62.3 mmol, 48.8% yield) pure $\text{SF}_5\text{CF}_2\text{CFBr}_2$. The reaction vessel was rinsed with acetone, and the rinsings were set aside to dry. The 3.83 g (2.11 mmol, 46.8% yield) solid material that was collected from these rinsings was the telomer $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$.

Reaction of $\text{CF}_3\text{CH}_2\text{I}$ with Na_2SO_3 in 50% ethanol

A 250 mL roundbottom flask containing 24.92 g (118.7 mmol) of $\text{CF}_3\text{CH}_2\text{I}$, 144 mL of 50% ethanol and 15.04 g (119.4 mmol) of Na_2SO_3 was equipped with a Fredrick condenser and a Teflon stir bar. The solution was refluxed for 3 days, then it was cooled. The mixture was transferred to a beaker and the solvent was removed by heating on a hot plate. Final drying was done under vacuum, without heating. A colorless solid (15.82 g) was obtained, but the minor weight gain indicated that little if any reaction had occurred.

ELEMENTAL ANALYSIS

The elemental analyses for $\text{SF}_5\text{CF}_2\text{CFBr}_2$ and $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$ are given below. The data for the monomer correspond to the calculated values closely, while the different chain lengths present in the telomer make matching the found percentages more difficult.

TABLE XX
ELEMENTAL ANALYSIS FOR $\text{SF}_5\text{CF}_2\text{CFBr}_2$ AND $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$

$\text{SF}_5\text{CF}_2\text{CFBr}_2$		Calc.	Found
	C	6.52	6.48
	H	0.0	<0.1
	F	41.3	41.5
	Br	43.47	43.43
	S	8.70	8.59
$\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$			
	C	13.22	13.56
	H	0.0	<0.1
	F	36.6	37.1
	Br	48.39	47.53
	S	1.77	1.85

IR SPECTRA

IR spectral data for $\text{SF}_5\text{CF}_2\text{CFBr}_2$ and $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$ are summarized in Tables XXI and XXII below and the spectra are reproduced in the appendix. Both spectra exhibit a strong SF_5^- vibrational mode in the region 850 to 910 cm^{-1} , and CF stretching frequencies between 1100 and 1210 cm^{-1} . Deformation modes for SF_5^- appear near 600 cm^{-1} for both the monomer and telomer.

TABLE XXI
IR DATA FOR $\text{SF}_5\text{CF}_2\text{CFBr}_2$ (cm^{-1})

peak	desc.	peak	desc.
1208	str	811	weak
1118	str	717	str
1031	weak	686	med
903	v str	643	weak
886	v str	602	str
828	med	575	weak

TABLE XXII
IR DATA FOR $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$ (cm^{-1})

peak	desc.	peak	desc.
1411	med	796	weak
1384	med	763	med
1249	str	712	med
1208	v str	683	med
1183	v str	653	med
1122	vs	636	w
1115	m	599	s
927	s	573	m
884	vs	532	w
841	s	495	w

^{19}F NMR SPECTRA

NMR data for $\text{SF}_5\text{CF}_2\text{CFBr}_2$ and $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$ are given in Tables XXIII and XXIV, and the spectra are reproduced in the appendix. The spectra exhibit an AB_4 pattern for the SF_5 - group, with a 9-line pattern at about 65 ppm, and a doublet with fine structure at about 50 ppm. These are within the expected range for these resonances. The monomer shows a CF resonance at about -86 ppm, while the CF_2 peak is at -78 ppm. The polymer shows a series of broad peaks of different sizes in this region, as would be expected for the many different CF_2 and CF groups present in the telomer.

Table XXIII
NMR DATA FOR $\text{F}^{\text{a}}\text{-SF}_4^{\text{b}}\text{-CF}_2^{\text{c}}\text{-CF}^{\text{d}}\text{Br}_2$

Chemical shifts (from CFCl_3) and relative areas.			
a	b	c	d
64.8	48.4	-86.1	-78.5
1.0	4.1	1.0	2.0
Coupling constants: $J_{\text{ab}} = 152 \text{ Hz}$, $J_{\text{ac}} = 5.4 \text{ Hz}$.			

Table XXIV
NMR DATA FOR $F^a-SF_4^b-(CF_2^c-CF^dBr)_{10}-Br$

Chemical shifts (from $CFCl_3$) and relative areas.			
a	b	c	d
65.1	46.0	*	*
1.0	4.0	*	*

* Broad peaks (with integration height) at 58.2 (14), 71.0 (11), 82.5 (9), 86.2 (5), 93.0 (17), 100.9 (70), 106.2 (53), 129.5 (52), 137.5 (7).

Coupling constant: $J_{ab} = 148$ Hz.

MASS SPECTRUM

The mass spectrum for $SF_5CF_2CFBr_2$ is given in Table XXV below. Since this compound contains bromine, isotope peaks with similar intensity separated by 2 mass units are expected, and observed. If there are two bromine atoms present in a fragment, three peaks in a 1:2:1 ratio, separated by two mass units, are seen.

This compound also contains an SF_5- group, and the mass peaks characteristic of this group are all apparent in this spectrum. A molecular ion peak is observed at 367.9, the calculated molecular weight is 367.88. The base peak is not SF_3^+ as in the other SF_5- containing compounds, but $CF_2CF_2Br^+$ ion. This can be explained by a cyclic bromonium ion structure, which stabilizes this fragment.

TABLE XXV
MASS SPECTRUM OF SF₅CF₂CBr₂

M/e	Rel. Int.	Type	M/e	Rel.Int.	Type
43.0	0.3	C ₂ F ⁺	142.9	2.5	C ₂ F ₂ Br ⁺
44.0	2.0	CS ⁺	159.9	39.2	C ₂ F ₃ Br ⁺
50.0	4.1	CF ₂ ⁺	161.9	38.2	C ₂ F ₃ Br ⁺
51.0	1.6	SF ⁺	169.8	0.3	CBr ₂ ⁺
62.0	1.7	C ₂ F ₂ ⁺	171.8	0.9	CBr ₂ ⁺
69.0	3.0	CF ₃ ⁺	173.8	0.3	CBr ₂ ⁺
69.9	5.9	SF ₂ ⁺	178.9	100.0	C ₂ F ₄ Br ⁺
78.9	2.3	Br ⁺	179.9	2.2	¹³ C ₂ F ₄ Br ⁺
80.9	2.4	Br ⁺	180.9	98.6	C ₂ F ₄ Br ⁺
81.0	2.7	C ₂ F ₃ ⁺	181.9	2.0	¹³ C ₂ F ₄ Br ⁺
89.0	33.1	SF ₃ ⁺	188.8	17.7	CFBr ₂ ⁺
90.9	4.4	CBr ⁺	190.8	33.5	CFBr ₂ ⁺
92.9	4.4	CBr ⁺	192.8	16.3	CFBr ₂ ⁺
100.0	2.3	C ₂ F ₄ ⁺	207.0	0.3	SF ₅ C ₂ F ₃ ⁺
108.0	0.2	SF ₄ ⁺	219.8	1.2	C ₂ F ₂ Br ₂ ⁺
109.9	12.2	CFBr ⁺	221.8	2.5	C ₂ F ₂ Br ₂ ⁺
111.9	12.3	CFBr ⁺	223.8	1.2	C ₂ F ₂ Br ₂ ⁺
121.9	0.8	C ₂ FBr ⁺	238.9	9.6	C ₂ F ₃ Br ₂ ⁺
123.9	1.0	C ₂ FBr ⁺	240.9	18.6	C ₂ F ₃ Br ₂ ⁺

TABLE XXV, cont.

127.0	18.6	SF ₅ ⁺	242.9	9.4	C ₂ F ₃ Br ₂ ⁺
128.9	23.8	CF ₂ Br ⁺	286.9	1.4	M-Br ⁺
130.9	23.1	CF ₂ Br ⁺	288.9	1.4	M-Br ⁺
140.9	2.7	C ₂ F ₂ Br ⁺	367.9	0.3	M ⁺

CHAPTER V

CONCLUSION

The reaction scheme used in this thesis has been shown to have general utility in the synthesis of SF_5 - containing fluoroalkanesulfonic acids from fluoroolefins. The compounds $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$, $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H}$, $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$, $\text{SF}_5\text{CHF}\text{CF}_2\text{SO}_3\text{H}$ and $\text{SF}_5\text{CHF}\text{CF}_2\text{SO}_3\text{Na}$ have been prepared using this method, though the difluoro- acid and salt have not yet been completely purified. It has not yet proved possible to extend this reaction scheme to perfluorinated systems, but there is spectroscopic and other evidence that the acids are being formed for this and the vinyl fluoride. The possibility of a competing carbene mechanism in the sulfite addition can give rise to a mixture of products, but these are usually separated by conversion to the acid and sublimation.

Preliminary studies into the utility of this reaction scheme for other mono- and di- brominated systems have been initiated, though there is much more to be done in this area. The SF_5Br addition to olefins can provide a wide variety of starting materials for these reactions, and this reaction was used to prepare the new compounds $\text{SF}_5\text{CF}_2\text{CFBr}_2$ and $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$.

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APPENDIX

INFRARED SPECTRA	PAGE
$\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$	65
$\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$	66
$\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	67
$\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$	68
$\text{SF}_5\text{CHFCH}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	69
$\text{SF}_5\text{CHFCH}_2\text{SO}_3\text{Na}$	70
$\text{SF}_5\text{CF}_2\text{CFBr}_2$	71
$\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$	72
NMR SPECTRA	
$\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$	73
$\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$	75
$\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	77
$\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$	80
$\text{SF}_5\text{CHFCH}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$	83
$\text{SF}_5\text{CHFCH}_2\text{SO}_3\text{Na}$	87
$\text{SF}_5\text{CF}_2\text{CFBr}_2$	91
$\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$	93

Infrared Spectrum of $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$

Infrared Spectrum of $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$

Infrared Spectrum of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$

Infrared Spectrum of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$

Infrared Spectrum of $\text{SF}_5\text{CHFCl}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$

Infrared Spectrum of $\text{SF}_5\text{CHFCl}_2\text{SO}_3\text{Na}$

Infrared Spectrum of $\text{SF}_5\text{CF}_2\text{CFBr}_2$

Infrared Spectrum of $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$

^1H NMR spectrum of $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$

^{19}F NMR Spectrum of $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ (SF_5 region)

^1H NMR spectrum of $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$

^{19}F NMR Spectrum of $\text{SF}_5\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ (SF_5 region)

^1H NMR spectrum of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$

^{19}F NMR Spectrum of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (SF_5 region)

^{19}F NMR Spectrum of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ (CF_2 region)

^1H NMR spectrum of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$

^{19}F NMR Spectrum of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$ (SF_5 region)

^{19}F NMR Spectrum of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$ (CF_2 region)

^1H NMR spectrum of $\text{SF}_5\text{CHF}_2\text{CF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$

^{19}F NMR Spectrum of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ (SF_5 region)

^{19}F NMR Spectrum of $\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ (CF_2 region)

^{19}F NMR Spectrum of $\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ (CF region)

^1H NMR spectrum of $\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3\text{Na}$

^{19}F NMR Spectrum of $\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{Na}$ (SF_5 region)

^{19}F NMR Spectrum of $\text{SF}_5\text{CHFCF}_2\text{SO}_3\text{Na}$ (CF_2 region)

^{19}F NMR Spectrum of $\text{SF}_5\text{CHF}_2\text{SO}_3\text{Na}$ (CF region)

^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CFBr}_2$ (SF_5 region)

^{19}F NMR Spectrum of $\text{SF}_5\text{CF}_2\text{CFBr}_2$ (CF_2 region)

^{19}F NMR Spectrum of $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$ (SF_5 region)

^{19}F NMR Spectrum of $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$ (CF_2 region)

^{19}F NMR Spectrum of $\text{SF}_5(\text{CF}_2\text{CFBr})_{10}\text{Br}$ (CF region)