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THE PREPARATION OF SOME NOVEL ELECTROLYTES: SYNTHESIS OF PARTIA--ETC(U)
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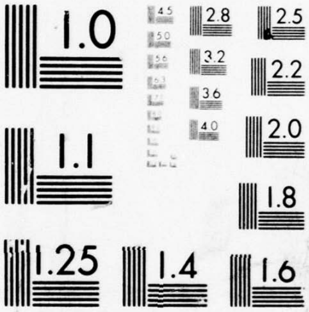

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THE PREPARATION OF SOME NOVEL ELECTROLYTES: SYNTHESIS OF PARTIALLY FLUORINATED ALKANE SULFONIC ACIDS AS POTENTIAL FUEL CELL ELECTROLYTES

First Interim Technical Report

by

Chaiyun Bunyagidj and M. H. Aldridge

March 1978

to

U.S. Army Mobility Equipment Research and
Development Command

Fort Belvoir, Virginia

Prepared by

The American University

Washington, D.C.

Contract No. DAAK-70-C-0047

DA Project/Task Area/Work Unit No. 1L161102AH51 PA 053 EF

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ACKNOWLEDGMENT

This research on the preparation of some novel fuel cell electrolytes has been sponsored by the U.S. Army Mobility Equipment Research and Development Command at Fort Belvoir, Virginia, under Contract No. DAAK70-77-C-0047 with The American University. The work was authorized under DA Project/Task Area/Work Unit No. 1L161102AH51 PA 053 EF.

ABSTRACT

The objective of this research was to prepare some strong acids for evaluation by Fort Belvoir as potential fuel cell electrolytes. The only acid other than phosphoric, H_3PO_4, currently under investigation by Fort Belvoir as a fuel cell electrolyte is TFMSA, $CF_3SO_3H \cdot H_2O$, trifluoromethanesulfonic acid monohydrate aqueous solutions and sodium salt mixtures. 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.

The following acids were prepared:

1. Methanedisulfonic acid,
2. Ethanesulfonic acid,
3. Ethane-1,2-disulfonic acid,
4. Propane-1,3-disulfonic acid,
5. Propane-1,2,3-trisulfonic acid,
6. Chlorotrifluoroethanesulfonic acid, and
7. 1,2,2-trifluoroethane-1,1,2-trisulfonic acid.

Yields were low because of purification difficulties and future work will be concerned with scaling up the preparations.

INTRODUCTION

Improvements in H_3PO_4 fuel cell performance over the last decade have been due principally to engineering refinements. The ultimate performance will depend to a certain degree upon the fuel cell electrolyte and recent studies have indicated that TFMSA monohydrate, $CF_3SO_3H \cdot H_2O$, is far superior to H_3PO_4 from the standpoint of electrode kinetics. The present research is concerned with electrolyte improvement.

The properties desired for the ideal fuel cell electrolyte based on previous studies are:

1. It must be a moderately strong, highly water-soluble acid
2. It must be thermally stable and non-volatile under fuel cell operating conditions
3. It must be non-oxidizing
4. It must be non-hydrolyzable
5. Its solutions must be highly conductive
6. It must be non-corrosive toward cell and electrode materials.

A literature search indicated several probable organic acid electrolytes, with their methods of preparation.

Barick (1, 2) and Coffman (3) prepared $CHF_2CF_2SO_3H$ in a 54% yield from tetrafluoroethylene by the addition of sodium sulfite using benzoyl peroxide as a catalyst. The reaction was carried out in an autogeneous pressure at 80° to 210°. The fluoroalkanesulfonic acid was generated from the sodium salt by sulfuric acid.

Kashar et al. (4) prepared $CF_3CFHCF_2SO_3H$, $C_3H_7CFHCF_2SO_3H$ and $C_5H_{11}CFHCF_2SO_3H$ in good yields from the fluoroolefins and sodium hydrogen sulfite and borax.

Haszeldine (5) using sodium bisulfite and borax, prepared $CFCl_2CF_2$ $CFHCF_2SO_3H$ and other chlorofluoroalkanesulfonic acids.

Another method for the preparation of fluoroalkanesulfonic acids was reported by Haszeldine and Kidd (6), who oxidized $(CF_3S)_2Hg$ with 35% hydrogen peroxide at 105°.

The end product of the oxidation of mercaptans, sulfides, disulfides, sulfoxides, sulfones, etc., is a sulfonic acid. Oxidation by potassium permanganate (7), chromic anhydride (7), bromine water (8), hydrogen peroxide (9), nitric acid (10), and alkalis (11) are reported.

Many halogen compounds react with sodium, potassium or ammonium sulfites to give high yields of sulfonic acid salts (12, 13, 14), i.e., alkylation of alkali sulfites (Strecker).

The first method that we selected for evaluation was Haszeldine's method, the addition of sodium hydrogen sulfite to alkenes in the presence of Borax, because a variety of fluorinated alkenes were available commercially (PCR)*. This procedure required the use of a Parr pressure reaction vessel and we soon encountered difficulties with leaks and corrosion. Other disadvantages to this procedure were the low yields due to the number of byproducts formed. For example,

$$\begin{aligned} 4\ CF_2{=}CFCl + 4\ NaHSO_3 \rightarrow\ & HCF_2CFClSO_3Na\ + \\ & HCF_2COONa + HCFClCF_2SO_3Na\ + \\ & HCFClCOONa + 2\ SO_2 + 4\ HF \end{aligned}$$

The difluoroacetic acid derivative apparently results from the lability of the fluorine atoms which are removed from the α-carbon atom

---

*PCR Research Chemicals, Inc., Gainesville, Florida.

by hydrolysis, i.e.:

$$HCFClCF_2SO_3Na + H_2O \rightarrow [\ HCFClCOSO_3Na + 2\ HF\ ] \rightarrow$$

$$HCFClCOONa + SO_2 + 2\ HF$$

The second method evaluated was Strecker's method involving the reactions of alkyl halides with alkali sulfites, i.e.:

$$RX + Na_2SO_3 \rightarrow RSO_3\ Na + NaX$$

Using this procedure, methane disulfonic acid, ethane sulfonic acid, ethane 1,2-disulfonic acid, propane 1,3-disulfonic acid, propane 1,2,3-trisulfonic acid and 1,2,2-trifluoroethane 1,1,2-trisulfonic acid have been prepared.

Products of organic reactions are seldom of high purity and in order to obtain reliable values for their physical properties it is necessary to purify them. All the classic methods of purification, recrystallization, distillation, ion-exchange, column chromatography, etc., were employed.

EXPERIMENTAL

1. Preparation of Alkanesulfonate Sodium Salt

The first method selected for evaluation was Haszeldine's involving the addition of an aqueous solution of sodium hydrogen sulfite to chlorotrifluoroethylene under pressure. A No. 4521 Parr Stirrer Type Pressure Reaction Apparatus with a 1 liter bomb of Carpenter 20 C b 3 metal was used. All attempts to increase the yields by increasing the temperature, liquifying the alkene gas or using a catalyst were disastrous--resulting in corrosion and leaks in the pressure gauge.

Five different techniques for converting the sodium salts to the corresponding sulfonic acids were evaluated.

The second method selected for evaluation was Strecker's, involving the alkylation of alkali sulfites ($RX + Na_2SO_3 \rightarrow RSO_3Na + NaX$). The yields were considerably better.

A. Scheme I: By Addition of $NaHSO_3$ to Gaseous $ClFC=CF_2$

A Parr pressure reaction vessel was charged with 100 g of sodium hydrogen sulfite, 200 g of distilled water, and evacuated to remove the air. The sodium bisulfite solution was buffered to pH 6 - 7 with Borax. The apparatus was then charged with gaseous chlorotrifluoroethylene so that the pressure was 180 lb/in^2 when the apparatus was heated to 120°C. The reaction proceeded smoothly overnight with constant stirring and the temperature maintained at 120°C. After cooling, the reaction mixture was filtered to remove the sodium fluoride and other unreacted materials. The filtrate was evaporated to dryness over a steam bath and the solid residue was extracted with hot absolute alcohol. The alcoholic extract was filtered and evaporated to dryness on a steam bath to obtain 17.5 g of the chlorotrifluoroethanesulfonic acid sodium salt.

Scheme I Chlorotrifluoroethanesulfonic Sodium Salt

$$ClFC{=}CF_2 + NaHSO_3 \longrightarrow ClFCHCF_2SO_3Na$$

$NaHSO_3 + H_2O$

↓ Buffer to pH 6 - 7 with Borax ($Na_2B_4O_7 \cdot 10\ H_2O$)

introduce into Parr reaction vessel

↓ $ClFC{=}CF_2$ gas is charged into reactor

with pressure

↓ 100 lb/in^2

Reaction proceeds smoothly overnight with a drop in pressure at temperature 120°C

↓

Cool, filter to remove the sodium fluoride and evaporate the filtrate to dryness over a steam bath

↓

Extract solid residue with hot absolute ethanol

↓

Evaporate alcohol extract to dryness over a steam bath to obtain the sodium salts

In an effort to increase the yield this reaction was repeated twice, increasing the temperature each time, but with disastrous results.

Table of Experiments and Products Using Gaseous Alkene

1. $NaHSO_3 + ClFC{=}CF_2 \xrightarrow[\text{with Borax}]{\text{Buffer to pH 6 - 7}} ClFCHCF_2SO_3Na$

   100 g gas 100 lb/in^2

Initial Condition		Final Condition	
Temperature	120°C	Temperature	120°C
Pressure	180 lb/in^2	Pressure	160 lb/in^2
Reaction Time	22 hours		

Yield: white solid, 17.5 g

2. $NaHSO_3 + ClFC{=}CF_2 \xrightarrow[\text{with Borax}]{\text{Buffer to pH 6 - 7}} ClFCHCF_2SO_3Na$

   100 g gas 85 lb/in^2

Initial Condition		Final Condition	
Temperature	170°C	Temperature	170°C
Pressure	240 lb/in^2	Pressure	280 lb/in^2
Reaction Time	19 hours		

Yield: white solid, 0.8 g; unreacted materials, 14.0 g

3. $NaHSO_3 + ClFC{=}CF_2 \xrightarrow[\text{with Borax}]{\text{Buffer to pH 6 - 7}} ClFCHCF_2SO_3Na$

   100 g gas 81 lb/in^2

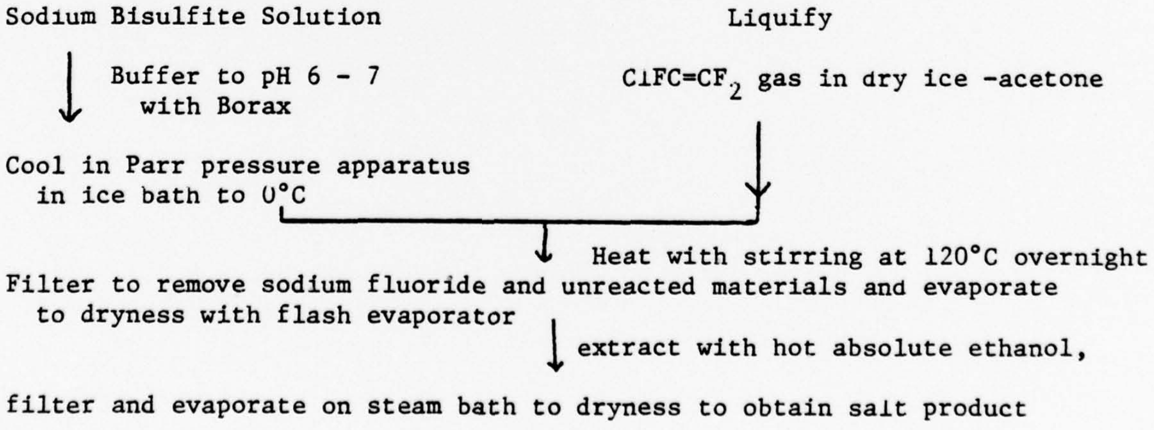
Initial Condition		Final Condition	
Temperature	200°C	Temperature	200°C
Pressure	310 lb/in^2	Pressure	330 lb/in^2
Reaction time	24 hours		

Yield: traces; unreacted solid, 25 g

B. Scheme II: By Addition of Sodium Hydrogen Sulfite to Liquified Chlorotrifluoroethylene

In a modified experiment for preparation of chlorotrifluoroethanesulfonate sodium salt, a solution of 100 g of sodium bisulfite and 200 g of distilled water was introduced into the Parr pressure reaction apparatus. The sodium bisulfite solution was buffered to pH 6 - 7 with Borax. The apparatus was cooled in an ice bath to a temperature of approximately 0°C. Chlorotrifluoroethylene gas was liquified in an acetone dry ice trap and then introduced into the cooled Parr pressure reaction apparatus which was then quickly closed and evacuated to remove the air. The apparatus was left standing to reach room temperature and then slowly heated to a temperature of 120°C. The reaction proceeded smoothly overnight with constant stirring and heating at a temperature of 120°C. The reaction mixture was filtered to remove sodium fluoride and other unreacted materials. The filtrate was evaporated to dryness with a flash evaporator and the solid residue was extracted with hot absolute ethanol. The alcohol extract was filtered and evaporated on a steam bath to obtain chlorotrifluoroethanesulfonate sodium salt.

<u>Scheme II</u>



C. Scheme III: By Addition of Sodium Hydrogen Sulfite to Liquified Chlorotrifluoroethylene in the Presence of Benzoyl Peroxide

A solution of 100 g of sodium bisulfite and 200 g of distilled water was introduced into the Parr pressure reaction apparatus. A sodium bisulfite solution buffered to pH 6 - 7 with Borax was added. Benzoyl peroxide (1 g) was added as a catalyst. The apparatus was tightly closed and evacuated to remove the air. It was then cooled in an acetone-dry ice bath for an hour while chlorotrifluoroethylene gas was being liquified in an acetone-dry ice trap. The liquified gas was then introduced into the apparatus by suction. The apparatus was left standing to reach room temperature, and then heated slowly to a temperature of 120°C. The reaction proceeded smoothly overnight with constant stirring and heating. The reaction mixture was filtered to remove sodium fluoride and other unreacted materials. The filtrate was evaporated to dryness with a flash evaporator and the solid residue was extracted with hot absolute alcohol. The alcohol extract was filtered and evaporated on a steam bath to obtain the chlorotrifluoroethanesulfonate sodium salt.

Table of Experiments Using Liquified Alkene

1. $NaHSO_3 + ClFC = CF_2 \xrightarrow[\text{with Borax}]{\text{buffer to pH 6-7}} ClFCH - CF_2 - SO_3Na$

104 g 116.5 g

Initital Condition

Temp. 120°C

Press. 240 lb/in^2

Reaction Time: 16 hours

Yield white solid 34.5 g

Final Condition

Temp. 120°C

Press. 0 lb/in^2

2. $Na_2SO_3 + ClFC = CF_2 \xrightarrow[\text{pH 7 - 7.5}]{\text{No buffer}} ClFCH - CF_2 - SO_3Na$

100 g 116.5 g

Initial Condition

Temp. 120°C

Press. 20 lb/in^2

Reaction time: 2 hours

Yield only traces

Final Condition

Temp. 120°C

Press. ~ 0 lb/in^2

3. $Na_2SO_3 + ClFC = CF_2 \xrightarrow[\text{No Buffer}]{\text{pH 7. -7-5}} ClFCH - CF_2 - SO_3Na$

100 g 116.5 g

Initial Condition

Temp. 120°C

Press. 40 lb/in^2

Reaction time: 18 hours

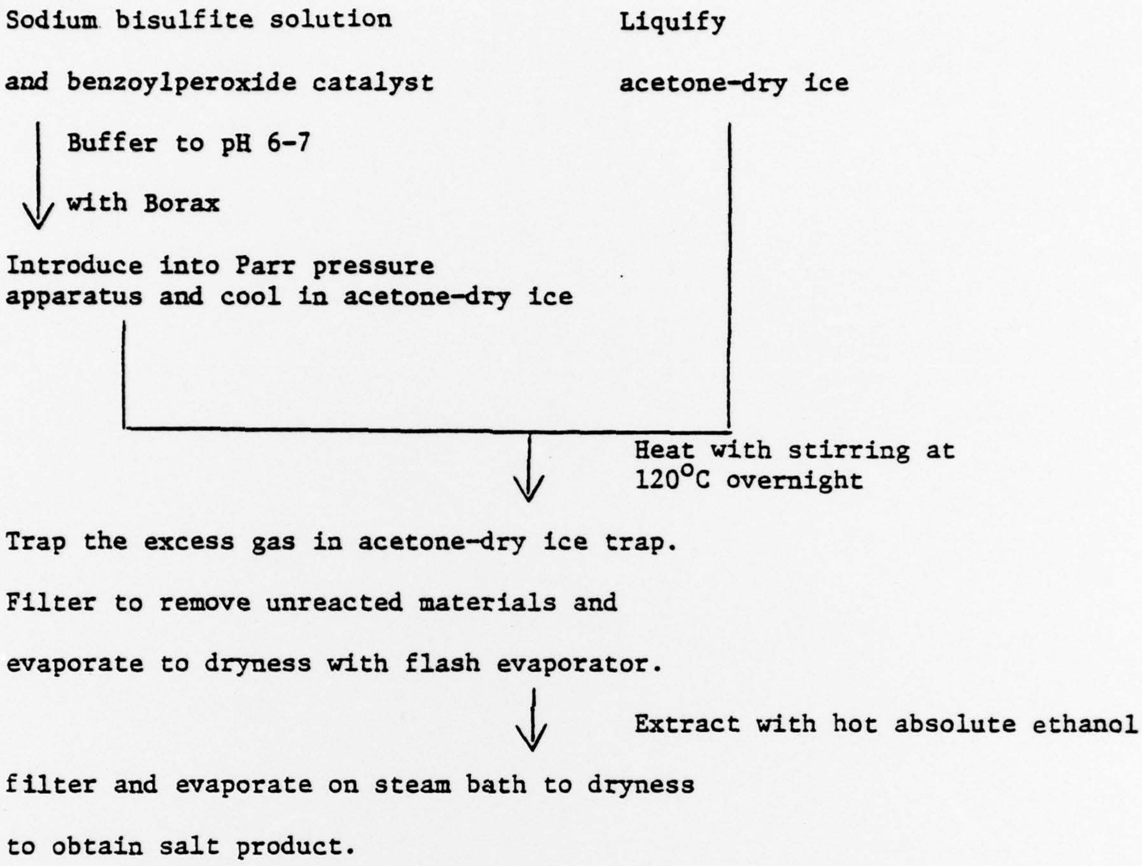
Yield: traces

Final Condition

Temp. 120°C

Press. ~ 30 lb/in^2

Scheme III



Sodium bisulfite solution
and benzoylperoxide catalyst

Buffer to pH 6-7
with Borax

Introduce into Parr pressure
apparatus and cool in acetone-dry ice

Liquify
acetone-dry ice

Heat with stirring at
120°C overnight

Trap the excess gas in acetone-dry ice trap.
Filter to remove unreacted materials and
evaporate to dryness with flash evaporator.

Extract with hot absolute ethanol

filter and evaporate on steam bath to dryness
to obtain salt product.

Table of Experiments and Products Using Modified Liquid Alkene

1. $Na_2SO_3 + ClFC = CF_2 \xrightarrow[\text{1 g}]{\text{Benzoyl peroxide}} ClFCHCF_2 - SO_3Na$

   100 g 116.5 g

Initial Condition

Temp. 120°C

Press. 30 lb/in^2

Final Condition

Temp. 120°C

Press. 0 lb/in^2

Reaction time: 18 hours

Yield: white solid 3 g

2. $NaHSO_3 + ClFC = CF_2 \xrightarrow[\text{Benzoyl peroxide}]{\text{Buffer with Borax}} ClFCH\ CF_2 - SO_3Na$

   100 g 116.5 g

Initial Condition

Temp. 120°C

Press. 480 lb/in^2

Final Condition

Temp. 120°C

Press. 270 lb/in^2

Reaction time: 18 hours

Unreacted materials 6 g.

Excess gas trapped 31 cc.

Yield: white solid 20 g.

3. $NaHSO_3 + ClFC = CF_2 \xrightarrow[\text{Benzoyl peroxide 0.5 g}]{\text{Buffer with Borax}} ClFCH - CF_2 - SO_3Na$

   100 g ~100 ml.

Initial Condition

Temp. 120°C

Press. 520 lb/in^2

Final Condition

Temp. 120°C

Press. ~0 lb/in^2

Unreacted material 6.5 g.

Excess gas trapped: 0 cc. Rxn. time: 24 hours

Yield: white solid 25 g.

4. $$\underset{100\text{g}}{\text{NaHSO}_3} + \underset{80\text{ cc.}}{\text{ClFC} = \text{CF}_2} \xrightarrow[\substack{\text{Benzoyl peroxide}\\ \text{1 gram}}]{\text{Buffer with Borax}} \text{ClFCHCF}_2 - \text{SO}_3\ \text{Na}$$

Initial Condition	Final Condition
Temp. 120°C	Temp. 120°C
Press. 300 lb/in^2	Press. 0 lb/in^2

Reaction Time: 18 hours

Yield: white solid 25.6 g.

2. Conversion of Chlorotrifluoroethanesulfonate Sodium Salt to the Corresponding Sulfonic Acid

A. By Acidification of the Crude Sodium Salt with 35% Sulfuric Acid

After extraction with hot absolute ethanol, 1 g of the crude sulfonate salt was pulverized and acidified with 35% H_2SO_4 under the hood. The colorless gas given off was assumed to be sulfur dioxide. All of the solid dissolved. The pH of the solution was very acidic. It was extracted several times with anhydrous ether and the ethereal layer was dried over anhydrous magnesium sulfate. Evaporation of the ether on a steam bath under the hood resulted in a light brown viscous liquid.

B. By Acidification of the Purified Sodium Salt with 35% Sulfuric Acid

i) Approximately 0.5 g of the pure white solid was pulverized, acidified with 35% H_2SO_4 and then extracted with anhydrous ether several times. The ether layer was collected and dried over anhydrous magnesium sulfate. After evaporation of the ether on a steam bath about 0.5 ml of a viscous brown liquid was obtained.

ii) Approximately 10 g of the white solid was pulverized and acidified with 20 g of 35% H_2SO_4; about half of the salt dissolved leaving a white solid in the acid solution. The acid solution was filtered through a sintered glass funnel to obtain 7.5 g of a solid residue. The filtrate was then extracted with anhydrous ether (100 ml portion, five times). The collected ether layers were dried over anhydrous magnesium sulfate. The ether solution was evaporated on a steam bath to a volume of 3 - 5 ml, and transferred to a small round-bottomed flask for distillation under reduced pressure.

C. By Acidification of the Sodium Salt with p-Toluenesulfonic Acid

Approximately 22.0 g (0.10 mole) of chlorotrifluoroethanesulfonate sodium salt was pulverized and dissolved in 50 ml of super dry ethyl alcohol. Approximately 17.22 g (0.10 mole) of p-toluenesulfonic acid was dissolved in 50 ml of super dry ethyl alcohol. These two solutions were mixed and heated on a steam bath, then filtered hot to remove undissolved materials. The ethyl alcohol was distilled off at atmospheric pressure and the remaining solution transferred to a smaller flask for distillation under reduced pressure.

D. By Conversion of the Sodium Salt to the Ammonium Salt and then Acidification with Hydrogen Chloride

A solution of 3 g of chlorotrifluoroethane sulfonate ammonium salt in 10 ml of water was saturated with hydrogen chloride. The precipitated sodium chloride was filtered off on a sintered glass funnel and the filtrate evaporated to a syrup on a steam bath. This syrup, after drying in the Abderhalden for 2 - 3 days was converted to light brown, hydroscopic crystals of chlorotrifluoroethanesulfonic acid hydrate.

E. By Using a Strong Acid Cation Exchange Technique

Chlorotrifluoroethanesulfonate sodium salt (19 g) was pulverized and dissolved in distilled water. The solution was passed through a glass column (3' x 1") packed with Amberlite IR 120 (H) resin at a very slow rate. The acid solution was collected and the water was removed by using a flash evaporator. The white solid obtained was somewhat hygroscopic and was kept in a desiccator. A very good yield, 90% conversion, was obtained. The product was dried overnight in the Abderhalden.

3. Preparation of Extremely Dry (or Super Dry) Ethyl Alcohol

Method I (Lund and Bjerrum, 1931).

This procedure depends upon the reactions:

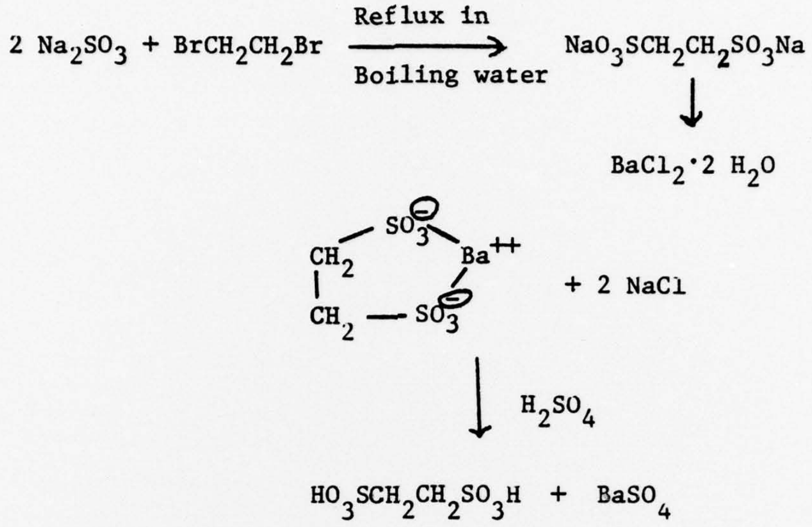
$$Mg + 2\ C_2H_5OH \rightarrow H_2 + Mg(OC_2H_5)_2 \qquad (1)$$

$$Mg(OC_2H_5)_2 + 2\ H_2O \rightarrow Mg(OH)_2 + 2\ C_2H_5OH \qquad (2)$$

Reaction 1 usually proceeds readily provided the magnesium is activated with iodine and the water content does not exceed over 1%. Subsequent interaction between the magnesium ethoxide and water gives the highly insoluble magnesium hydroxide; only a slight excess of magnesium is therefore necessary.

A dry 1.5 or 2 liter round-bottomed flask is fitted with a double surface condenser and a drying tube (the latter may contain either cotton wool or anhydrous $CaCl_2$ between plugs of glass wool). Clean dry magnesium turnings (5 g) and 0.5 g of iodine are placed in the flask, followed by 50 - 75 ml of the $99^+\%$ alcohol (U.S.I. absolutely pure ethyl alcohol U.S.P.). The mixture is warmed until the iodine has disappeared: if a lively evolution of hydrogen does not set in, a further 0.5 g of iodine is added. Heating is continued until all the magnesium is converted into the ethylate. The absolute alcohol (900 ml) is then added and the mixture is refluxed for 30 minutes. The alcohol is distilled off directly into the vessel in which it is to be stored. The purity of the alcohol exceeds 99.95% provided adequate precautions are taken to protect the distillate from atmospheric moisture. The super dry alcohol is exceedingly hygroscopic.

4. Preparation of Ethane 1,2-Disulfonic Acid



Approximately 200 g of sodium sulfite and 650 ml of water were introduced into a 1 liter three-necked flask, equipped with a mechanical stirrer and a reflux condenser. To this rapidly stirred and boiling solution, 150 g of 1,2-dibromoethane (ethylene bromide) was added over a period of two hours. The solution then was refluxed for an hour after the organic layer had disappeared. On cooling the resulting aqueous solution to 5°C, crystals of sodium ethanedisulfonate separated and were filtered off. After a second crop of crystals was removed, the filtrate was evaporated to incipient crystallization, cooled to 0°C and the third crop of crystals separated. The three crops of crystals were combined and recrystallized from water by dissolving in the minimum amount of boiling water required to remove the sodium bromide. The yield of sodium ethanedisulfonate after drying at 140°C amounted to 200 g.

A hot saturated aqueous solution of 100 g of this salt was treated with a hot saturated aqueous solution of 105 g of barium chloride dihydrate. The heavy granular precipitate which separated was filtered from the cooled solution. The barium salt was suspended in water and treated with an equivalent of sulfuric acid and, after filtering off the precipitated barium sulfate on a sintered glass funnel, the filtrate was evaporated to dryness on a steam bath. The residue (about 50 g) was recrystallized from acetic acid containing a small amount (5 - 10%) of acetic anhydride. A yield of 40 - 45 g (41 - 46%) of the ethane 1,2-disulfonic acid dihydrate was obtained.

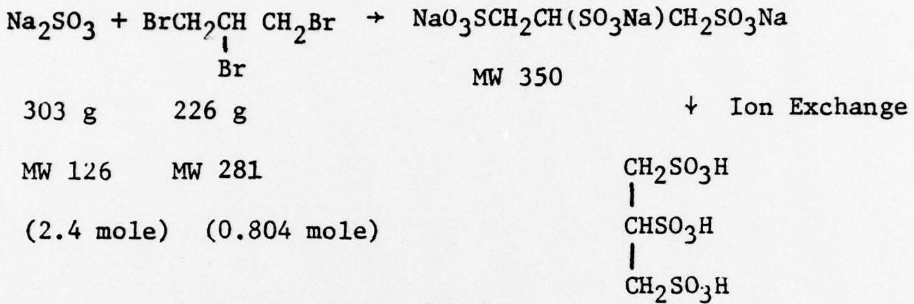
5. Preparation of Propane 1,3-Disulfonic Acid

Approximately 165 g of sodium sulfite and 550 ml of water were introduced into a 1 liter three-necked flask equipped with a mechanical stirrer and a reflux condenser. To this vigorously stirred and boiling solution, 132 g of 1,3-dibromopropane was added slowly over a period of 1 1/2 hours. After another hour of refluxing and stirring, the organic layer disappeared. On cooling to 0°C no salt crystallized from the solution. The solution was again heated to boiling, 88 g of sodium sulfite and 70 g of 1,3-dibromopropane were added, and the mixture was allowed to reflux overnight. After cooling to room temperature, some crystals separated and were filtered off. The filtrate was treated with 10 ml of 40% hydrobromic acid to destroy any remaining sulfite and then evaporated on a steam bath until crystals began to appear in the hot solution. On cooling to room temperature, and further in an ice bath, a second crop of crystals separated and were filtered off. Recrystallization of the disodium propane 1,2-disulfonate from a minimum amount of hot water to remove the sodium bromide resulted in a yield of 85 g.

Approximately 3.32 g of recrystallized propane 1,3-disulfonate sodium salt dissolved in 10 ml of water was saturated with hydrogen chloride and evaporated on a steam bath until a white precipitate appeared.

The precipitate was collected on a sintered glass funnel and the filtrate was evaporated on a steam bath to a syrup. This syrup, after drying in the Abderhalden for 2 to 3 days, was converted to light brown, hygroscopic crystals of propane 1,3-disulfonic acid hydrate.

6. Preparation of Propane 1,2,3-Trisulfonic Acid



$$Na_2SO_3 + BrCH_2\underset{\underset{Br}{|}}{CH}\,CH_2Br \rightarrow NaO_3SCH_2CH(SO_3Na)CH_2SO_3Na \xrightarrow{\text{Ion Exchange}} \begin{array}{c} CH_2SO_3H \\ | \\ CHSO_3H \\ | \\ CH_2SO_3H \end{array}$$

303 g 226 g

MW 126 MW 281 MW 350

(2.4 mole) (0.804 mole)

Theoretical yield: 28150 g

Experimental yield: 175.5 g

% yield: 62.35%

Approximately 200 g of sodium sulfite and 700 ml of water were introduced into a three-necked 1 liter flask equipped with a mechanical stirrer and a reflux condenser. To a boiling solution of sodium sulfite, 150 g of 1,2,3-tribromopropane was added over a period of 1 hour, then refluxed for an additional hour after the organic layer disappeared. The reaction mixture was cooled to 5°C in an ice bath but no crystals of sodium propane trisulfonate separated. The mixture was then reheated and the above process was repeated with the addition of 103 g of sodium sulfite and 76 g of 1,2,3-tribromopropane.

After the addition was completed, the resulting solution was refluxed overnight. On cooling to room temperature no crystals separated but, upon evaporation on a steam bath, crystals began to appear in the hot solution. On cooling to room temperature, the first crop of crystals was filtered off, and further cooling the filtrate in an ice bath resulted in a second crop of crystals. Recrystallization of the sulfonate from a minimum quantity of hot water removed the sodium bromide. After drying in the oven at 100°C overnight, the yield was 175.5 g (62.5%).

Conversion to sulfonic acid

1. HCl gas method.
2. Ion exchange method.
   a) 76.94% conversion of a 10% solution of the sodium salt.
   b) 92% conversion of a 5% solution of the sodium salt.

Propane 1,2,3-trisulfonic acid was obtained by using the strong acid cation exchange resin. Only a 77% conversion was obtained using a 10% solution of the sodium salt but a 92% conversion was obtained with a 5% solution of the sodium salt.

7. Preparation of Methanedisulfonic Acid

$$\underset{\text{MW } 173.86}{CH_2Br_2} + \underset{\text{MW } 126}{Na_2SO_3} + H_2O \rightarrow \underset{\text{MW } 220}{NaO_3SCH_2SO_3Na}$$

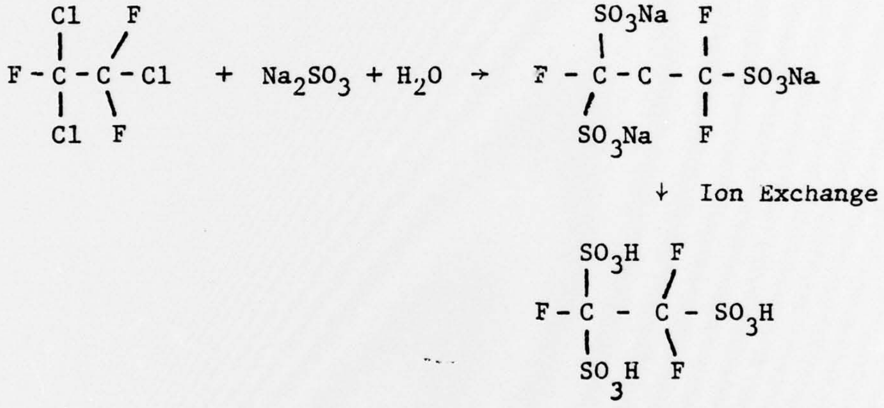
$$\downarrow \text{ ion exchange}$$

$$CH_2(SO_3H)_2$$

Approximately 126 g of sodium sulfite and 600 ml of water were introduced into a 1 liter three-necked flask equipped with a mechanical stirrer and a reflux condenser. Dibromomethane (87 g) was added to a vigorously boiled and stirred sodium sulfite solution over a period of 1 hour. Refluxing with stirring was continued overnight. After cooling to about 0°C disodium methanesulfonate crystals separated and were filtered off. The filtrate was evaporated on the steam bath until crystals started to form. Upon cooling in an ice bath, more crystals separated and a second drop was collected. The two crops of crystals were combined and recrystallized from a minimum amount of hot water. After drying in the oven at 100°C overnight the yield of disodium methanesulfonate was 70 g (63.63%).

Using the cation exchange resin, a conversion of 84% was obtained with a 10% solution of the salt.

8. Preparation of 1,2,2-Trifluoroethane-1,1,2-trisulfonic Acid



$$\mathrm{F-\overset{Cl}{\underset{Cl}{C}}-\overset{F}{\underset{F}{C}}-Cl} + Na_2SO_3 + H_2O \rightarrow \mathrm{F-\overset{SO_3Na}{\underset{SO_3Na}{C}}-C-\overset{F}{\underset{F}{C}}-SO_3Na}$$

$$\downarrow \text{Ion Exchange}$$

$$\mathrm{F-\overset{SO_3H}{\underset{SO_3H}{C}}-\overset{F}{\underset{F}{C}}-SO_3H}$$

Approximately 126 g of sodium sulfite and 300 ml of water were introduced into a three-necked flask equipped with a mechanical stirrer and a reflux condenser. To the vigorously boiling solution, 62.5 g of 1,1,2-trichloro-1,2,2-trifluoroethane was added slowly over a period of one hour. The refluxing was continued for a whole day; upon cooling to 0°C, crystals separated and were filtered off. The filtrate was then evaporated until more crystals appeared and the second crop of crystals was collected after cooling in an ice bath.

The two crops of crystals were combined and recrystallized with a minimum amount of hot water. The salt product was collected and dried in the oven at 100°C overnight. The yield was 69.0 g (53.9%).

Using the cation exchange resin, a conversion of 36.52% was obtained with a 10% solution of the salt.

9. Preparation of Ethanesulfonic Acid

$$\begin{array}{ccccc} CH_3CH_2Br & + & Na_2SO_3 & \rightarrow & CH_3CH_2SO_3Na \\ \text{MW } 108.97 & & \text{MW } 126 & & \\ & & & & \downarrow \text{ Ion Exchange} \\ & & & & CH_3CH_2SO_3H \end{array}$$

Approximately 73 g of sodium sulfite and 375 ml of water were introduced into a three-necked flask equipped with a mechanical stirrer and a reflux condenser. To the vigorously boiling sodium sulfite solution, 55 g of bromoethane was added slowly over a period of 1 hour. The refluxing was continued with stirring overnight; upon cooling to room temperature no crystals separated. The solution was evaporated on a steam bath until crystals appeared. The solution was then cooled in an ice bath and the crystals collected with suction filtration; this was repeated for the second crop. The two crops of crystals were combined and recrystallized from the minimum amount of hot water. After drying in the oven at 100°C overnight sodium ethanesulfonate, 72 g, was obtained (over 90% yield).

Conclusions:

Since the alkanesulfonate sodium salts are so difficult to purify efforts should be directed toward finding a better method of preparation for the alkanesulfonic acids.

Future work:

Future work will be concerned with an evaluation of the methods involving the oxidation of thiols (RSH) under acidic conditions.

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