

A comparative study of the electrochemical fluorination (ECF) of 1,*n*-alkanebis(sulfonylfluorides) (*n* = 1–3)

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Abstract

Synthetic methods for the preparation of α,ω -alkanebis(sulfonylfluorides) and their electrochemical fluorination (ECF) are described in detail. Factors affecting the yield of the perfluoro- α,ω -alkanebis(sulfonylfluorides) are also discussed. Spectral data (^{13}C and ^{19}F NMR and mass spectra) and other hitherto unknown physical properties of difluoromethanebis(sulfonylfluoride) (1), 1,1,2,2-tetrafluoroethane-1,2-bis(sulfonylfluoride) (2) and 1,1,2,2,3,3-hexafluoropropane-1,3-bis(sulfonylfluoride) (3) are measured and compared. © Elsevier Science S.A.

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1. Introduction

Perfluoro- α,ω -alkanedisulfonic acids and their derivatives have received considerable attention in recent years because of their application as fuel cell electrolytes [1,2], polymerization catalysts [3,4], etc. Syntheses of the precursors of perfluorodisulfonic acids, namely perfluorobis(sulfonylfluorides), are mainly carried out by electrochemical fluorination (ECF) [5,6] of the corresponding α,ω -alkanebis(sulfonylfluorides). However, difluoromethanebis(sulfonylfluoride) (1) has been prepared by both chemical [7,8] and electrochemical [9–11] methods from methanebis(sulfonylfluoride) (4). Although the ECF of the α,ω -alkanebis(sulfonylfluorides) 5 and 6 has been reported [1,12,13], no details have been given for 1,2-ethanebis(sulfonylfluoride) (5) and the perfluorinated homolog 2 [1].

In general, the methods of preparation of the α,ω -alkanebis(sulfonylfluorides) and their ECF appear to be the same. However, the exact experimental conditions differ from one compound to another depending on the solubility of the sulfonylfluoride in anhydrous hydrogen fluoride and other factors.

The objectives of this work are to compare the ECF of α,ω -alkanebis(sulfonylfluorides) and the physical properties

(^{13}C and ^{19}F NMR, IR, mass spectra) of perfluoro- α,ω -alkanebis(sulfonylfluorides) containing one to three carbon atoms.

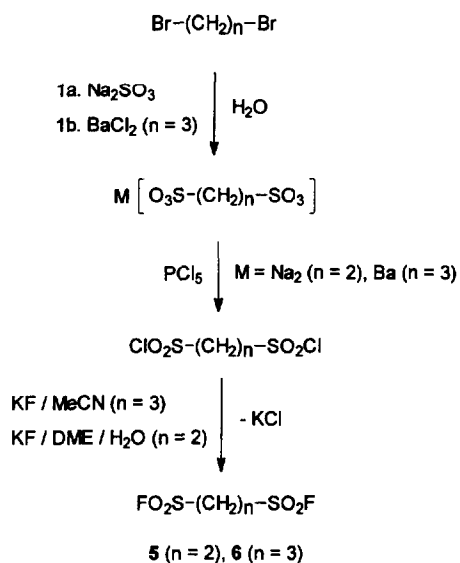
2. Results and discussion

The general methods of preparation of α,ω -alkanebis(sulfonylfluorides) are described in Refs. [13,14]. The preparation of 1,2-ethanebis(sulfonylfluoride) (5) and 1,3-propanebis(sulfonylfluoride) (6) differs from the preparation of the corresponding methanebis(sulfonylfluoride) (4). The synthesis of the α,ω -alkanebis(sulfonylfluorides) 5 and 6 essentially consists of three steps starting from the corresponding dibromoalkanes (Scheme 1).

In the first chemical step using the Strecker reaction [15], involving the synthesis of alkane disulfonates, the sodium salt of propane disulfonic acid appears to be significantly more soluble in cold water than does di-sodium-1,2-ethane-disulfonate, which is nearly insoluble in cold water. Hence propane disulfonate is precipitated as a barium salt from aqueous solution to separate it from sodium bromide.

Conversion of the alkane sulfonates to the sulfonylchlorides (second step) is quite easy to handle. In the last step, the nucleophilic chloride to fluoride exchange reaction also exhibits certain differences between the ethane and propane systems. Fluoride exchange under conventional conditions using potassium fluoride in acetonitrile at 75–80 °C proceeds

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Scheme 1. Preparation of α,ω -alkanebis(sulfonylfluorides) **5** and **6**.

smoothly for 1,3-propanebis(sulfonylfluoride) (**6**) with 80% yield. However, very little conversion yield of 1,2-ethanebis(sulfonylfluoride) (less than 5%) is achieved under the same conditions, and gas evolution, probably due to the decomposition of the reactant molecule, is observed. Hence for the synthesis of 1,2-ethanebis(sulfonylfluoride) (**5**), a biphasic reaction medium, using potassium fluoride–water solution and dimethoxyethane (DME) as solvent for the sulfonylchloride at significantly lower temperature (10 °C), was employed. Even under these conditions, the conversion efficiency is only around 45%. This exceptional situation of 1,2-ethanebis(sulfonylfluoride) (**5**) can also be shown by comparing the ^1H and ^{19}F NMR spectra of the sulfonylfluorides **4–6**. The methane (**4**) and propane (**6**) spectra are easy to interpret, whereas the ethane (**5**) spectrum is more complicated [14].

Table 2

Physical data of perfluoro-1,*n*-alkanebis(sulfonylfluorides) ($n=1-3$) (^{13}C (75.5 MHz) and ^{19}F (75.4 MHz) NMR in CD_3CN , 25% w/w)

Physical data	$n=1$	$n=2$	$n=3$
Molecular weight (g mol^{-1})	216.12	266.13	316.14
Density at 20 °C (g ml^{-1})	1.712	1.747	1.775
Melting point (°C)	-93	-64	-75
Melting enthalpy (kJ mol^{-1})	12.4	9.1	13.5
Boiling point (°C)	58	80	108
Viscosity at 20 °C (mPa s)	0.90	1.20	1.49
Refractive index n	1.3298	1.3278	1.3261
$\delta^{13}\text{C}$ NMR (ppm)	117.17 (tt) $^1J_{\text{CF}}=332.5$ Hz $^2J_{\text{CF}}=41.6$ Hz	118.56 (tdt) $^1J_{\text{CF}}=301.2$ Hz $^2J_{\text{CF}}=38.6$ Hz $^2J_{\text{CF}}=34.7$ Hz	119.32 (tqa) $^1J_{\text{CF}}=306.0$ Hz $^2J_{\text{CF}}=37.4$ Hz
$\delta^{19}\text{F}$ NMR (ppm)	47.64 (t, 6.7 Hz) -96.82 (t, 6.7 Hz)	48.81 (qi, 7.5 Hz) -105.97 (t, 7.1 Hz)	48.04 (m) -106.53 (m) -117.58 (m)

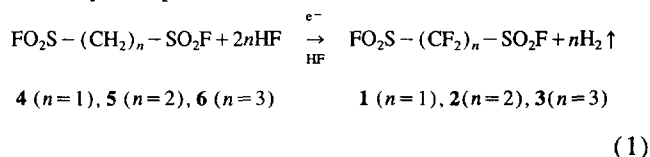
Table 1

Results of the ECF of 1,*n*-alkanebis(sulfonylfluorides) ($n=1-3$) (total amount of starting material added, 200 g)

Experimental parameters	$n=1$	$n=2$	$n=3$
Concentration of starting material (% w/w)	20	5	15
Temperature of the cell (°C)	0	10	0
Current density (A dm^{-2})	0.80	0.50	0.75
Yield (g)	180	134	179
Yield (%)	75	49	59
Current yield (%)	60	39	47

In the case of methanebis(sulfonylfluoride), only two steps are necessary. The preparation of the chloride [16] and the corresponding fluoride **1** has been described previously [11].

The preparation of the perfluorinated sulfonylfluorides **1–3** may be represented as follows



The results of ECF are given in Table 1.

The solubility of 1,2-ethanebis(sulfonylfluoride) (**5**) in anhydrous hydrogen fluoride is considerably lower than that of the other sulfonylfluorides **4** and **6**. Hence, for the ECF process itself, it is not possible to start with a high concentration of reactant for 1,2-ethanebis(sulfonylfluoride) (**5**). Even for a 5% reactant concentration, the cell temperature must be raised to 10 °C. Under these conditions, the reactant slowly adsorbs on the nickel anode [17], and the thin insulating film formed during ECF inhibits the electrode process and decreases the current of the cell. This film is easily observed after the completion of the ECF operation. The solubility problem leads to a poor overall yield of the ECF

product in the case of 1,2-ethanebis(sulfonylfluoride) (5) when compared with the other compounds (Table 1).

The physical properties of the perfluorinated α,ω -alkanebis(sulfonylfluorides) 1–3 are summarized in Table 2.

For the perfluorinated α,ω -alkanebis(sulfonylfluorides) 1–3, most of the physical properties (except the NMR data) can be predicted from a knowledge of the data for the perfluorinated methanebis(sulfonylfluoride) (1) and ethanebis(sulfonylfluoride) (2). For example, the differences in viscosity are nearly the same at 0.30 mPa s (20 °C). The only exceptions are the melting point and melting enthalpy of 1,1,2,2-tetrafluoroethanebis(sulfonylfluoride) (2). The reason may be the higher symmetry of the ethane system 2 compared with 1 and 3.

Comparing the NMR data, the methanesulfonylfluoride 1 plays a special role. In ^{13}C NMR, very large coupling constants $^1J_{\text{CF}}$ and $^2J_{\text{CF}}$ exist, implying a stronger interaction within this molecule compared with the other sulfonylfluorides 2 and 3. The ^{19}F NMR spectrum of the perfluorinated ethanesulfonylfluoride 2 is very easy to understand, in contrast with the complicated fluorine spectrum of the ethane sulfonylfluoride 5 reported previously [14].

3. Experimental details

3.1. Apparatus

The ECF cell and the techniques used have been described previously [1,6,18].

3.2. Analytical procedures

IR spectra were recorded from 4000 to 225 cm^{-1} on a Nicolet 20 DXB instrument. NMR spectra were taken on Bruker WP 80 SY (80.1 MHz ^1H , 75.4 MHz ^{19}F) and Bruker WM 300 (300.1 MHz ^1H , 64.5 MHz ^{13}C) instruments in acetonitrile- d_3 (^{13}C and ^{19}F) and benzene- d_6 with tetramethylsilane (TMS) (^1H) and CD_3CN (^{13}C) as internal standard and C_6F_6 (^{19}F) as external standard. Mass spectral data were determined with a Varian MAT 311A (EI, 70 eV) and an AMD Intektra DP10 V 0.86 data system. Elemental analysis was performed with an elemental analyzer from Carlo Erba (Carlo Erba, model 1106).

3.3. Chemicals

Methanebis(sulfonylfluoride) (4) ($d^{25\text{ °C}} = 1.84 \text{ g ml}^{-1}$, m.p. -10 °C , b.p. $86\text{--}87\text{ °C}/14\text{ Torr}$) was prepared as described previously [11].

3.4. Preparation of 1,2-ethanebis(sulfonylfluoride) (5)

To a cold (10 °C) solution of crude 1,2-ethanebis(sulfonylchloride) (227 g) [19] in 250 ml of DME, potassium fluoride (122 g) in 250 ml of water was added

slowly. Throughout the addition of potassium fluoride the reaction temperature should be kept around 15 °C. After warming the suspension to room temperature, 75 ml of diethylether and 300 ml of water were added to the reaction mixture. The organic phase was separated and the aqueous phases were extracted three times with diethylether. The combined organic phases were dried using anhydrous sodium sulfate and filtered. The light yellow crude product obtained after evaporation of the organic solvent was dissolved in 200 ml of toluene and refluxed with activated charcoal for at least 1 h. After filtration of the hot toluene solution, the filtrate was allowed to cool to 0 °C with stirring to obtain very tiny crystals. Colourless 1,2-ethanebis(sulfonylfluoride) (5) was filtered and dried in vacuum.

Yield: 87 g (45%); m.p.: 74 °C. ^1H NMR (CD_3CN , 80.1 MHz, 39% w/w) δ : 4.19 (m) [14]. ^{13}C NMR (CD_3CN , 75.5 MHz, 39% w/w) δ : 45.38 (d, $^2J_{\text{CF}} = 20.3\text{ Hz}$). ^{19}F NMR (CD_3CN , 75.4 MHz, 39% w/w) δ : 57.15 (m) [14]. IR (KBr) $\tilde{\nu}$: 3005m, 2953m, 1422sst, 1407sst, 1261st, 1217st, 1194sst, 858st, 817st, 799st, 758st, 725st, 527st, 504m, 483m. MS (EI, 70 eV, 30 °C) m/e : 194 (2%, M^+), 175 (47%, $\text{M}^+ - \text{F}$), 111 (100%, $\text{M}^+ - \text{SO}_2\text{F}$), 67 (83%, SO_2F^+) and other fragments.

3.5. Preparation of 1,3-propanebis(sulfonylfluoride) (6)

3.5.1. Barium-1,3-propanedisulfonate

To a suspension of sodium sulfite (252 g) in 600 ml of water, 202 g of 1,3-dibromopropane was added with constant stirring. This mixture was refluxed until it formed a homogeneous solution (4–5 h). A warm aqueous barium chloride dihydrate solution (244 g in 400 ml of water) was added to the hot solution. A white precipitate of barium-1,3-propanedisulfonate was formed and was allowed to settle at room temperature; it was filtered and dried at 140 °C for about 24 h.

Yield: 251 g (80%). $\text{C}_3\text{H}_6\text{BaO}_6\text{S}_2$ (339.53); calculated: C, 10.61%; H, 1.78%; found: C, 10.24%; H, 1.98%.

3.5.2. 1,3-Propanebis(sulfonylchloride)

Powdered barium-1,3-propanedisulfonate (340 g) and fresh powdered phosphorus pentachloride (458 g) were heated in a 1 l flask under refluxing conditions until homogeneous (105–110 °C, 3 h). This mixture was allowed to cool to room temperature with stirring. The contents of the flask were poured carefully into a beaker containing approximately 1.5 kg of ice. An oily layer separated out and crystallized. The solid crude 1,3-propanebis(sulfonylchloride) was decanted from the aqueous barium phosphate water suspension and washed several times with cold water.

Yield: 171 g (71%); m.p.: 48 °C [20]. ^1H NMR (C_6D_6 , TMS, 80.1 MHz) δ : 2.17 (q, $^3J_{\text{HH}} = 7.0\text{ Hz}$, 2H), 3.17 (t, $^3J_{\text{HH}} = 7.0\text{ Hz}$, 4H).

3.5.3. 1,3-Propanebis(sulfonylfluoride) (6)

To a stirred solution of crude 1,3-propanebis(sulfonylchloride) (241 g) in 250 ml of acetonitrile, potassium fluoride (122 g) was added slowly. This suspension was refluxed at 80 °C for about 1 h. After cooling to room temperature, the suspension was filtered. A yellow oil was formed after evaporation of the acetonitrile. This oil was recrystallized in the same manner as described for 1,2-ethanebis(sulfonylfluoride) (6).

Yield: 167 g (80%); m.p.: 33–34 °C. ¹H NMR (CD₃CN, 300.1 MHz, 27% w/w) δ: 2.51 (q, ³J_{HH} = 7.5 Hz, 2H), 3.78 (dt, ³J_{HH} = 7.4 Hz, ³J_{HF} = 5.8 Hz, 4H). ¹³C NMR (CD₃CN, 75.5 MHz, 27% w/w) δ: 19.16, 48.85 (d, ²J_{CF} = 17.7 Hz). ¹⁹F NMR (CD₃CN, 75.4 MHz, 27% w/w) δ: 54.27 (t, ³J_{FF} = 5.5 Hz). MS (EI, 70 eV, 50 °C) *m/e*: 208 (0.2%, M⁺), 189 (0.5%, M⁺ – F), 125 (10%, M⁺ – SO₂F), 111 (5%, M⁺ – CH₂SO₂F), 97 (4%, M⁺ – CH₂CH₂SO₂F), 67 (17%, SOF⁺), 41 (100%) and other fragments.

3.6. ECF of α,ω-alkanebis(sulfonylfluorides)

Anhydrous hydrogen fluoride (200 g) was introduced into the ECF cell (volume, 280 ml) and dried for about 30 h by passing a current to remove the moisture and to condition the Ni electrodes. A cell voltage of 4.5–4.8 V was maintained for this drying process. The temperature of the cell was held at 0 °C in the case of **1** and **3** and 10 °C in the case of the ethane compound **2**. The temperature of the condenser was maintained at –30 °C in all the experiments.

In the case of methanebis(sulfonylfluoride) (**4**), 30 g of liquid sulfonylfluoride was added directly to the cell. For ethane-1,3-bis(sulfonylfluoride) (**5**) and propane-1,3-bis(sulfonylfluoride) (**6**), 5% and 15 wt.% solutions respectively of the sulfonylfluorides in anhydrous hydrogen fluoride were transferred into the cell. The solubility of 1,2-ethanebis(sulfonylfluoride) is very poor in anhydrous hydrogen fluoride, even at a higher temperature of 10 °C.

Electrolysis was carried out under galvanostatic conditions. The cell voltage was maintained between 4.8 and 5.3 V. Subsequent addition of the starting material was performed after passing 120%–130% of theoretical current. The perfluoro compound formed during ECF was removed periodically through the bottom valve of the ECF cell. The electrofluorination was stopped after nearly 1 mol of compound had been electrofluorinated. The perfluoroalkanebis(sulfonylfluorides) obtained were separated from the hydrogen fluoride phase, washed with cold water, 2% sodium hydrogen carbonate solution and again with water and finally dried using anhydrous sodium sulfate. After filtration, the clear and colourless liquid was distilled.

The results of ECF of α,ω-alkanebis(sulfonylfluorides) are given in Table 1. Physical data are given in Table 2, except for the mass spectra and IR data.

3.6.1. Difluoromethanebis(sulfonylfluoride) (1)

IR (KBr) $\tilde{\nu}$: 1471sst, 1259m, 1236st, 1213m, 1202m, 1153st, 956s, 835st, 807st.

MS (EI, 70 eV, 116 °C) *m/e*: 133 (16%, CF₂SO₂F⁺), 83 (34%, SO₂F⁺), 69 (18%, CF₃⁺), 67 (100%, SOF⁺), 64 (21%, SO₂⁺), 50 (4%, CF₂⁺), 48 (17%, SO⁺) and other fragments.

3.6.2. 1,1,2,2-Tetrafluoroethane-1,2-bis(sulfonylfluoride) (2)

IR (KBr) $\tilde{\nu}$: 1470sst, 1244sst, 1212sst, 1146sst, 878m, 825st, 801st, 780st, 767m.

MS (EI, 70 eV, 116 °C) *m/e*: 133 (47%, CF₂SO₂F⁺), 119 (53%, C₂F₅⁺), 100 (50%, C₂F₄⁺), 83 (7%, SO₂F⁺), 69 (49%, CF₃⁺), 67 (100%, SOF⁺), 64 (9%, SO₂⁺), 50 (8%, CF₂⁺), 48 (20%, SO⁺) and other fragments.

3.6.3. 1,1,2,2,3,3-Hexafluoropropane-1,3-bis(sulfonylfluoride) (3)

IR (KBr) $\tilde{\nu}$: 1468sst, 1245sst, 1220sst, 1149sst, 843st, 820st, 789m, 745m.

MS (EI, 70 eV, 116 °C) *m/e*: 169 (10%, C₃F₇⁺), 133 (2%, CF₂SO₂F⁺), 119 (30%, C₂F₅⁺), 100 (24%, C₂F₄⁺), 83 (2%, SO₂F⁺), 69 (52%, CF₃⁺), 67 (100%, SOF⁺), 64 (6%, SO₂⁺), 50 (1%, CF₂⁺), 48 (2%, SO⁺) and other fragments.

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