## ORIGINAL PAPER

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# Electrochemical synthesis of polyfluorinated compounds with functional groups

**Abstract** The electrochemical fluorination of alkane-disulfonyl fluorides, alkanesulfonyl amides and alkanedisulfonyl amides is described. Detailed analysis of the products and the electrolyte and new information on higher nickel fluorides have led to a new insight into the mechanism of electrochemical fluorination.

**Key words** Electrochemical fluorination · Anhydrous hydrogen fluoride · Perfluoroalkanesulfonyl fluorides Perfluoroalkanesulfonyl dimethylamides

## Introduction

Electrolytical methods play an important role in the preparation of the title compounds. With increasing degree of fluorine substitution the progress of fluorination slows down or is totally stopped. Only a few methods of producing highly fluorinated or perfluorinated compounds are available. Among them, the Simons process of electrochemical fluorination [1, 2] plays a key role. Its main advantage is perfluorination of the starting material with preservation of functional groups. For organic compounds the term "perfluorination" means that all hydrogen bonded to carbon is replaced by fluorine. Thus, carboxylic acids and sulfonic acids, when used in the Simons process, give perfluoro carboxylic acids and sulfonic acid fluorides respectively. Much confusion has been caused by the use of unclear nomenclature as shown in the following table, since the term "electrofluorination" is used for the three different procedures without further explanation.

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## Experimental details

The electrochemical cell, its instrumentation and the cell operating procedure have been described elsewhere [2]. Special details of the electrochemical fluorination of the compounds described in this text and of identification procedures are given in [9, 10].

Only electrochemical reactions in anhydrous hydrogen fluoride on nickel anodes lead to poly- and perfluorinated functional compounds. The reactions are performed in undivided cells with current densities of 0.2–5.5 $A/dm^2$. The chemical properties of the electrolyte restrict the number of starting materials. Only a few functional groups are stable against substitution in aHF (anhydrous hydrogen fluoride).

Aliphatic amines, carboxylic and sulfonic acids are the most commonly used starting materials. Their main products are perfluorinated amines, carboxylic acid fluorides and sulfonic acid fluorides respectively, with ideally poly- or perfluorinated aliphatic radicals of identical chain length.

## Results

Our research in this field has been focussed on three new fields of electrochemical fluorination.

1. Preparation of perfluoroalkane-α, ω-disulfonyl difluorides
2. Behaviour of alkanesulfonyl amides towards electrochemical fluorination
3. Semifluorinated starting materials for electrochemical fluorination.

α,ω-Perfluoroalkane disulfonyl difluorides. $FSO_2(CF_2)_n SO_2F$ (n = 1, 2...)

The synthesis of these compounds via electrochemical fluorination depends on the availability of the unfluorinated starting materials.
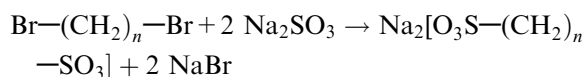
Whereas $FSO_2CH_2SO_2F$ is readily available from the reaction of acetic acid with $POCl_3/ClSO_3H$ [3, 4] to give $ClSO_2(CH_2)SO_2Cl$ followed by reaction with $KHF_2$,

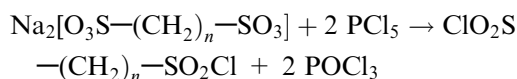**Table 1** Electrolyte systems for electrochemical fluorinations

| Procedure | Electrolyte | Temperature | Anode | Potential |
|---|---|---|---|---|
| Electrofluorination: Simons process of electrochemical perfluorination | anhydrous $(HF)_x$ | $-10$ to $+20$ °C | Ni | 5–7 V |
| Molten salt electrofluorination | $NH_4F \cdot HF$ or $KF \cdot 2HF$ | 100 °C | C porous | 5–7 V |
| Electrofluorination in polar solvents (electrochemical fluorination) | $CH_3COOH/KF \cdot HF$ $HF/BF_3$ $[(C_2H_5)_4N]F \cdot 3HF/CH_3CN$ $AgF/CH_3CN$ $[(C_2H_5)_3NH]SiF_6/CH_3CN$ | 20 to $+50$ °C | Pt | up to 50 V |

compounds with $n > 2$ are synthesized in a somewhat different way by a combination of known procedures. Compounds $FSO_2(CH_2)_nSO_2F$ with $n = 1,3,4, ...$ are easily accessible to electrochemical fluorination. In the case of $n = 2$ the situation is somewhat different, because the solubility of this compound in aHF is surprisingly low. The resulting perfluoroalkanedisulfonyl difluorides are stable liquids insoluble in aHF, and are thus isolated from the bottom of the electrolysis cell.
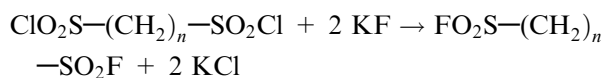
### Disodiumalkane-1,n-disulfonates

$$Br—(CH_2)_n—Br + 2\ Na_2SO_3 \rightarrow Na_2[O_3S—(CH_2)_n—SO_3] + 2\ NaBr$$

### Alkane-1,n-disulfonyl dichlorides

$$Na_2[O_3S—(CH_2)_n—SO_3] + 2\ PCl_5 \rightarrow ClO_2S—(CH_2)_n—SO_2Cl + 2\ POCl_3$$

### Alkane-1,n-disulfonyl difluorides

$$ClO_2S—(CH_2)_n—SO_2Cl + 2\ KF \rightarrow FO_2S—(CH_2)_n—SO_2F + 2\ KCl$$

**Scheme 1** Preparation of perfluoroalkane-1,n-disulfonyl difluorides

They can be converted by alkaline hydrolysis into their alkali or alkaline earth salts, and these on treatment with strongly acidic ion exchange resins into the corresponding perfluoroalkanedisulfonic acids and other derivatives as shown in Scheme 2.

### Behaviour of alkanesulfonylamides towards electrochemical fluorination

Difficulties caused by poor solubilities etc. of some of the starting sulfonyl fluorides prompted us to investigate the corresponding amides as starting materials. They are stable in aHF solution, but in the course of electrolysis fission of S—N bonds occurs quantitatively and, as a result of electrochemical fluorination, $NF_3$ and perfluoroalkanesulfonyl fluorides are formed in comparable quantities and yields [5] based on sulfonyl fluorides. Preliminary experiments with methanesulfonyl bistrimethylamide gave somewhat similar results. The solution of $CH_3SO_2N(CH_3)_2$ is stable in aHF, but, on electrolysis, quantitative decomposition occurs, giving $SO_2F_2$, $CF_4$, $NF_3$ etc. This has been the subject of further investigation.

### Semifluorinated materials for electrochemical fluorination

$CF_3SO_2N(CH_3)_3$ was chosen as the first starting compound. This substance, too, is stable indefinitely in aHF. Under conditions of electrochemical fluorination, however, the perfluorinated product $CF_3SO_2N(CF_3)_2$ is formed in good yield. Moreover, very interesting hydrogen-containing polyfluorinated compounds are also formed:

The overall yield of these products (ca. 60.7%) is reduced by the production of fission products such as $CF_3SO_2F$, $FSO_2N(CF_3)_2$, $FN(CF_3)_2$, $CF_4$ and $SO_2F_2$.

**Table 2** Physical properties of Perfluoroalkan-α,ω-disulfonyl difluorides

| | b.p. [°C] | Current yield [%] |
|---|---|---|
| Perfluoromethanedisulfonyl difluoride | 58 | 60 |
| Perfluoroethane-1,2-disulfonyl difluoride | 80 | 39 |
| Perfluoropropane-1,3-disulfonyl difluoride | 108 | 47 |
| Perfluorobutane-1,4-disulfonyl difluoride | 120 | 21 |
| Perfluoropentane-1,5-disulfonyl difluoride | 143 | 25 |

**Scheme 2** Survey of new reactions of perfluoro alkane disulfonic acids and their derivatives ($n = 3$ to $5$ if not otherwise stated)

$M_2[O_3S-(CF_2)_n-SO_3]$    $CF_3CH_2O_3S-(CF_2)_n-SO_3CH_2CF_3$    $Ba[O_3S-(CF_2)_n-SO_3]$

$M = Li, Cs$

MOH, CaO | $H_2O$     $CF_3CH_2OH$ / $Et_3N, CH_2Cl_2$     $Ba(OH)_2, CaO$ | $H_2O$

$FO_2S-(CF_2)_n-SO_2F$

$Na_2SO_3$ $H_2O$ / Dioxan     KOH, CaO | $H_2O$     $Ag_2CO_3, CaO$ | $H_2O$

$Na_2[O_2S-(CF_2)_n-SO_2]$     $K_2[O_3S-(CF_2)_n-SO_3]$     $Ag_2[O_3S-(CF_2)_n-SO_3]$

$Na_2SO_3$ $H_2O$ / Dioxan

Lewatit S100     $Ag_2CO_3$

$PCl_5$ / $POCl_3$

$HO_3S-(CF_2)_n-SO_3H$

$R_3SiCl$    $R_3SiCl$ / $CH_2Cl_2$

$ClO_2S-(CF_2)_n-SO_2Cl$

$P_4O_{10}$

$R_3SiO_3S-(CF_2)_n-SO_3SiR_3$

$R = Me, Ph$

$(CF_2)_3 \begin{smallmatrix} SO_2 \\ \quad O \\ SO_2 \end{smallmatrix}$    $(Me_3Si)_2O$

$RO_3S-(CF_2)_n-SO_3R$  ←  $RI, CH_2Cl_2$

$R = Me, Et$

$Br_2, H_2O$ → $BrO_2S-(CF_2)_n-SO_2Br$

$R_4NX, X = Br, I$

$R_4NO_3S-(CF_2)_n-SO_3NR_4$

$R = Me, Et, n\text{-}Bu, (C_6H_5CH_2) (n\text{-}BU)3$

Lewatit S100   $HO_2S-(CF_2)n-SO_2H$

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The temperature of electrolysis has a remarkable effect on product partition:

The concept of semifluorinated starting materials also holds for longer $R_f$-chains, as shown with $C_4F_9SO_2N(CH_3)_2$.

Again, the overall yield of ca. 52.8% is balanced by similar fission products as before. Based on these procedures, perfluorinated groups such as $-N(CF_3)_2$ are now available for synthetic work. Moreover, a series of experiments was conducted to elucidate the long-dis-

**Table 3** Temperature dependence of product partition

| Cell temperature | $F_3CSO_2N\begin{smallmatrix}CF_3\\CF_3\end{smallmatrix}$ | $F_3CSO_2N\begin{smallmatrix}CHF_2\\CF_3\end{smallmatrix}$ | $F_3CSO_2N\begin{smallmatrix}CHF_2\\CHF_2\end{smallmatrix}$ | others |
|---|---|---|---|---|
| $-15\ °C$ | 35% | 36% | 20% | 9% |
| $+5\ °C$ | 64% | 21% | 7% | 8% |

**Scheme 3** Relative contents of per- and partially fluorinated products in the reaction mixture in the electrolyte during the steady state of electrolysis

$$CF_3SO_2N\begin{array}{c}CH_3\\CH_3\end{array} \xrightarrow[aHF]{e^{\ominus}}$$

$CF_3SO_2N\begin{array}{c}CF_3\\CF_3\end{array}$    b.p. 55–56°C

35%

$CF_3SO_2N\begin{array}{c}CHF_2\\CF_3\end{array}$    b.p. 71–72°C

17.6%

$CF_3SO_2N\begin{array}{c}CHF_2\\CHF_2\end{array}$    b.p. 93–94°C

6.2%

$CF_3SO_2N\begin{array}{c}CHF_2\\CH_2F\end{array}$    b.p. 108–109°C

1.9%
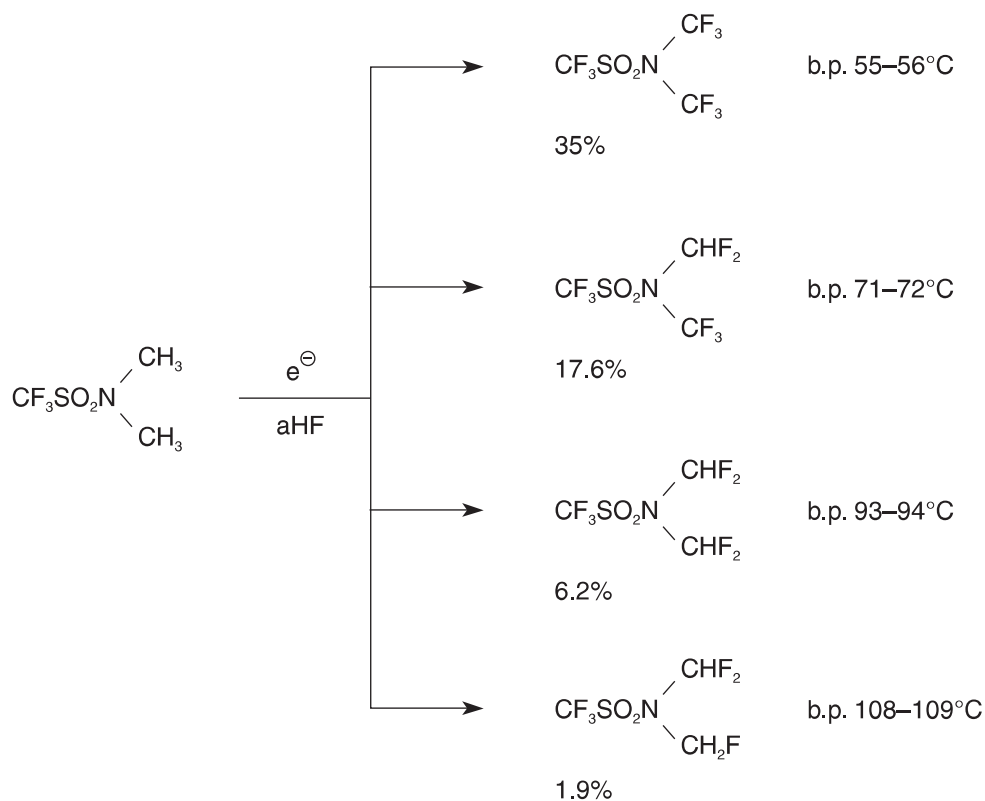
puted mechanism of electrochemical fluorination. This has before preferentially been discussed in the "normal" fashion of electrochemical reactions and cumulated in the ECEC mechanism [6, 7]. Based on this, the pattern of partially fluorinated reaction products should show different compounds, for example, $CF_3SO_2N(CH_3)(CF_3)$ as one of the prominent products.
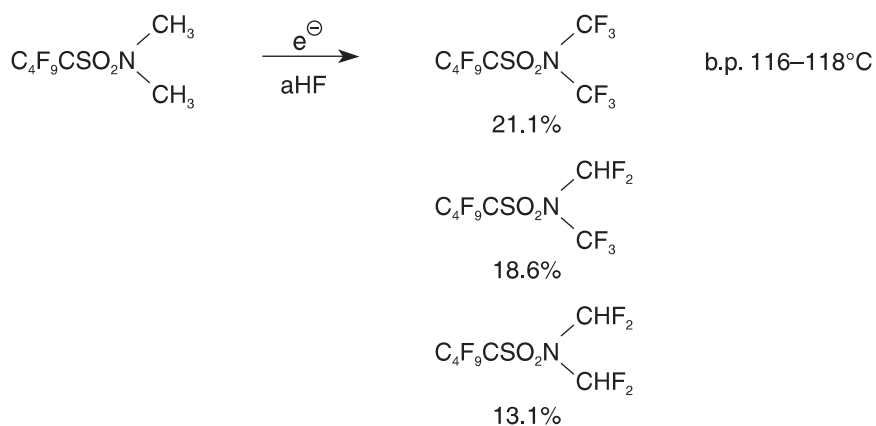
However, this compound is never found in products or reaction mixture and is not present during electrolysis in the electrolyte. The course of electrolysis and the product pattern is consistent with a different mechanism, in which nickel fluorides play a key role. It has long been a matter of confusion that many other metals have been claimed to be suitable anode materials.

In practice, however, only nickel gave results as expected from electrochemical fluorination. This is understandable now, since Zemva et al. [8] have described the preparation and properties of the thermodynamically unstable nickel fluorides $RNiF_3$ and $NiF_4$.

## Conclusions

We now understand the action of nickel in this particular process as follows:

1. As mentioned above, higher nickel fluorides are formed on the anode surface during electrolysis and act

$$C_4F_9CSO_2N\begin{array}{c}CH_3\\CH_3\end{array} \xrightarrow[aHF]{e^{\ominus}}$$

$C_4F_9CSO_2N\begin{array}{c}CF_3\\CF_3\end{array}$    b.p. 116–118°C

21.1%

$C_4F_9CSO_2N\begin{array}{c}CHF_2\\CF_3\end{array}$

18.6%

$C_4F_9CSO_2N\begin{array}{c}CHF_2\\CHF_2\end{array}$

13.1%

114

**Scheme 4** Reaction sequence based on the assumption of the ECEC mechanism [6, 7] leading to $F_3CSO_2N(CH_3)(CF_3)$

$$CF_3SO_2N(CH_3)_2 \xrightarrow[\text{aHF}]{e^{\ominus}} \left[ CF_3SO_2N(CH_3)_2 \right]^{\cdot +} \xrightarrow{-H^{\oplus}} CF_3SO_2N(CH_2^{\bullet})(CH_3)$$

$$CF_3SO_2N(CH_2^{\oplus})(CH_3) \xleftarrow{-e^{\ominus}}$$

$$CF_3SO_2N(CH_2^{\oplus})(CH_3) \xrightarrow{F^{\ominus}} CF_3SO_2N(CH_2F)(CH_3)$$

Prefered site of deprotonation

$$CF_3SO_2N(CHF_2)(CH_3) \longrightarrow \longrightarrow CF_3SO_2N(CF_3)(CH_3)$$
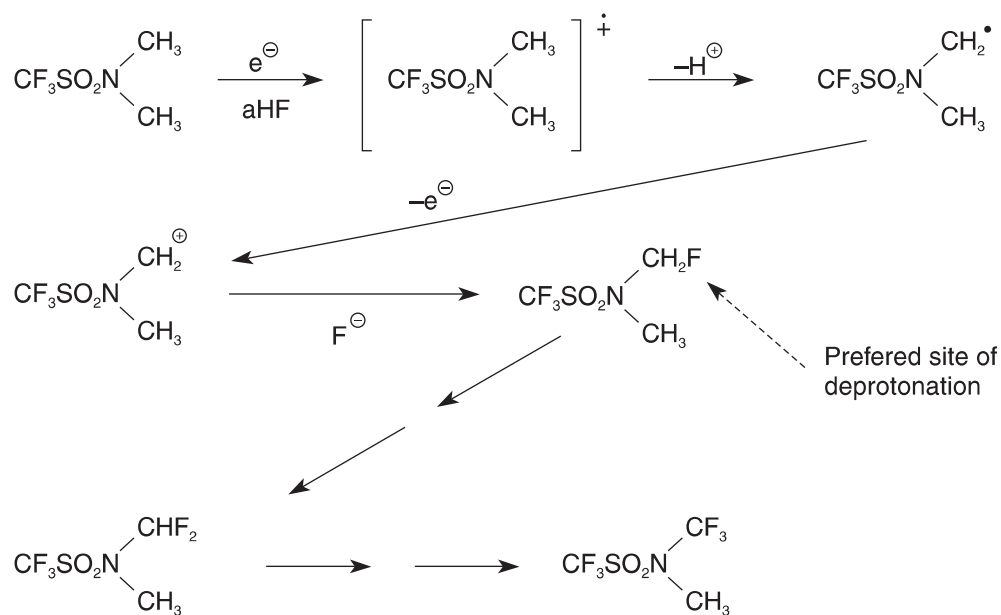
**Scheme 5** Stepwise fluorination by $NiF_3$ ($NiF_4$) film

$$Ni + 3\ HF \xrightarrow{-3e^-} NiF_3 + 3\ H^+$$

$$F_3CSO_2N(CH_3)_2 + 2\ NiF_3 \longrightarrow F_3CSO_2N(CH_2F)(CH_3) + 2\ NiF_2 + HF$$

$$NiF_2 + HF \xrightarrow{-e^-} NiF_3 + H^+$$

$$F_3CSO_2N(CH_3)_2 \xrightarrow[\text{HF}]{NiF_X} F_3CSO_2N(CH_2F)(CH_3) \longrightarrow \text{stepwise fluorination}$$

$$\longrightarrow F_3CSO_2N(CH_2F)(CH_2F) \longrightarrow F_3CSO_2N(CH_2F)(CHF_2) \longrightarrow$$

$$\longrightarrow F_3CSO_2N(CHF_2)(CHF_2) \longrightarrow F_3CSO_2N(CHF_2)(CF_2) \longrightarrow$$

$$\longrightarrow F_3CSO_2N(CF_3)(CF_3)$$
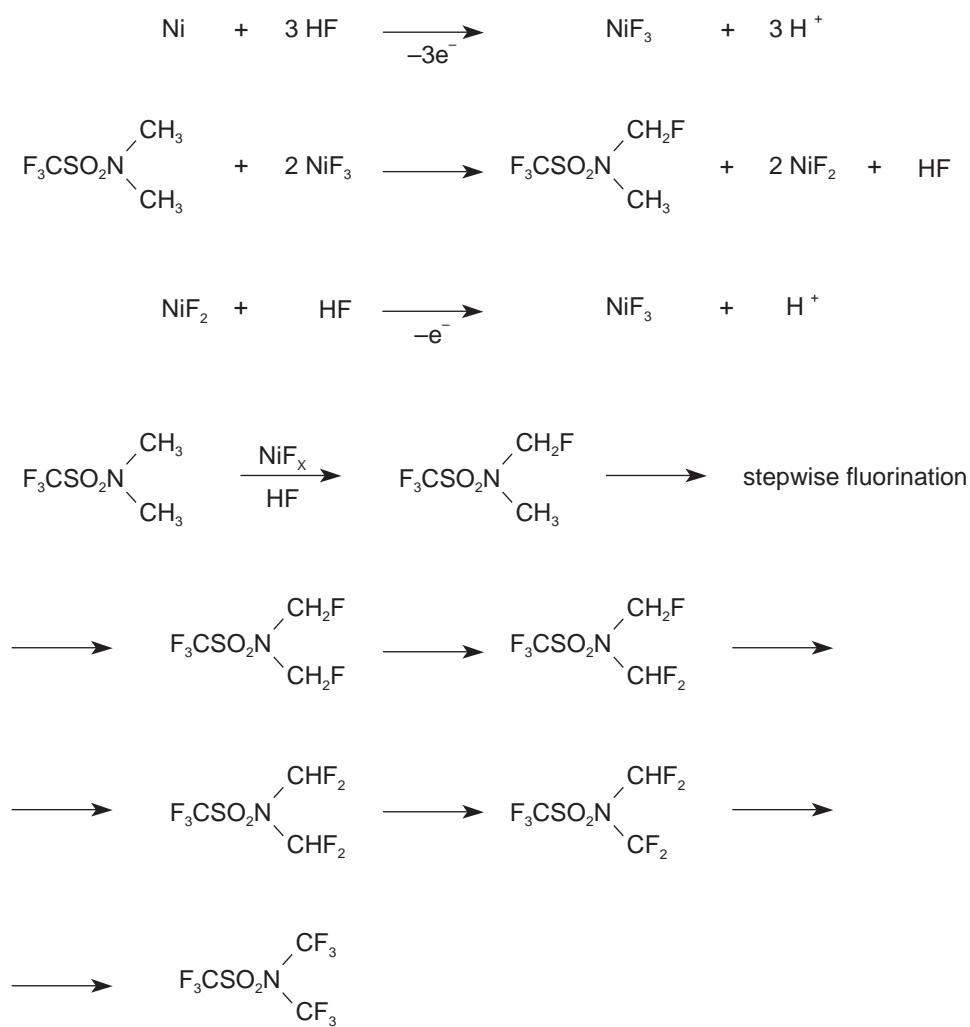
**Scheme 6** Electrochemical fluorination of $N,N,N',N'$-tetramethyldifluoromethane-disulfonamide. Similar results and confirmation were obtained by using the less complex starting material $N,N,N',N'$-tetramethylsulfondiamide

$$CH_xF_{3-x} \quad \backslash N—SO_2CF_2SO_2—N \diagup CH_{x''}F_{3-x''}$$
$$CH_{x'}F_{3-x'} \diagup \qquad \backslash CH_{x'''}F_{3-x'''}$$

$x, x', x'', x''' = 1, 2, 3$

Starting compound
$x, x', x'', x''' = 3$

Electrochemical Fluorination (ECF)
$(NiF_x)$ / HF

$$CH_2F \quad \backslash N—SO_2CF_2SO_2—N \diagup CHF_2$$
$$CHF_2 \diagup \qquad \backslash CHF_2$$

ECF $(NiF_x)$ / HF

$$CH_2F \quad \backslash N—SO_2CF_2SO_2—N \diagup CF_3$$
$$CHF_2 \diagup \qquad \backslash CHF_2$$

**not** found in the reaction mixture

$$CHF_2 \quad \backslash N—SO_2CF_2SO_2—N \diagup CHF_2$$
$$CHF_2 \diagup \qquad \backslash CHF_2$$

m.p. 51–52°C

ECF $(NiF_x)$ / HF

$$CF_3 \quad \backslash N—SO_2CF_2SO_2—N \diagup CHF_2$$
$$CHF_2 \diagup \qquad \backslash CHF_2$$

ECPF $(NiF_x)$ / HF

$$CF_3 \quad \backslash N—SO_2CF_2SO_2—N \diagup CHF_2$$
$$CF_3 \diagup \qquad \backslash CHF_2$$

**not** found in the reaction mixture

$$CF_3 \quad \backslash N—SO_2CF_2SO_2—N \diagup CF_3$$
$$CHF_2 \diagup \qquad \backslash CHF_2$$

m.p. 36–37°C

as mediators to transfer oxidation equivalent from the anode and fluorine from the solvent to substrate molecules.

2. Specific adsorption of the starting material on the anodic surface is very important. The orientation of organic molecules on the anode surface is dominated by the formation of NiF—H—C—R structures based on F—H bridges.

3. Consequently, the initial fluorination takes place preferably at the most hydrogen-bearing position.
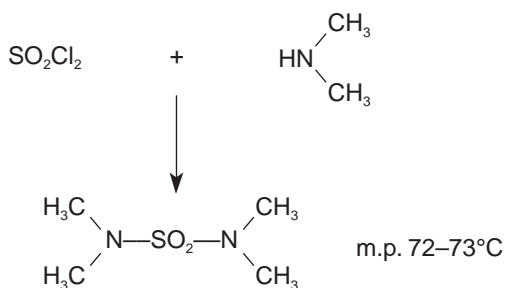
4. Moreover, electrochemical fluorination is a radical process. Radicals are formed by abstraction of hydrogen by higher nickel fluorides. Thus, the results of electrochemical fluorination depend on the stability of the radicals formed. Stable radical intermediates can give cyclic and isomeric products, as observed during electrochemical fluorinations. According to this assumption, the electrochemical fluorination of $CF_3SO_2N(CH_3)_2$ should proceed as in Scheme 5 [9].

5. Our assumptions were confirmed by the results of electrochemical fluorination of difunctional semi-fluorinated starting compounds. Thus, $N,N,N',N'$-tetramethyl difluoromethane disulfonamide $(CH_3)_2NSO_2$ $CF_2SON_2(CH_3)_2$ m.p. 71 °C on electrochemical fluorination gave a product pattern that was very complex but consistent with our assumptions in every case. Examination of the electrolyte during electrolysis and of reaction products isolated showed that the number of reaction products was large but that some characteristic compounds were absent, as illustrated in Scheme 6 [10]. Again the absence of $(CHF_2)_2NSO_2N(CF_3)_2$ and the presence of the isomer $(CF_3)(CHF_2)NSO_2N(CF_3)$ $(CHF_2)$ was very characteristic.
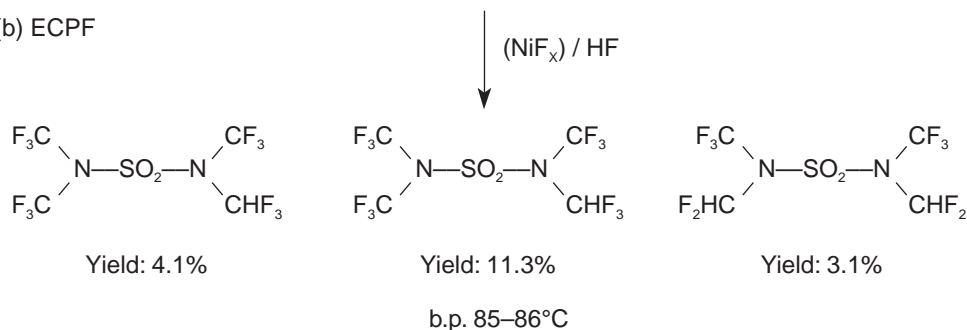
Additional proof of our proposal for the mechanism of electrochemical fluorination could be given as follows:

By pre-electrolysis of neat aHF, the anodes were charged by formation of $NiF_3/NiF_4$ film. After
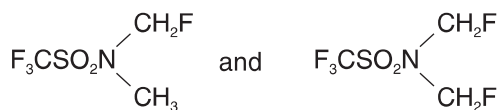
(a) Synthesis

$$SO_2Cl_2 \quad + \quad HN\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

$$\begin{matrix} H_3C \\ H_3C \end{matrix}N-SO_2-N\begin{matrix} CH_3 \\ CH_3 \end{matrix} \qquad \text{m.p. } 72\text{–}73°C$$

(b) ECPF

$(NiF_x) / HF$

$$\begin{matrix} F_3C \\ F_3C \end{matrix}N-SO_2-N\begin{matrix} CF_3 \\ CHF_3 \end{matrix}$$

Yield: 4.1%

$$\begin{matrix} F_3C \\ F_3C \end{matrix}N-SO_2-N\begin{matrix} CF_3 \\ CHF_3 \end{matrix}$$

Yield: 11.3%

$$\begin{matrix} F_3C \\ F_2HC \end{matrix}N-SO_2-N\begin{matrix} CF_3 \\ CHF_2 \end{matrix}$$

Yield: 3.1%

b.p. 85–86°C

Total yield: 18.5% (GC)

By-products:

$$FSO_2N\begin{matrix} CF_3 \\ CF_3 \end{matrix} \qquad \text{Yield: 7.5%}$$

$$FSO_2N\begin{matrix} CF_3 \\ CHF_2 \end{matrix} \qquad \text{Yield: 2.4%}$$

termination of electrolysis $CF_3SO_2N(CH_3)_2$ was injected into the cell. After a short time the presence of compounds

$$F_3CSO_2N\begin{matrix} CH_2F \\ CH_3 \end{matrix} \quad \text{and} \quad F_3CSO_2N\begin{matrix} CH_2F \\ CH_2F \end{matrix}$$

in the reaction mixture could be shown by $^{19}F$-NMR. Moreover, the polarization potential between anode and cathode now decreased rapidly. Similar observations could be made using difunctional semifluorinated starting materials.

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