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Carbon-chain isomerization during the electrochemical fluorination in anhydrous hydrogen fluoride—a mechanistic study

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Dedicated to Professor Dr. Dieter Naumann on the occasion of his 60th birthday

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Abstract

The compounds *i*-$C_4H_9SO_2F$, *i*-$C_3H_7SO_2F$ and *cyclo*-$C_3H_7C(O)F$ have been subjected to electrochemical fluorination in anhydrous hydrogen fluoride. The resulting products were fully analyzed by NMR spectroscopy. From the reaction balances, literature data and quantum chemical calculations, a new mechanism for carbon-chain isomerization during the electrochemical fluorination (ECF) is proposed. The key step in the formation of isomeric products is believed to be a ring closure reaction involving carbo-cationic or biradical intermediates.
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Keywords: Electrochemical fluorination; Simons process; Isomerization; Mechanism

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1. Introduction

Isomerization of the carbon frameworks via cyclization or chain branching during electrochemical fluorination (ECF) of the Simons type reduces the yields of target fluorochemicals produced by this method [1–7]. Cyclic compounds formed by ECF of carboxylic acid derivatives [8–11], primary aliphatic alcohols and aldehydes [12] or substituted alkylamines [13,14] are sometimes the main products and can be isolated in reasonable yield. To suppress the formation of cyclic or other isomerized products, partially fluorinated compounds [5,15–21] or those containing a nitrogen atom in an appropriate position may be used as the starting material for ECF [22–24].

Possible mechanisms of the isomerization process during the ECF have been discussed in the literature. Plashkin et al. [25] rationalized the isomerization of a branched alkyl chain into the linear one by the migration of a methyl (alkyl) group to the neighboring carbon atom. This simple approach does not explain the isomerization of a linear alkyl group into an *i*-alkyl group observed by the electrochemical fluorination of different compounds [5,22,26,27].

A carbo-cationic mechanism of the isomerization in the Simons process was proposed by Gambaretto et al. [26] based on the hypothetical four-step (EC_bEC_N) route for the electrochemical fluorination in anhydrous HF. According to this approach, the first step in the Simons process is the electrochemical oxidation (E—electrochemical step) of the organic compounds on the nickel anode to a radical cation, which eliminate a proton (C_b—chemical step) resulting in the formation of the corresponding radical. The second (E) electrochemical step leads to the oxidation of the radical into a carbo-cation followed by fluorination (addition of fluoride anion—C_N step) or isomerization [26]. The key step in this mechanism is the direct electrochemical oxidation of the starting material on the surface of nickel anode (further possible mechanisms of the Simons process are reviewed in [1,28]).

Recently, we have demonstrated that the Simons process does not proceed via direct electrochemical oxidation [19]. According to the ECEC mechanism [1,26] the first step in the Simons' process cannot proceed in the absence of electrical current flowing through the cell. We have shown [19] that fluorination takes place (after pre-electrolysis in pure HF) if the Simons' cell is disconnected from the power supply. We therefore proposed a NiF_2/NiF_3 (NiF_4) mediated process. [29,30].

High oxidation state nickel fluorides have been synthesized by Žemva et al. [31]) and could mediate the electrochemical

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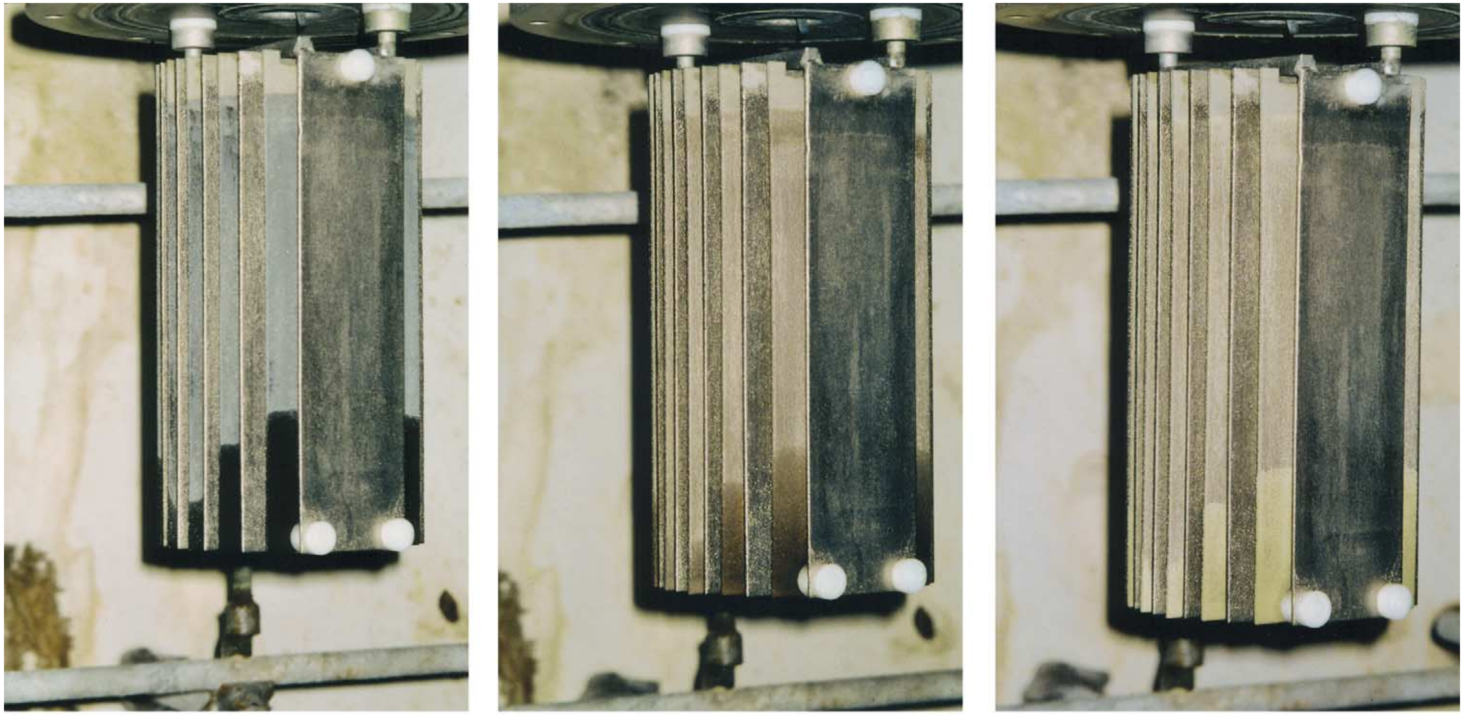
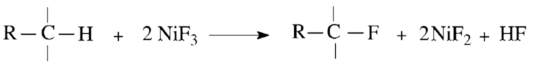

(a) (b) (c)

Fig. 1. (a) Nickel electrodes immediately after opening of the cell. Black area on the surface of the anode coat of the high oxidation state nickel fluorides, protected from the air and moisture by the film of perfluorinated material. (b) Nickel electrodes in 2–3 min after opening of the cell. Perfluorinated material is evaporated and high oxidation state nickel fluorides are partially destroyed. (c) Nickel electrodes in 30 min after opening of the cell. High oxidation state nickel fluorides are completely converted into NiF_2.

process in anhydrous HF. The key step in the Simons process is a chemical fluorination, similar to that demonstrated by Bartlett et al. [32] in the fluorination of organic compounds with NiF_3 and NiF_4.

According to our proposed [29,30] mechanism, fluorination takes place on the black nickel fluoride film (see Fig. 1) of the nickel anode. The organic molecule is adsorbed and orientated on the surface of the anode so that the carbon atom bearing a hydrogen is in contact with two NiF_3 formula units which convert the C–H bond into a C–F bond. This anode process is formulated in Eqs. (1) and (2) [29]:



$$R-\overset{|}{\underset{|}{C}}-H + 2\,NiF_3 \longrightarrow R-\overset{|}{\underset{|}{C}}-F + 2NiF_2 + HF \qquad (1)$$

$$2NiF_2 + 2HF \rightarrow 2NiF_3 + 2H^+ + 2e^- \qquad (2)$$

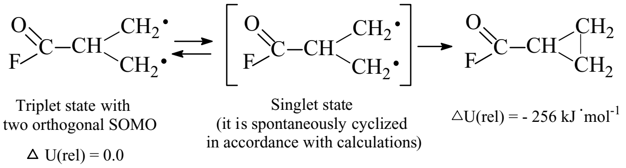
Reaction (1) proceeds in two steps within the Ni coordination sphere with the formation of an intermediate radical species [29]. In some cases these radicals are stable [33–35] and leave the surface of the anode without picking up a fluorine atom [36] or even can be detected by ESR in crude products after ECF of trialkylamines [37,38].

2. Results and discussion

2.1. The proposed reaction mechanism

If the geometry of the organic molecule permits adsorption on the nickel anode at two sites, formation of a biradical (**A**) is possible. In this case, the intramolecular interaction of both radical centers may lead to the formation of cyclic products, having for example a *cyclo*-propane structure (**D**) (see Scheme 1).

Žemva et al. [31] found the Ni–Ni distance in solid NiF_3 to be about 3.5 Å. Calculation shows the distances between the different hydrogen atoms bonded to 1 and 3 carbons in the *i*-alkane structure are in the range 2.6–3.8 Å. This distance fits with the 1,3-coordination of *i*-alkane derivatives on the surface of Ni anode, covered with NiF_3 (see Scheme 1). Quantum chemical calculations demonstrate that cyclization of β-biradicals into *cyclo*-propane derivatives is thermodynamically favored process, (Scheme 2).



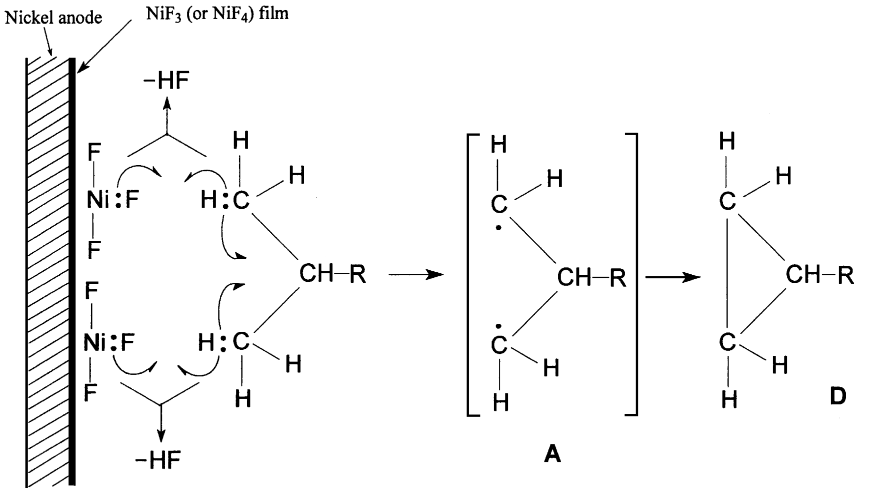
Scheme 2.

1,3-Biradicals readily undergo cyclization [39,40], for example ring closure to *cyclo*-propanes [40].

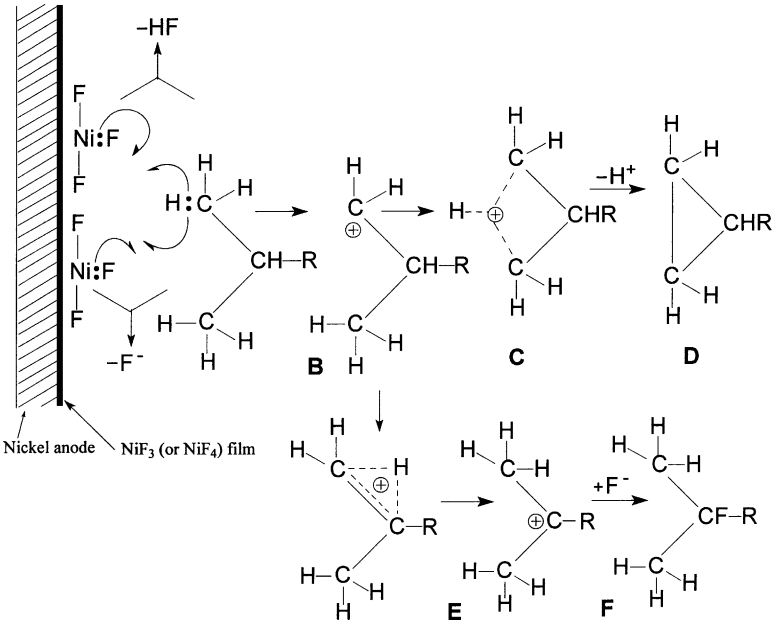
The formation of a *cyclo*-propane derivative (structure **D**) is also possible by a two-electron oxidation of one methyl group (one-site oxidation) via the intermediate formation of a "non-classical" carbo-cation ion **C** (Scheme 3), of the type, proposed by Olah [41]. **C** is a protonated *cyclo*-propane which can be diverted to **D** via deprotonation with fluoride, generated in the process (see Scheme 3).

Carbo-cation **B** can be stabilized also via hydrogen migration giving **E**, which by addition of fluoride anion is converted to the mono-fluorinated product (**F**) (Scheme 3). That is probably the route to the formation of mono-fluorinated sulfonyl fluoride $(CH_3)_2CFCH_2SO_2F$, which is present in a low but significant amount in the product after ECF of *i*-butylsulfonyl fluoride (I) (see Table 1).

Both, the radical (Scheme 1) and carbo-cation (Scheme 3) route to **D**, are reasonable but the radical route may be more favorable due to the facile single-electron oxidation rather than a two-electron oxidation (Scheme 3), assuming that oxidation on each site (biradical formation) proceeds independently. It is possible that during the early stages of fluorination when the molecule is still hydrogen-rich the carbo-cation route predominates but that after introduction of more fluorine into the molecule, the radical path way becomes more favorable.



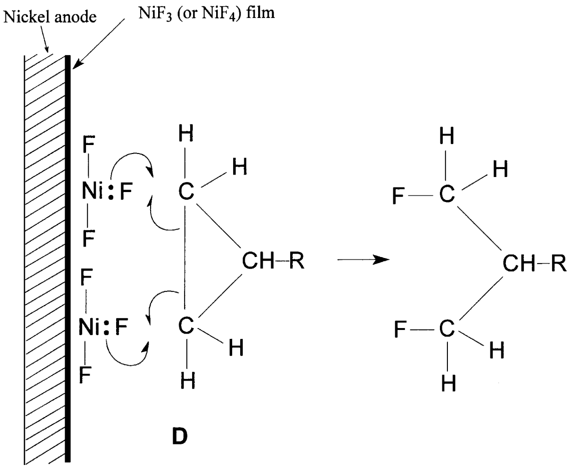
Scheme 1.



Scheme 3.

ECF of the *cyclo*-propane carboxylic acid fluoride (see Section 2.4) resulted in *cyclo*-propane ring opening. Possibly, it proceeds in a way similar to the addition of two fluorine atoms in olefinic or aromatic systems during the Simons process [28,42]. A possible mechanism involves attachment of **D** to the electrochemically recovered NiF_3 (or NiF_4) layer on the anode surface then addition of 2 F (Scheme 4).

The process represented by Scheme 4 can proceed over several steps and electron transfer may not be concerted. In some respects high oxidative state nickel fluorides are stronger fluorinating agents than diluted F_2 [29]. The mechanism of isomerization based on intermediate *cyclo*-propane ring formation has been briefly presented previously [7,43] to rationalize the isomerization of *i*-butyl to *n*-butyl during the electrochemical fluorination of tri-*i*-butylphosphine [7].



Scheme 4.

More experimental support for this mechanism (Schemes 1 and 3) is now presented. Three compounds, *i*-butylsulfonyl fluoride (I), *i*-propylsulfonyl fluoride (II) and *cyclo*-propane carboxylic acid fluoride (III) were subjected to electrochemical fluorination in anhydrous HF under typical Simons conditions.

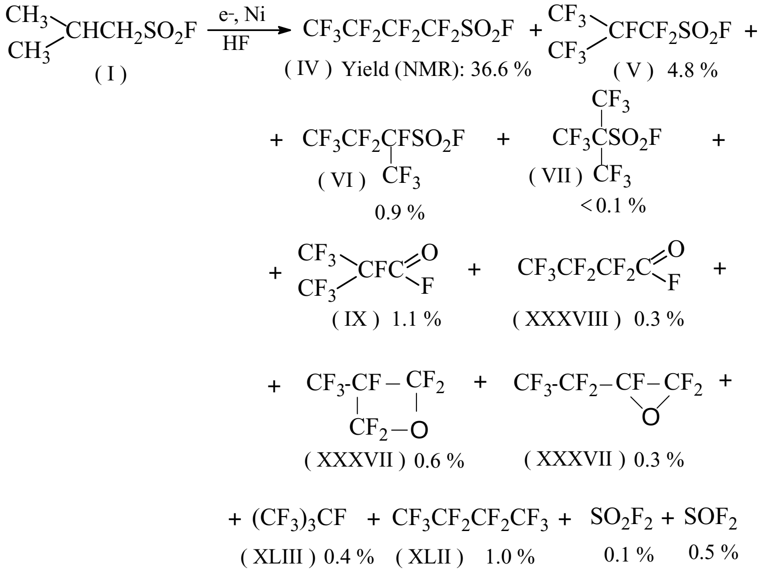
2.2. Electrochemical fluorination of i-butylsulfonyl fluoride (I)

ECF of *i*-butylsulfonyl fluoride (I) resulted in the formation of *n*-, *i*-, *s*- and *t*-perfluorobutylsulfonyl fluorides (IV–VII) together with small quantities of perfluoroacyl fluorides, perfluoroalkanes, SO_2F_2 and SOF_2 (Scheme 5) and partially fluorinated products (Tables 1 and 2). The yields of the products were estimated by ^{19}F NMR spectroscopy.

The total yield of all isolated products (see Table 1) was 59.3%, usually viewed as a good yield from the Simons process. The remainder, 41%, were volatile perfluorinated (or polyfluorinated) small molecules, such as CF_4, C_2F_6, SO_2F_2, etc. These molecules have low boiling points and cannot be completely trapped at −78 °C. Trapping with liquid nitrogen is dangerous due to the possible co-trapping of OF_2 which can cause a severe explosion.

Our main aim was to elucidate the distribution pattern of per- and poly-fluorinated products originating from the starting compound, the mass loss in balance deficiency due to loss of small perfluorinated molecules has no great influence on the origins of isomeric products. We assume that carbon-chain isomerization takes place before the final molecular degradation, because the C–H bonds are fluorinated prior to C–C.

Extensive chain isomerization revealed by the ratio of (IV)-to-(V) (Scheme 5) is proposed to arise through the



Scheme 5.

Table 1
Composition of the mixtures obtained after electrochemical fluorination of *i*-$C_4H_9SO_2F$

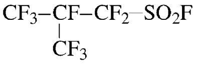
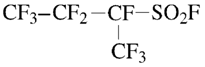
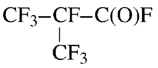
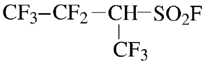
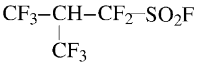
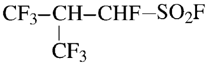
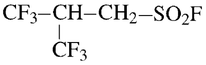
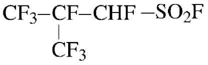
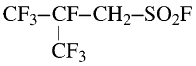
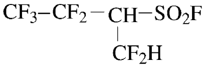
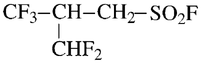
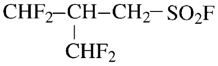
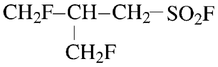
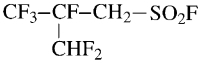
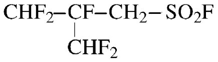
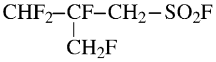
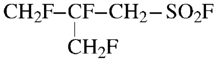
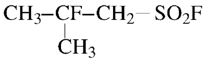
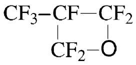
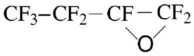
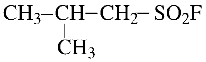
Compound	bp (°C)	Contents (mol%)			Total in the mixture (mol%, 152 g)
		Product separated from HF in the cell (70 g)	Product dissolved in HF from the cell (58 g)	Product trapped at −78 °C (24 g)	
$CF_3{-}CF_2{-}CF_2{-}CF_2{-}SO_2F$ (IV)	64 [44]	81.3	49.4	42.3	61.7
 $CF_3{-}\underset{\underset{\displaystyle CF_3}{\vert}}{C}F{-}CF_2{-}SO_2F$ (V)	–	10.4	6.3	6.5	8.1
 $CF_3{-}CF_2{-}\underset{\underset{\displaystyle CF_3}{\vert}}{C}F{-}SO_2F$ (VI)	–	1.8	1.0	1.9	1.5
$(CF3)_3C{-}SO_2F$ (VII)	–	≈0.1	<0.1	0.3	≈0.1
$CF_3{-}CF_2{-}CF_2{-}SO_2F$ (VIII)	36 [44]	0.2	≈0.2	2.3	0.5
 $CF_3{-}\underset{\underset{\displaystyle CF_3}{\vert}}{C}F{-}C(O)F$ (IX)	0–2 [60]	0.2	–	10.8	1.9
 $CF_3{-}CF_2{-}\underset{\underset{\displaystyle CF_3}{\vert}}{C}H{-}SO_2F$ (X)	–	≈0.1	0.3	–	0.2
 $CF_3{-}\underset{\underset{\displaystyle CF_3}{\vert}}{C}H{-}CF_2{-}SO_2F$ (XI)	–	0.8	0.8	–	0.6
 $CF_3{-}\underset{\underset{\displaystyle CF_3}{\vert}}{C}H{-}CHF{-}SO_2F$ (XII)	–	≈0.1	<0.1	–	<0.1
 $CF_3{-}\underset{\underset{\displaystyle CF_3}{\vert}}{C}H{-}CH_2{-}SO_2F$ (XIII)	–	≈0.1	0.8	–	0.4
 $CF_3{-}\underset{\underset{\displaystyle CF_3}{\vert}}{C}F{-}CHF{-}SO_2F$ (XIV)	–	<0.1	≈0.1	–	<0.1
 $CF_3{-}\underset{\underset{\displaystyle CF_3}{\vert}}{C}F{-}CH_2{-}SO_2F$ (XV)	–	≈0.2	1.2	–	0.6
$CF_3{-}CF_2{-}CF_2{-}CHF{-}SO_2F$ (XVI)	51–55/150 mbar [61]	0.9	1.3	–	0.9
$CF_3{-}CHF{-}CF_2{-}CF_2{-}SO_2F$ (XVII)	–	≈0.1	–	–	<0.1
$CF_3{-}CF_2{-}CF_2{-}CH_2{-}SO_2F$ (XVIII)	77–79/150 mbar [61]	1.4	8.5	–	4.0
$CF_3{-}CH_2{-}CF_2{-}CF_2{-}SO_2F$ (XIX)	–	0.4	0.7	–	0.4
$CF_3{-}CH_2{-}CF_2{-}CHF{-}SO_2F$ (XX)	–	≈0.1	0.7	–	0.3
$CF_3{-}CHF{-}CF_2{-}CH_2{-}SO_2F$ (XXI)	–	≈0.1	2.3	–	1.0
$CF_3{-}CH_2{-}CF_2{-}CH_2{-}SO_2F$ (XXII)	–	0.4	4.6	–	2.0

Table 1 (*Continued*)

Compound	bp (°C)	Contents (mol%)			Total in the mixture (mol%, 152 g)
		Product separated from HF in the cell (70 g)	Product dissolved in HF from the cell (58 g)	Product trapped at −78 °C (24 g)	
 $CF_3{-}CF_2{-}CH(CF_2H){-}SO_2F$ (XXIII)	–	–	0.4	–	0.2
 $CF_3{-}CH(CHF_2){-}CH_2{-}SO_2F$ (XXIV)	–	–	0.5	–	0.2
 $CHF_2{-}CH(CHF_2){-}CH_2{-}SO_2F$ (XXV)	–	–	≈0.3	–	≈0.1
 $CH_2F{-}CH(CH_2F){-}CH_2{-}SO_2F$ (XXVI)	–	–	0.4	–	0.2
 $CF_3{-}CF(CHF_2){-}CH_2{-}SO_2F$ (XXVII)	–	–	1.2	–	0.5
 $CHF_2{-}CF(CHF_2){-}CH_2{-}SO_2F$ (XXVIII)	–	–	0.5	–	0.2
 $CHF_2{-}CF(CH_2F){-}CH_2{-}SO_2F$ (XXIX)	–	–	0.9	–	0.3
 $CH_2F{-}CF(CH_2F){-}CH_2{-}SO_2F$ (XXX)	–	–	≈0.3	–	≈0.1
$CHF_2{-}CF_2{-}CF_2{-}CH_2{-}SO_2F$ (XXXI)	–	–	0.6	–	0.2
$CHF_2{-}CH_2{-}CF_2{-}CH_2{-}SO_2F$ (XXXII)	–	–	0.9	–	0.3
$CH_2F{-}CH_2{-}CF_2{-}CH_2{-}SO_2F$ (XXXIII)	–	–	0.4	–	0.2
 $CH_3{-}CF(CH_3){-}CH_2{-}SO_2F$ (XXXIV)	–	–	4.3	–	1.7
$CF_3{-}CF_2{-}SO_2F$ (XXXV)	8 [44]	–	–	2.2	0.4
$CF_3{-}SO_2F$ (XXXVI)	−21 [62]	–	–	≈0.1	<0.1
 (XXXVII)	–	–	–	5.6	1.0
$CF_3{-}CF_2{-}CF_2{-}COF$ (XXXVIII)	7–9 [63]	–	–	2.7	0.4
 (XXXIX)	–	–	–	2.9	0.5
$CF_3{-}CF_2{-}COF$ (XL)	−27 [64]	–	–	0.4	<0.1
$CF_3{-}COF$ (XLI)	−53—50 [65]	–	–	≈0.2	<0.1
 $CH_3{-}CH(CH_3){-}CH_2{-}SO_2F$ (I) starting material	47/16 mbar [66]	–	7.9	–	3.2
$CF_3{-}CF_2{-}CF_2{-}CF_3$ (XLII)	−1 [67]	<0.1	–	9.7	1.7
$(CF_3)_3CF$ (XLIII)	−1 to 1 [68]	<0.1	<0.1	3.5	0.7
$(CF_3)_3CH$ (XLIV)	10–12 [69]	<0.1	<0.01	≈0.2	<0.1
$CF_3{-}CF_2{-}CF_3$ (XLV)	−38 [67]	<0.1	–	2.3	0.4
$CF_3{-}CF_3$ (XLVI)	−78 [67]	–	–	≈0.1	<0.1
SO_2F_2	−55 [70]	<0.1	<0.1	0.4	≈0.1
OSF_2	−44 [70]	≈0.2	–	4.7	0.9
Others		≈0.5	≈3.0	≈1.0	≈1.6

formation of a *cyclo*-propane intermediate (Id), ring-opening fluorination of which preferentially gives a linear product (Scheme 6).

According to Scheme 6 the linear compound should be formed in double the quantity compared with the *i*-structure, assuming that in each ring opening process both ways (**1** and **2**) are equally likely (that probably not a case if a bulky fluorinated group is bonded directly to *i*-position, see Section 2.3). The *cyclo*-propane structure can be formed not only initially but also, to some extent, later, from partially fluorinated compounds that are intermediates in perfluorination (Scheme 7).

From Scheme 7 the upper limit of the product ratio linear-to-branched structure is 26:1. As the probabilities of cyclization-opening process occurring during the second (step **B**) and third (step **C**) fluorinations run are low, although not zero, the

Table 2
NMR data[a] of the compounds identified in the mixture after electrochemical fluorination of i-$C_4H_9SO_2F$ and i-$C_3H_7SO_2F$

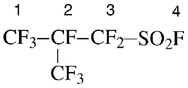
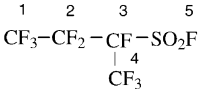
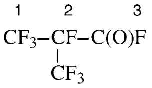
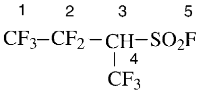
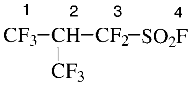
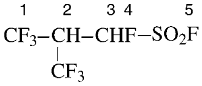
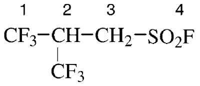
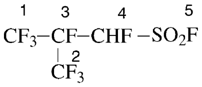
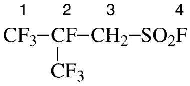
Compound	^{19}F (δ, ppm)	^{1}H (δ, ppm)
$\overset{1}{\mathrm{CF_3}}-\overset{2}{\mathrm{CF_2}}-\overset{3}{\mathrm{CF_2}}-\overset{4}{\mathrm{CF_2}}-\overset{5}{\mathrm{SO_2F}}$ (IV)	46.36 t, t, (SO_2F); −81.01 t, t ($3F^1$); −107.87 m ($2F^4$); −120.57 m ($2F^3$); −125.59 m ($2F^2$); $^{3}J_{F^4,F^5} = 6.0$ Hz; $^{4}J_{F^3,F^5} = 8.6$ Hz; $^{4}J_{F^1,F^3} = 10.2$ Hz; $^{5}J_{F^1,F^4} = 2.0$ Hz	
 (V) $\overset{1}{\mathrm{CF_3}}-\underset{\mathrm{CF_3}}{\overset{2}{\mathrm{CF}}}-\overset{3}{\mathrm{CF_2}}-\overset{4}{\mathrm{SO_2F}}$	44.94 d, t, sep (SO_2F); −71.90 d, t, d ($6F^1$); −100.13 d, d, sep ($2F^3$); −182.88 d, sep, t (F^2); $^{3}J_{F^3,F^4} = 4.1$ Hz; $^{3}J_{F^1,F^2} = 6.6$ Hz; $^{3}J_{F^2,F^3} = 5.8$ Hz; $^{4}J_{F^2,F^4} = 9.2$ Hz; $^{4}J_{F^1,F^3} = 10.6$ Hz; $^{5}J_{F^1,F^4} = 2.6$ Hz	
 (VI) $\overset{1}{\mathrm{CF_3}}-\overset{2}{\mathrm{CF_2}}-\underset{\mathrm{CF_3}\,4}{\overset{3}{\mathrm{CF}}}-\overset{5}{\mathrm{SO_2F}}$	57.57 m (SO_2F); −70.59 d, d, d, q, d ($3F^4$); −80.13 d, q, d ($3F^1$); −115.27 d, m ($1F^{2A}$); −116.82 d, m ($1F^{2B}$); −163.96 m ($1F^3$); $^{2}J_{F^{2A},F^{2B}} = 304$ Hz; $^{3}J_{F^3,F^4} = 6.6$ Hz; $^{4}J_{F^1,F^3} = 11.3$ Hz; $^{4}J_{F^4,F^5} = 6.9$ Hz; $^{4}J_{F^4,F^{2A}} = 13.4$ Hz; $^{4}J_{F^4,F^{2B}} = 13.2$ Hz; $^{5}J_{F^1,F^4} = 6.7$ Hz; $^{5}J_{F^1,F^5} = 2.7$ Hz	
$(CF_3)_3C-SO_2F$ (VII)	65.75 dec (SO_2F); −62.95 d ($3CF_3$); $^{4}J_{F,F} = 10.6$ Hz; [b]65.24 dec (SO_2F); −62.82 d ($3CF_3$); $^{4}J_{F,F} = 10.2$ Hz	
 (IX) $\overset{1}{\mathrm{CF_3}}-\underset{\mathrm{CF_3}}{\overset{2}{\mathrm{CF}}}-\overset{3}{\mathrm{C(O)F}}$	32.60 d, sep ($1F^3$); −74.51 d, d ($6F^1$); −180.75 d, sep ($1F^2$); $^{3}J_{F^2,F^3} = 21.8$ Hz; $^{3}J_{F^1,F^2} = 7.5$ Hz; $^{4}J_{F^1,F^3} = 6.6$ Hz	
 (X) $\overset{1}{\mathrm{CF_3}}-\overset{2}{\mathrm{CF_2}}-\underset{\mathrm{CF_3}\,4}{\overset{3}{\mathrm{CH}}}-\overset{5}{\mathrm{SO_2F}}$	66.33 m (SO_2F); −60.82 m ($3F^4$); −83.03 d, q ($3F^1$); −109.35 d, m ($1F^{2A}$); −114.64 d, m ($1F^{2B}$); $^{2}J_{F^{2A},F^{2B}} = 293$ Hz; $^{5}J_{F^1,F^4} = 6.2$ Hz; $^{5}J_{F^1,F^5} = 2.3$ Hz	
 (XI) $\overset{1}{\mathrm{CF_3}}-\underset{\mathrm{CF_3}}{\overset{2}{\mathrm{CH}}}-\overset{3}{\mathrm{CF_2}}-\overset{4}{\mathrm{SO_2F}}$	38.08 t, sep (SO_2F); −61.57 t, d, d ($6F^1$); −96.44 d, d, sep ($2F^3$); $^{3}J_{F^3,F^4} = 6.3$ Hz; $^{3}J_{H^2,F^1} = 7.0$ Hz; $^{3}J_{H^2,F^3} = 11.3$ Hz; $^{4}J_{F^1,F^3} = 10.8$ Hz; $^{5}J_{F^1,F^4} = 4.0$ Hz	4.23 t, sep (H^2) $^{3}J_{H,F^3} = 11.8$ Hz $^{3}J_{H,F^1} = 6.9$ Hz
 (XII) $\overset{1}{\mathrm{CF_3}}-\underset{\mathrm{CF_3}}{\overset{2}{\mathrm{CH}}}-\overset{3\,4}{\mathrm{CHF}}-\overset{5}{\mathrm{SO_2F}}$	44.72 m (SO_2F); −67.00 d, d, d ($6F^1$); −187.70 d, m ($1F^4$); $^{2}J_{H^3,F^4} = 43$ Hz; $^{3}J_{H^2,F^1} = 11.6$ Hz; $^{4}J_{F^1,F^4} = 11.6$ Hz; $^{5}J_{F^1,F^5} = 2.6$ Hz	
 (XIII) $\overset{1}{\mathrm{CF_3}}-\underset{\mathrm{CF_3}}{\overset{2}{\mathrm{CH}}}-\overset{3}{\mathrm{CH_2}}-\overset{4}{\mathrm{SO_2F}}$	58.68 sep (SO_2F); −67.87 d, d ($6F^1$); $^{3}J_{H^2,F^1} = 7.5$ Hz; $^{5}J_{F^1,F^4} = 4.3$ Hz	3.70 d (CH_2) $^{3}J_{H^2,H^3} = 4.7$ Hz; signal of CH_2 group is overlapped with another signals
 (XIV) $\overset{1}{\mathrm{CF_3}}-\underset{\mathrm{CF_3}\,2}{\overset{3}{\mathrm{CF}}}-\overset{4}{\mathrm{CHF}}-\overset{5}{\mathrm{SO_2F}}$	62.52 d, m (SO_2F); −77.45 d, q, d, d (CF_3); −183.59 m ($1F^3$); $^{3}J_{F^1,F^3} = 5.8$ Hz; $^{4}J_{F^1,F^2} = 5.9$ Hz; $^{4}J_{F^1,F^4} = 10.0$ Hz; $^{4}J_{F^3,F^5} = 13.8$ Hz; $^{5}J_{F^1,F^5} = 3.9$ Hz; signal of CHF is overlapped with another signals	
 (XV) $\overset{1}{\mathrm{CF_3}}-\underset{\mathrm{CF_3}}{\overset{2}{\mathrm{CF}}}-\overset{3}{\mathrm{CH_2}}-\overset{4}{\mathrm{SO_2F}}$	66.59 d, sep (SO_2F); −76.54 d, d ($6F^1$) −183.70 d, t, sep (F^2); $^{3}J_{H^3,F^2} = 15.6$ Hz; $^{3}J_{F^1,F^2} = 6.9$ Hz; $^{4}J_{F^2,F^4} = 11.9$ Hz; $^{5}J_{F^1,F^4} = 3.2$ Hz	3.67 d, d (CH_2) $^{3}J_{H^3,F^2} = 15.6$ Hz $^{3}J_{H^3,F^4} = 3.1$ Hz
$\overset{1}{\mathrm{CF_3}}-\overset{2}{\mathrm{CF_2}}-\overset{3}{\mathrm{CF_2}}-\overset{4}{\mathrm{CHF}}-\overset{5}{\mathrm{SO_2F}}$ (XVI)	55.60 d, d, d, d (SO_2F); −80.88 d, d, d ($3F^1$); −126.22 d, d, d ($2F^2$); −119.12 d, m ($1F^{3A}$); −125.20 d, m ($1F^{3B}$); −189.50 d, m ($1F^4$); $^{2}J_{H,F^4} = 44.0$ Hz; $^{2}J_{F^{3A},F^{3B}} = 297$ Hz; $^{3}J_{H,F^5} = 2.3$ Hz; $^{3}J_{F^4,F^5} = 6.3$ Hz; $^{3}J_{F^2,F^{3A}} = 2.6$ Hz; $^{3}J_{F^2,F^{3B}} = 4.5$ Hz; $^{4}J_{F^1,F^{3A}} = 11.1$ Hz; $^{4}J_{F^1,F^{3B}} = 8.7$ Hz; $^{4}J_{F^2,F^4} = 13.4$ Hz; $^{4}J_{F^5,F^{3A}} = 6.3$ Hz; $^{4}J_{F^5,F^{3B}} = 12.0$ Hz; $^{5}J_{F^1,F^4} = 2.4$ Hz	5.96 d, d, d, d (H) $^{2}J_{H,F^4} = 44.0$ Hz $^{3}J_{H,F^{3A}} = 17.0$ Hz $^{3}J_{H,F^{3B}} = 2.2$ Hz $^{3}J_{H,F^5} = 2.0$ Hz
$\overset{1}{\mathrm{CF_3}}-\overset{2\,3}{\mathrm{CHF}}-\overset{4}{\mathrm{CF_2}}-\overset{5}{\mathrm{CF_2}}-\overset{6}{\mathrm{SO_2F}}$ (XVII)	46.75 m (SO_2F); −74.20 d, t, d, t ($3F^1$); −107.67 m ($2F^5$); −211.36 d, m ($1F^3$); $^{2}J_{H^2,F^3} = 43$ Hz; $^{3}J_{H^2,F^1} = 5.4$ Hz; $^{3}J_{F^1,F^3} = 10.9$ Hz; $^{4}J_{F^1,F^4} = 10.4$ Hz; $^{5}J_{F^1,F^5} = 1.6$ Hz; signals of $CF_2{}^4$ group (A, B system) are overlapped with another signals	
$\overset{1}{\mathrm{CF_3}}-\overset{2}{\mathrm{CF_2}}-\overset{3}{\mathrm{CF_2}}-\overset{4}{\mathrm{CH_2}}-\mathrm{SO_2F}$ (XVIII)	66.47 t, t, t (SO_2F); −80.46 t ($3F^1$); −113.64 m ($2F^3$); −126.94 m ($2F^2$); $^{3}J_{H,F^4} = 3.5$ Hz; $^{4}J_{F^3,F^4} = 12.4$ Hz; $^{4}J_{F^1,F^3} = 9.9$ Hz; $^{5}J_{F^2,F^4} = 1.1$ Hz	4.13 t, d, t (CH_2) $^{3}J_{H,F^4} = 3.7$ Hz $^{3}J_{H,F^3} = 15.2$ Hz $^{4}J_{H,F^2} = 0.8$ Hz
$\overset{1}{\mathrm{CF_3}}-\overset{2}{\mathrm{CH_2}}-\overset{3}{\mathrm{CF_2}}-\overset{4}{\mathrm{CF_2}}-\overset{5}{\mathrm{SO_2F}}$ (XIX)	45.79 t, t (SO_2F); −61.26 t, t, t ($3F^1$); −110.70 d, m ($2F^4$); −111.50 d, t, q ($2F^3$); $^{3}J_{F^4,F^5} = 5.3$ Hz; $^{3}J_{H^2,F^1} = 9.3$ Hz; $^{3}J_{H^2,F^3} = 16.7$ Hz; $^{4}J_{F^1,F^3} = 9.3$ Hz; $^{4}J_{F^3,F^5} = 8.8$ Hz; $^{5}J_{F^1,F^4} = 2.1$ Hz	

Table 2 (*Continued*)

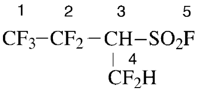
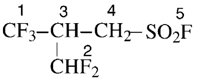
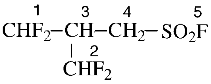
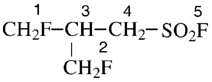
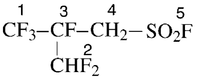
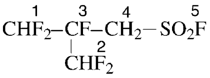
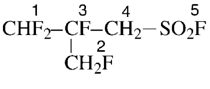
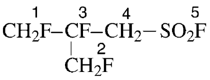
Compound	^{19}F (δ, ppm)	^{1}H (δ, ppm)
$\overset{1}{CF_3}-\overset{2}{CH_2}-\overset{3}{CF_2}-\overset{4\,5}{CHF}-\overset{6}{SO_2F}$ (XX)	54.43 d, d, d (SO$_2$F), −61.53 t, t, d (3F^1); −106.52 d, m (1F^{3A}); −109.33 d, m (1F^{3B}); −187.60 d, m (1F^5); $^2J_{F^{3A},F^{3B}} = 282$ Hz; $^2J_{H^4,F^5} = 44$ Hz; $^3J_{H^2,F^1} = 9.3$ Hz; $^3J_{F^5,F^6} = 7.2$ Hz; $^4J_{F^{3A},F^6} = 11.1$ Hz; $^4J_{F^{3B},F^6} = 7.3$ Hz; $^4J_{F^1,F^3} = 9.3$ Hz; $^5J_{F^1,F^5} = 2.4$ Hz	
$\overset{1}{CF_3}-\overset{2\,3}{CHF}-\overset{4}{CF_2}-\overset{5}{CH_2}-\overset{6}{SO_2F}$ (XXI)	64.95 d, d, d, t, (SO$_2$F); −74.32 t, d, d (3F^1); −106.56 d, m (1F^{4A}); −109.06 d, m (1F^{4B}); −209.78 d, m (1F^3); $^2J_{F^{4A},F^{4B}} = 280$ Hz; $^2J_{H^2,F^3} = 44$ Hz; $^3J_{H^2,F^1} = 5.6$ Hz; $^3J_{H^5,F^6} = 2.7$ Hz; $^4J_{H^5,F^3} = 2.0$ Hz; $^3J_{F^1,F^3} = 9.1$ Hz; $^4J_{F^1,F^4} = 11.1$ Hz; $^4J_{F^{4A},F^6} = 13.9$ Hz; $^4J_{F^{4B},F^6} = 11.2$ Hz; $^5J_{F^3,F^6} = 5.3$ Hz	5.15 d, d, d, q (CHF) $^2J_{H^2,F^3} = 43.8$ Hz $^3J_{H^2,F^{4A}} = 5.6$ Hz $^3J_{H^2,F^{4B}} = 14.3$ Hz $^3J_{H^2,F^1} = 5.6$ Hz; signal of CH$_2$ group is overlapped with another signals
$\overset{1}{CF_3}-\overset{2}{CH_2}-\overset{3}{CF_2}-\overset{4}{CH_2}-\overset{5}{SO_2F}$ (XXII)	63.83 t, t (SO$_2$F); −61.94 t, t (3F^1); −92.72 m (2F^3)[c]; $^3J_{H^4,F^5} = 3.8$ Hz; $^4J_{F^3,F^5} = 12.9$ Hz; $^3J_{H^2,F^1} = {}^4J_{F^1,F^3} = 9.5$ Hz	3.08 t, q (CH$_2^2$) 4.04 t, d (CH$_2^4$) $^3J_{H^2,F^3} = 14.4$ Hz $^3J_{H^2,F^1} = 9.6$ Hz $^3J_{H^4,F^5} = 4.0$ Hz $^3J_{H^4,F^3} = 13.0$ Hz
 $\overset{1}{CF_3}-\overset{2}{CF_2}-\underset{\underset{CF_2H}{\vert\,4}}{\overset{3}{CH}}-\overset{5}{SO_2F}$ (XXIII)	66.08 t, m (SO$_2$F); −80.06 t (3F^1); −123.79 d, d, d, m (1F^{4A}); −124.24 d, d, d, m (1F^{4B}); $^2J_{F^{4A},F^{4B}} = 295$ Hz; $^2J_{H^4,F^4} = 54$ Hz; $^3J_{H^3,F^4} = 15.5$ Hz; $^4J_{F^2,F^5} = 11.6$ Hz; $^4J_{F^4,F^5} = 3.4$ Hz; $^5J_{F^1,F^4} = 7.9$ Hz; signals of CF$_2^2$ group (A, B system) are overlapped with another signals	
 $\overset{1}{CF_3}-\underset{\underset{CHF_2}{\vert\,2}}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{SO_2F}$ (XXIV)	58.36 m (SO$_2$F); −68.10 t, d, d (3F^1); −122.4 d, d, d, q, d (1F^{2A}); −125.5 d, d, d, q, d (1F^{2B}); $^2J_{F^{2A},F^{2B}} = 298$ Hz; $^2J_{H^2,F^2} = 54$ Hz; $^3J_{H^3,F^1} = 6.8$ Hz; $^3J_{H^3,F^{2A}} = 8.2$ Hz; $^3J_{H^3,F^{2B}} = 19.7$ Hz; $^4J_{F^1,F^{2A}} = 7.1$ Hz; $^4J_{F^1,F^{2B}} = 7.9$ Hz; $^5J_{F^1,F^5} = 4.2$ Hz; $^5J_{F^{2A},F^5} = 7.0$ Hz; $^5J_{F^{2B},F^5} = 2.2$ Hz	
 $\overset{1}{CHF_2}-\underset{\underset{CHF_2}{\vert\,2}}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{SO_2F}$ (XXV)	57.56 quin (SO$_2$F); −124.10 d, d, m (4F^{1,2}); $^2J_{H,F} \approx 53$ Hz; $^3J_{H^3,F^1} \approx 12$ Hz $^5J_{F^1,F^5} = 4.0$ Hz	
 $\overset{1}{CH_2F}-\underset{\underset{CH_2F}{\vert\,2}}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{SO_2F}$ (XXVI) (XXVI)	57.29 m (SO$_2$F); −225.82 t, d, t (2F^{1,2}); $^2J_{H,F} = 47$ Hz; $^3J_{H^3,F^1} = 21.2$ Hz; $^4J_{F^1,H^2} = 1.4$ Hz	
 $\overset{1}{CF_3}-\underset{\underset{CHF_2}{\vert\,2}}{\overset{3}{CF}}-\overset{4}{CH_2}-\overset{5}{SO_2F}$ (XXVII)	65.2 d, m (SO$_2$F); −76.31 d, d, d, d (3F^1); −129.9 d, d, d, q, d (1F^{2A}); −131.6 d, d, d, q, d (1F^{2B}); −184.2 m (F^3); $^2J_{F^{2A},F^{2B}} = 309$ Hz; $^2J_{H^2,F^2} = 53$ Hz; $^3J_{F^1,F^3} = 9.1$ Hz; $^3J_{F^{2A},F^3} = 7.6$ Hz; $^3J_{F^{2B},F^3} = 7.6$ Hz; $^4J_{F^1,F^{2A}} = 7.9$ Hz; $^4J_{F^1,F^{2B}} = 7.5$ Hz; $^4J_{F^3,F^5} = 15.3$ Hz; $^5J_{F^1,F^5} = 2.6$ Hz; $^5J_{F^{2A},F^5} = 4.8$ Hz; $^5J_{F^{2B},F^5} = 3.6$ Hz	3.86 d, d (CH$_2$) 6.32 t, d, q (CHF$_2$) $^2J_{H^2,F^2} = 52.9$ Hz $^3J_{H^2,F^3} = 4.0$ Hz $^3J_{H^4,F^3} = 8.5$ Hz $^3J_{H^4,F^5} = 3.6$ Hz $^4J_{H^2,F^1} = 1.1$ Hz
 $\overset{1}{CHF_2}-\underset{\underset{CHF_2}{\vert\,2}}{\overset{3}{CF}}-\overset{4}{CH_2}-\overset{5}{SO_2F}$ (XXVIII)	65.94 d, m (SO$_2$F); −132.62 d, d, d (4F^{1,2}); −184.73 m (1F^3); $^2J_{H,F} = 54$ Hz; $^3J_{F^1,F^3} = 7.8$ Hz; $^4J_{F^3,F^5} = 14.3$ Hz; $^5J_{F^1,F^5} = 3.5$ Hz	6.30 t, d, t (CHF$_2$) $^2J_{H,F} = 55.4$ Hz $^3J_{H^1,F^3} = 4.0$ Hz $^4J_{H^1,F^2} = 1.8$ Hz
 $\overset{1}{CHF_2}-\underset{\underset{CH_2F}{\vert\,2}}{\overset{3}{CF}}-\overset{4}{CH_2}-\overset{5}{SO_2F}$ (XXIX)	−132.18 d, d, d, m (1F^{1A}); −133.55 d, d, d, m (1F^{1B}); ≈−184.8 m (1F^3); −228.20 t, d, m (1F^2); $^2J_{H^1,F^{1A}} = 56$ Hz; $^2J_{H^1,F^{1B}} = 55$ Hz; $^2J_{H^2,F^2} = 47$ Hz; $^3J_{F^2,F^3} = 12.5$ Hz; $^3J_{F^{1A},F^3} = 7.6$ Hz; $^3J_{F^{1B},F^3} = 7.2$ Hz; signal of SO$_2$F group is overlapped with another signal	
 $\overset{1}{CH_2F}-\underset{\underset{CH_2F}{\vert\,2}}{\overset{3}{CF}}-\overset{4}{CH_2}-\overset{5}{SO_2F}$ (XXX)	≈−185 m (1F^3); −238.78 t, d, m (2F^{1,2}); $^2J_{H,F} = 46$ Hz; $^3J_{F^1,F^3} = 13.8$ Hz; signal of SO$_2$F group is overlapped with another signal	
$\overset{1\,2}{CHF_2}-\overset{3}{CF_2}-\overset{4}{CF_2}-\overset{5}{CH_2}-\overset{6}{SO_2F}$ (XXXI)	65.48 t, t (SO$_2$F); −114.20 m (2F^4); −130.33 m (2F^3); −137.22 d, t, t (2F^2); $^2J_{H^1,F^2} = 52$ Hz; $^3J_{F^2,F^3} = 5.2$ Hz; $^3J_{H^5,F^6} = 3.8$ Hz; $^4J_{F^2,F^4} = 7.9$ Hz; $^4J_{F^4,F^6} = 11.4$ Hz	
$\overset{1\,2}{CHF_2}-\overset{3}{CH_2}-\overset{4}{CF_2}-\overset{5}{CH_2}-\overset{6}{SO_2F}$ (XXXII)	63.76 t, t (SO$_2$F); −92.60 m (2F^4); −115.65 d, t, t (2F^2); $^2J_{H^1,F^2} = 55$ Hz; $^3J_{H^3,F^2} = 15.3$ Hz; $^3J_{H^5,F^6} = 3.6$ Hz; $^4J_{F^2,F^4} = 5.7$ Hz; $^4J_{F^4,F^6} = 12.9$ Hz	

Table 2 (*Continued*)

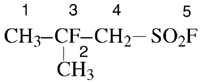
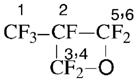
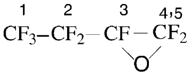
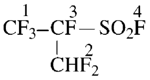
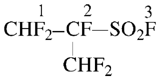
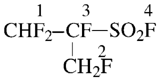
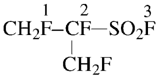
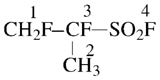
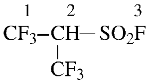
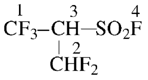
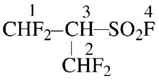
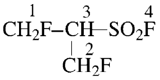
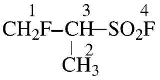
Compound	^{19}F (δ, ppm)	^{1}H (δ, ppm)
$\overset{1}{CH_2}\overset{2}{F}-\overset{3}{CH_2}-\overset{4}{CF_2}-\overset{5}{CH_2}-\overset{6}{SO_2F}$ (XXXIII)	63.05 t, t (SO_2F); −94.50 m ($2F^4$); −241.76 t, t, t ($1F^2$); $^{2}J_{H^1,F^2} = 46$ Hz; $^{3}J_{H^3,F^2} = 15.2$ Hz; $^{3}J_{H^5,F^6} = 3.6$ Hz; $^{4}J_{F^2,F^4} = 5.5$ Hz; $^{4}J_{F^4,F^6} = 12.6$ Hz	
 $\overset{1}{CH_3}-\underset{\underset{CH_3}{\vert\,2}}{\overset{3}{CF}}-\overset{4}{CH_2}-\overset{5}{SO_2F}$ (XXXIV)	63.21 d, t (SO_2F); −136.88 m (F^3); $^{3}J_{H^4,F^5} = 3.1$ Hz; $^{3}J_{H^1,F^3} = 21.3$ Hz; $^{3}J_{H^4,F^3} = 15.8$ Hz; $^{4}J_{F^3,F^5} = 12.9$ Hz	1.62 d ($2CH_3$) 3.73 d, d (CH_2) $^{3}J_{H^1,F^3} = 21.3$ Hz $^{3}J_{H^4,F^3} = 15.8$ Hz
 (XXXVII) (mixture of two isomers)	[b]−75.98 d, d, t ($3F^1$); −82.43 d, m ($2F^{3},^{4}$); −82.94 d, m ($2F^{5,6}$); −183.39 m ($1F^2$) $^{2}J_{F^3,F^4} = {}^{2}J_{F^5,F^6} = 102$ Hz $^{3}J_{F^1,F^2} = 8.8$ Hz; $^{4}J_{F^1,F^{3,5}} = 8.7$ Hz $^{4}J_{F^1,F^{4,6}} = 4.2$ Hz	
 (XXXIX)	[b]−80.99 d, d, m ($3F^1$); −79.83 d, d, t ($1F^4$); −84.79 d, d, t ($1F^5$); −124.16 d, d, d, d, q ($1F^{2A}$) −126.21 d, m ($1F^{2B}$); −133.62 m ($1F^3$); $^{2}J_{F^{2A},F^{2B}} = 217$ Hz; $^{2}J_{F^4,F^5} = 91$ Hz; $^{3}J_{F^1,F^{2A}} = 1.0$ Hz; $^{3}J_{F^1,F^{2B}} = 10.0$ Hz; $^{3}J_{F^3,F^4} = 9.0$ Hz; $^{3}J_{F^3,F^5} = 8.6$ Hz; $^{3}J_{F^{2A},F^3} = 6.0$ Hz; $^{4}J_{F^{2A},F^4} = 8.1$ Hz; $^{4}J_{F^{2A},F^5} = 14.1$ Hz; $^{4}J_{F^1,F^3} = 3.0$ Hz; $^{4}J_{F^{2B},F^5} \approx {}^{4}J_{F^{2B},F^4} = 8.6$ Hz	
$\overset{1}{CF_3}-\overset{2}{CF_2}-\overset{3}{CHF}-\overset{4}{SO_2F}$ (L)	[d]55.82 d, d, d, q (SO_2F); −82.14 d, m (CF_3); −120.78 d, m; (CF_2, F^A); −127.81 d, m;(CF_2, F^B); −190.85 d, m (CHF) $^{2}J_{FAFB} = 288$ Hz; $^{2}J_{H,F} = 44.0$ Hz; $^{3}J_{H,F^4} = 2.7$ Hz; $^{3}J_{F^3,F^4} = 6.5$ Hz; $^{4}J_{F^{2A},F^4} = 12.3$ Hz; $^{4}J_{F^{2B},F^4} = 5.9$ Hz	5.22 d, m
$\overset{1}{CF_3}-\overset{2}{CF_2}-\overset{3}{CH_2}-\overset{4}{SO_2F}$ (LI)	[d]66.28 m (SO_2F); −84.91 m (CF_3); −116.09 dt (CF_2); $^{3}J_{H,F^4} = 4.3$ Hz; $^{3}J_{H,F^2} = 15.5$ Hz; $^{4}J_{H,F^1} = 0.6$ Hz; $^{4}J_{F^2,F^4} = 11.9$ Hz	4.73 t, d, q
$\overset{1}{CF_3}-\overset{2}{CH_2}-\overset{3}{CF_2}-\overset{4}{SO_2F}$ (LII)	[d]42.50 t, m (SO_2F); −60.39 quin, d (CF_3); −97.72 d, t, q (CF_2); $^{3}J_{H^2,F^1} = 9.0$ Hz; $^{3}J_{H^2,F^3} = 17.1$ Hz; $^{3}J_{F^3,F^4} = 8.5$ Hz; $^{4}J_{F^1,F^3} = 8.8$ Hz; $^{5}J_{F^1,F^4} = 1.4$ Hz	
$\overset{1}{CHF_2}-\overset{2}{CF_2}-\overset{3}{CH_2}-\overset{4}{SO_2F}$ (LIII)	[d]65.75 t, t, t (SO_2F); −115.89 d, t, d, t (CF_2); −136.65 d, m (CF_2H); $^{2}J_{H,F^1} = 52.5$ Hz; $^{3}J_{H^3,F^4} = 4.3$ Hz; $^{4}J_{F^2,F^4} = 11.8$ Hz; $^{5}J_{F^1,F^4} = 1.0$ Hz	
 $\overset{1}{CF_3}-\underset{\underset{CHF_2}{\vert\,2}}{\overset{3}{CF}}-\overset{4}{SO_2F}$ (LIV)	[d]56.40 sex, d (SO_2F); −73.25 d, d, d, m (CF_3); −167.80 m (CF); $^{3}J_{F^1,F^3} \approx 7$ Hz; $^{3}J_{F^3,F^4} = 3.9$ Hz; $^{4}J_{F^1,F^4} = 10.1$ Hz; signals of CHF_2 group (A, B system) are overlapped with stronger signals	
 $\overset{1}{CHF_2}-\underset{\underset{CHF_2}{\vert}}{\overset{2}{CF}}-\overset{3}{SO_2F}$ (LV)	[d]56.20 quin, d, t (SO_2F); −131.29 dt (CHF_2); −175.39 quin, t, d (CF); $^{2}J_{H,F} = 52$ Hz; $^{3}J_{H^1,F^2} = 6.2$ Hz; $^{4}J_{H^1,F^3} = 2.1$ Hz; $^{3}J_{F^2,F^3} = 4.1$ Hz; $^{3}J_{F^1,F^2} = 10.2$ Hz; $^{4}J_{F^1,F^3} = 10.5$ Hz	
 $\overset{1}{CHF_2}-\underset{\underset{CH_2F}{\vert\,2}}{\overset{3}{CF}}-\overset{4}{SO_2F}$ (LVI)	[d]52.68 d, t, m (SO_2F); −131.1 d, d, d, d, d, t (CHF_2, F^A); −132.2 d, d, d, d, d, t (CHF_2, F^B); −171.67 m (CF); −240.55 t, d, d, t, d (CH_2F); $^{2}J_{F^A,F^B} \approx 300$ Hz; $^{2}J_{H^1,F^1} = 52$ Hz; $^{2}J_{H^2,F^2} = 46$ Hz; $^{4}J_{H^1,F^2} = 1.6$ Hz; $^{4}J_{H^2,F^1} = 1.2$ Hz; $^{3}J_{F^1,F^3} = 9.9$ Hz; $^{3}J_{F^2,F^3} = 14.9$ Hz; $^{4}J_{F^1,F^2} = 2.6$ Hz; $^{4}J_{F^1,F^4} = 9.9$ Hz; $^{4}J_{F^2,F^4} = 13.5$ Hz	
 $\overset{1}{CH_2F}-\underset{\underset{CH_2F}{\vert}}{\overset{2}{CF}}-\overset{3}{SO_2F}$ (LVII)	[d]49.22 t, m (SO_2F); −166.46 m (CF); −236.78 t, d, d, m (CH_2F); $^{2}J_{H^1,F^1} = 46$ Hz; $^{3}J_{F^1,F^2} = 14.4$ Hz; $^{3}J_{F^2,F^3} = 2.6$ Hz; $^{4}J_{F^1,F^3} = 13.0$ Hz	
 $\overset{1}{CH_2F}-\underset{\underset{CH_3}{\vert\,2}}{\overset{3}{CF}}-\overset{4}{SO_2F}$ (LVIII)	[d]40.68 d, m (SO_2F); −158.83 q, d, d, d, d (CF); −229.94 t, d, d, q (CH_2F); $^{2}J_{H^1,F^1} = 46$ Hz; $^{3}J_{F^1,F^3} = 6.4$ Hz; $^{3}J_{H^2,F^3} = 22.8$ Hz; $^{3}J_{H^{1A},F^3} = 10.8$ Hz; $^{3}J_{H^{1B},F^3} = 9.6$ Hz; $^{3}J_{F^3,F^4} = 2.4$ Hz; $^{4}J_{F^1,F^4} = 16.2$ Hz	
 $\overset{1}{CF_3}-\underset{\underset{CF_3}{\vert}}{\overset{2}{CH}}-\overset{3}{SO_2F}$ (LIX)	[d]66.26 sep, d (SO_2F); −62.13 dd ($2CF_3$); $^{3}J_{H^2,F^3} = 1.9$ Hz; $^{3}J_{H^2,F^1} = 7.0$ Hz; $^{4}J_{F^1,F^3} = 10.9$ Hz	6.08 sep, d
 $\overset{1}{CF_3}-\underset{\underset{CHF_2}{\vert\,2}}{\overset{3}{CH}}-\overset{4}{SO_2F}$ (LX)	[d]≈66.3 m (SO_2F); −61.84 d, d, d, d, d (CF_3); −122.0 d, m (CHF_2, F^A); −123.0 d, m (CHF_2, F^B); $^{2}J_{F^A,F^B} \approx 300$ Hz; $^{2}J_{H^2,F^2} = 52$ Hz; $^{3}J_{F^1,H^3} = 8.3$ Hz; $^{4}J_{F^1,F^4} = 9.8$ Hz; $^{4}J_{F^1,F^2} \approx 9$ Hz; $^{4}J_{F^1,H^2} \approx 1.9$ Hz	

Table 2 (*Continued*)

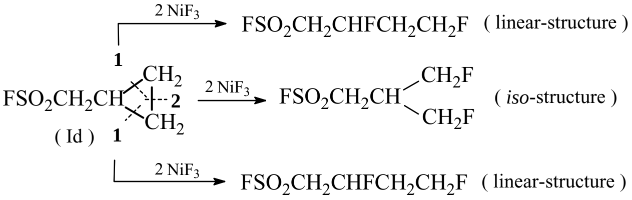
Compound	^{19}F (δ, ppm)	^{1}H (δ, ppm)
 $\overset{1}{CHF_2}-\underset{\overset{\mid\,2}{CHF_2}}{\overset{3}{CH}}-\overset{4}{SO_2F}$ (LXI)	^{d}65.97 sep, d, t (SO_2F); −121.60 d, m ($2CHF_2$); $^{2}J_{H^1,F^1} = 53$ Hz; $^{3}J_{H^3,F^4} = 3.5$ Hz; $^{4}J_{F^{1,2},F^4} = 10.8$ Hz; $^{4}J_{H^1,F^4} = 1.9$ Hz	
 $\overset{1}{CH_2F}-\underset{\overset{\mid\,2}{CH_2F}}{\overset{3}{CH}}-\overset{4}{SO_2F}$ (LXII)	^{d}−230.12 t, d, d, t ($2CH_2F$); $^{2}J_{H^1,F^1} = 46$ Hz; $^{3}J_{F^1,H^3} = 26.9$ Hz; $^{4}J_{F^{1,2},F^4} = 11.6$ Hz; $^{4}J_{F^1,H^2} = 4.2$ Hz; signal of SO_2F group is overlapped with another signal	
 $\overset{1}{CH_2F}-\underset{\overset{\mid\,2}{CH_3}}{\overset{3}{CH}}-\overset{4}{SO_2F}$ (LXIII)	^{d}49.00 d, m (SO_2F); −225.91 t, d, d, q (CH_2F); $^{2}J_{H^1,F^1} = 46.5$ Hz; $^{3}J_{F^1,H^3} = 22.1$ Hz; $^{4}J_{F^1,F^4} = 14.5$ Hz; $^{4}J_{F^1,H^2} \approx 1$ Hz	

[a] Spectra were recorded for a neat liquid with CD_3CN-film. CCl_3F and TMS served as internal references.

[b] ^{19}F and ^{1}H NMR spectra were recorded at −30 °C for a neat liquid.

[c] Position of the signal depends on the concentration.

[d] Solvent: CD_3CN, CCl_3F internal.

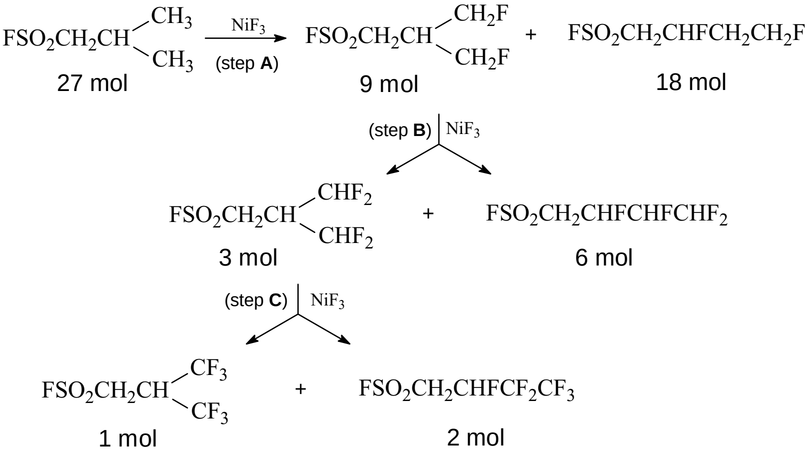


Scheme 6.

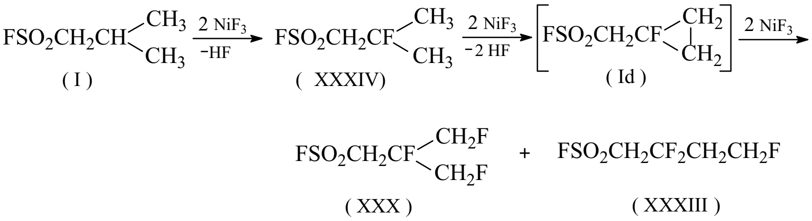
real molar ratio linear-to-*i*-structure in the resulting mixture should be substantially less than 26:1 but higher than 2:1.

Analysis of the reaction mixture obtained from ECF of *i*-butylsulfonyl fluoride (I) indicated that the molar ratio, *n*-nonafluorobutylsulfonyl fluoride (IV)-to-*i*-nonafluorobutylsulfonyl fluoride (V) was about 7.6:1 (see Scheme 5 and Table 1). Taking into consideration all partially fluorinated products present in the mixture (see Table 1) and the products, which are formed from the *i*-structure by loss of methyl groups or conversion to acyl fluorides and *s*-butylsulfonyl fluorides, the corrected ratio is about 4.3:1. This is in good agreement with the prediction of our model (Schemes 1 and 3).

Remarkably, all partially fluorinated compounds of the *n*-butyl-type, XVI–XXII and XXXI–XXXIII bear a $-CF_2-$ group in the β-position to the SO_2F group (Tables 1 and 2). At the same time fluorination in the γ- and especially the



Scheme 7.



Scheme 8.

α-positions has occurred later, in accordance with the proposed mechanism (see Schemes 6 and 7). By opening of the *cyclo*-propane- to the *n*-butyl-structure, the fluorine atoms occupy positions β and ω, but not positions α and γ in respect to the SO_2F group (Scheme 8).

Both XXX and XXXIII are found among the other products (see Table 1).

The concentrations of products $CF_3CH_2CF_2CH_2SO_2F$ (XXII) and $CF_3CF_2CF_2CH_2SO_2F$ (XVIII) in the resulting mixture is much higher than those of the corresponding compounds, containing one additional fluorine atom (Table 1). This observation indicates that by the opening of the *cyclo*-propane structure into the linear *n*-butyl structure (Scheme 8) the fluorine atoms are placed preferably on the β- and ω-positions but not into positions α and γ with respect to the SO_2F group and the fluorination process on the positions α and γ is hindered by the presence of the bulky fluorinated SO_2F group and neighboring CF_2 and CF_3 groups.

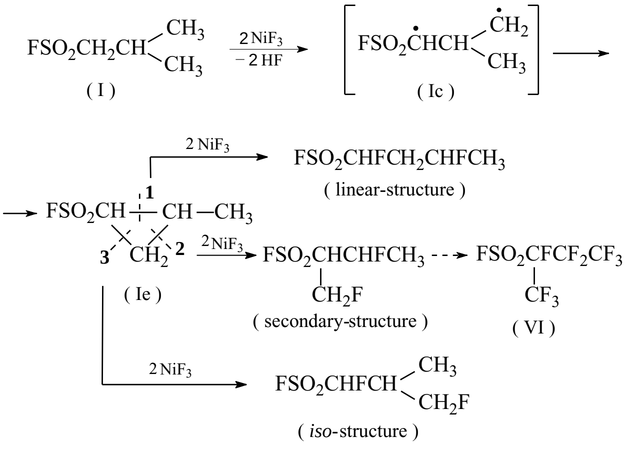
In $(CF_3)_2CHCF_2SO_2F$ (XI), replacement of the last hydrogen atom in the *i*-position is difficult and therefore the content of this compound in the mixture is relatively high (Table 1).

The presence of perfluoro-(1-methylpropane)sulfonyl fluoride (VI) in the mixture indicates that during the ECF process, *i*-butylsulfonyl fluoride (I) isomerizes, not only to the linear *n*-butyl structure but also to the *s*-butyl structure, possibly according to the mechanism (Scheme 9).

Formation of biradical (Ic) on the surface of Ni/NiF_x anode could be hindered by the bulky FSO_2 group, possibly explaining why perfluoro-*s*-butylsulfonyl fluoride (VI) is a minor product in the mixture after ECF of *i*-butylsulfonyl fluoride. Compound $FSO_2CH(CH_2F)CHFCH_3$ (Scheme 9) can undergo additional fluorination or participate in the next step of *cyclo*-propane ring-contraction/ring-opening reactions. The probability of the *cyclo*-propane ring contraction described by Scheme 9 is low. Therefore, the concentration of perfluoro-*s*-butylsulfonyl fluoride (VI) is low and is extremely low for perfluoro-*t*-butylsulfonyl fluoride (VII) (see Table 1 and Scheme 5).

Formation of perfluoroacyl fluorides during electrochemical fluorination of alkanesulfonyl fluorides is a phenomenon which appears have been mentioned only once previously in the literature [44] but was not investigated. Recently, Behr and Cheburkov [45] have published the conversion of perfluoroalkanesulfonyl fluorides into perfluoroacyl fluorides catalyzed by SbF_5.

A possible mechanism of this process is based on the intermediate formation of fluorosulfinic acid perfluoalkylesters [45]. A similar process can take place in the electrochemical cell.



Scheme 9.

At the early stage of fluorination, formation of carbo-cations of type **B** (Scheme 3) is possible. For carbo-cation (Ia) (Scheme 10) no optimized open-chain geometry was found (no energy minimum) by quantum chemical calculations [46]. Assuming a reasonable starting geometry for cation (Ia) led directly to the cyclic structure (Ib) (Scheme 10).

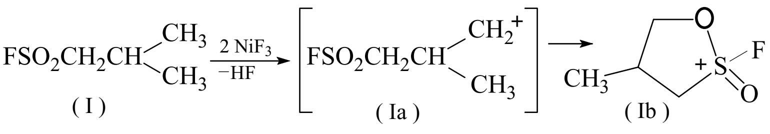
Possibly, cyclocations such as (Ib) could be intermediates in the conversion of fluorinated sulfonyl fluorides into acyl fluorides (Scheme 11).

Formation of cyclic cations like (Ib) is possible, not only from carbo-cations generated directly from the starting material (I) but also from the later stage of the fluorination process. Sulfonium salts of type (Ib) are known in the literature and the equilibrium between the sulfonium salt (Ib) and the sulfurane (If) is well established [47,48]. Nucleophilic attack by fluoride ion on the activated α-carbon atom in (Ib) should open irreversibly the cyclic into the *i*-structure (Ig) (Scheme 11).

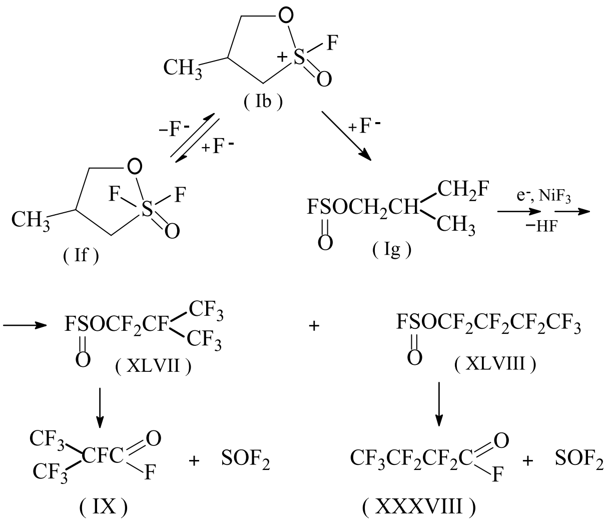
The mechanism of formation of perfluorooxetane (XXXVII) and perfluorooxirane (XXXIX) is not clear.

2.3. Electrochemical fluorination of *i*-propylsulfonyl fluoride

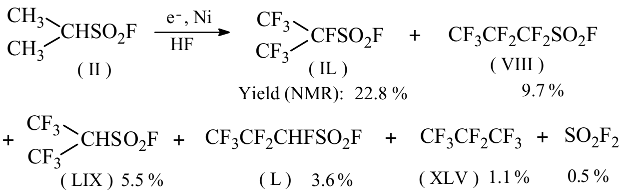
ECF of *i*-propylsulfonyl fluoride (II) results in branched and linear fluoropropylsulfonyl fluorides (see Scheme 12 and Table 3) together with partially fluorinated compounds bearing one or two hydrogen atoms.



Scheme 10.



Scheme 11.



Scheme 12.

The ratio of linear-to-branched molecules is about 1:3 (see Table 3). This ratio is not consistent with the prediction of our *cyclo*-propane model (Schemes 1 and 3), probably due to hindrance to *cyclo*-propane ring formation opening by the neighboring FSO_2 group (Scheme 13).

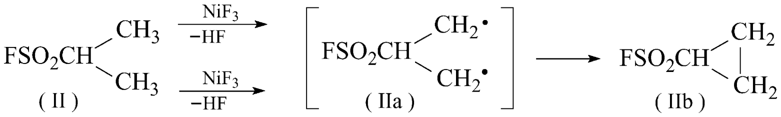
Electrochemical fluorination of *i*-propylsulfonyl fluoride (II) is preferred over one-site (methyl group) fluorination, which leads to the enrichment of compounds with the *i*-structure. The presence of compounds (for example,

Table 3
Composition of the mixture obtained after electrochemical fluorination of *i*-$C_3H_7SO_2F$

Compound	bp (°C)	Contents (mol%)		Total in the mixture (mol%)
		Product from the cell (24.4 g)	Product from trapped at −78 °C (23.2 g)	
$CF_3\text{–}\underset{CF_3}{\underset{\mid}{CF}}\text{–}SO_2F$ (IL)	–	38.5	57.6	48.0
$CF_3\text{–}CF_2\text{–}CF_2\text{–}SO_2F$ (VIII)	36 [44]	21.4	19.7	20.6
$CF_3\text{–}CF_2\text{–}CHF\text{–}SO_2F$ (L)	77 [71]	1.5	–	0.8
$CF_3\text{–}CF_2\text{–}CH_2\text{–}SO_2F$ (LI)	–	3.4	–	1.7
$CF_3\text{–}CH_2\text{–}CF_2\text{–}SO_2F$ (LII)	–	<0.1	–	<0.1
$CHF_2\text{–}CF_2\text{–}CH_2\text{–}SO_2F$ (LIII)	–	0.3	–	≈0.1
$CF_3\text{–}\underset{CHF_2}{\underset{\mid}{CF}}\text{–}SO_2F$ (LIV)	–	2.9	–	1.5
$CHF_2\text{–}\underset{CHF_2}{\underset{\mid}{CF}}\text{–}SO_2F$ (LV)	–	1.9	–	0.9
$CHF_2\text{–}\underset{CH_2F}{\underset{\mid}{CF}}\text{–}SO_2F$ (LVI)	–	0.6	–	0.3
$CH_2F\text{–}\underset{CH_2F}{\underset{\mid}{CF}}\text{–}SO_2F$ (LVII)	–	≈0.1	–	<0.1
$CH_2F\text{–}\underset{CH_3}{\underset{\mid}{CF}}\text{–}SO_2F$ (LVIII)	–	≈0.1	–	<0.1
$CF_3\text{–}\underset{CF_3}{\underset{\mid}{CH}}\text{–}SO_2F$ (LIX)	–	23.2	–	11.7
$CF_3\text{–}\underset{CHF_2}{\underset{\mid}{CH}}\text{–}SO_2F$ (LX)	–	0.9	–	0.5
$CHF_2\text{–}\underset{CHF_2}{\underset{\mid}{CH}}\text{–}SO_2F$ (LXI)	–	0.3	–	≈0.1
$CH_2F\text{–}\underset{CH_2F}{\underset{\mid}{CH}}\text{–}SO_2F$ (LXII)	–	0.2	–	≈0.1
$CH_2F\text{–}\underset{CH_3}{\underset{\mid}{CH}}\text{–}SO_2F$ (LXIII)	–	≈0.1	–	<0.1
$CH_3\text{–}\underset{CH_3}{\underset{\mid}{CH}}\text{–}SO_2F$ (II, starting material)	32–33/13 mbar [72]	4.2	–	2.2
$CF_3\text{–}CF_2\text{–}SO_2F$ (XXXV)	8 [44]	–	2.7	1.3
$CF_3\text{–}SO_2F$ (XXXVI)	−21 [62]	–	<0.1	<0.1

Table 3 (*Continued*)

Compound	bp (°C)	Contents (mol%)		Total in the mixture (mol%)
		Product from the cell (24.4 g)	Product from trapped at −78 °C (23.2 g)	
CF_3–CF_2–COF (XL)	−27 [64]	–	1.8	0.9
CF_3–CF_2–CF_3 (XLV)	−38 [67]	–	4.9	2.4
CF_3–CHF–CF_3 (LXIV)	−16 [73]	–	0.8	0.4
CF_3–CH_2–CF_3 (LXV)	−0.5 [74]	–	1.8	0.9
CF_3–CF_2–CHF_2 (LXVI)	−17 [75]	–	1.1	0.5
CF_3–CF_3 (XLVI)	−78 [67]	–	0.5	0.2
SO_2F_2	−55 [70]	–	2.2	1.1
OSF_2	−44 [70]	–	6.8	3.4



Scheme 13.

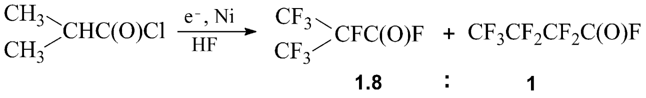
$CF_3CH_2CF_2SO_2F$) in the reaction mixture (see Table 3) confirms, that the process of *cyclo*-propane ring contraction–additional fluorination still takes place to an extent.

Gambaretto et al. (Scheme 14; [26]) have observed the same phenomenon in electrochemical fluorination of *i*-butyryl chloride.

The ratio of the linear-to-*i*-structure of about 1:1.8 [26] is at variance with the prediction of our model. We suggest that a bulky fluorinated –C(O)F group α- to the reaction center, as in the –SO_2F group case, hinders isomerization via the intermediate *cyclo*-propane ring contraction, ring-opening process. Isomerization of *i*-butyryl chloride is higher (36% [26]) than found for *i*-propylsulfonyl fluoride, as the –C(O)F group is less bulky. In order to investigate this further we carried out the electrochemical fluorination of a similar compound, that has the *cyclo*-propane-ring, *cyclo*-propane carboxylic acid fluoride (III).

2.4. Electrochemical fluorination of cyclo-propane carboxylic acid fluoride (III)

The electrochemical fluorination of compound (III) leads to the formation of a mixture of perfluorobutyryl fluorides with linear (XXXVIII) (NMR yield 27.5%) and *i*-structures (IX) (yield 11.9%). Other compounds formed include of perfluoroethane (yield 4.8%), propane (yield 2.0%), and cyclobutane (yield 3.5%). A rationalization is given in Scheme 15.



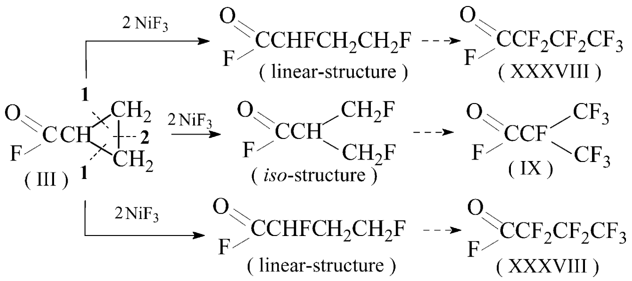
Scheme 14.

Contrary to ECF of *i*-butyryl chloride [26] (see above), *n*-heptafluorobutyryl fluoride (XXXVIII) and *i*-heptafluorobutyryl fluoride (IX) are formed in a molar ratio of 2.3:1. This is in good agreement with the prediction of our model (Schemes 1 and 3).

2.5. Comparisons with other studies

The following is an attempt to determine the applicability of our model to published data.

In 1974, Plashkin et al. reported the isomerization of heterocyclic *N*-*i*-alkylamines during electrochemical fluorination; the migration of the alkyl group was proposed [25]. The molar ratio of the perfluoro-*N*-(*n*-butyl)pyrrolidine and perfluoro-*N*-(*i*-butyl)pyrrolidine resulting from ECF of *N*-*i*-butylpyrrolidine is 2:1, in harmony with our model. The analysis of the reaction mixture after electrochemical fluorination of *N*-*i*-butylpiperidine [25] gives a similar result. The molar ratio of the sum of the products perfluoro-*N*-(*n*-butyl)piperidine plus perfluoro-*N*-(*n*-butyl)-3-(trifluoromethyl)pyrrolidine having an *n*-structure and the sum of product perfluoro-*N*-(*i*-butyl)piperidine plus



Scheme 15.

perfluoro-*N*-(*n*-propyl)piperidine is again 2:1. Perfluoro-*N*-(*n*-propyl)piperidine is formed by splitting off the methyl group in the position 2 of the *i*-butyl chain and should be included into the sum of the products with a branched structure.

The picture is different for the mixture obtained by the electrochemical fluorination of *N*-*i*-propylpiperidine [25]. The ratio of the products perfluoro-*N*-(*n*-propyl)piperidine plus perfluoro-*N*-(*n*-propyl)-3-(trifluoromethyl)pyrrolidine to perfluoro-*N*-(*i*-propyl)piperidine plus perfluoro-*N*-(*n*-ethyl)-piperidine is 1.17:1, less than predicted by our model. It seems that nitrogen in the aliphatic chain hinders the ring closing–ring opening reactions similar to the SO_2F group in $FSO_2CH(CH_3)_2$. That leads to a larger content of the *i*-product in the mixture. The influence of the nitrogen on the efficiency of five and six-membered ring formation during ECF is known [22–24]. Abe et al. [24] have proposed the strategic incorporation of a nitrogen atom in the aliphatic chain to prevent the intramolecular cyclization.

In the mixture from ECF of *N*-*t*-butylpyrrolidine [25] the higher probability of *cyclo*-propane ring formation involving all three methyl groups in the starting compound should be considered. The molar ratio between the sum of isomeric products perfluoro-*N*-(*s*-butyl)pyrrolidine, perfluoro-*N*-(*i*-butyl)pyrrolidine, perfluoro-*N*-(*n*-butyl)pyrrolidine and the product perfluoro-*N*-(*t*-butyl)pyrrolidine with the structure of the starting material is 5.25:1, in good agreement with our prediction.

ECF of *N*-(ω-chloroalkyl)-hexahydroazepines yields the mixture of corresponding fluoro-(*N*-alkyl-hexahydroazepines) together with isomeric fluoro-(1-alkyl-methylpiperidines) [49]. According to our model, the formation of biradicals is possible by the simultaneous oxidation of two C–H bonds with NiF_3 on the surface of the anode at the positions 2 and 4; 3 and 5; 4 and 6; 5 and 7 of the hexahydroazepine ring. Ring closure reactions at these positions with subsequent C–C bond cleavage in the *cyclo*-propane derivatives formed lead to the formation of the mixed perfluoro-1-alkyl-methylpiperidines with predicted molar ratio, $3\text{-}CF_3$:$4\text{-}CF_3$:$2\text{-}CF_3$ of 1:0.5:0.5, respectively. Due to the influence of the nitrogen atom, the yield of the $2\text{-}CF_3$ compound may be lower. Consequently, the experimental product distribution, 1:0.53:0.29 [49,50], is in good agreement with our model.

ECF of N-substituted piperidines, leads to the formation of perfluoro-$3\text{-}CF_3$-pyrrolidine derivatives [6,27,51]. Obviously, *cyclo*-propane ring closure reaction between the positions 2 and 4, 4 and 6 of the piperidine ring is hindered by nitrogen. The only possibility is ring formation between the positions 3 and 5. In this case, subsequent *cyclo*-propane ring opening reactions during ECF can give either $3\text{-}CF_3$-pyrrolidine derivatives or compounds with the structure of the starting material, in harmony with experimental results [6,27,51]. Our proposed model (Schemes 1 and 3) is able to explain not only the isomerization of branched alkyl chains into linear chains or ring contraction isomerizations, but also the isomerization of *n*-alkyl into *i*-alkyl groups.

The formation of cyclic products in the production of perfluorooctanoic acid, $C_7F_{15}COOH$, with the Simons method is well known. Approximately 60% of the starting material, $C_7H_{15}C(O)F$, is converted into perfluorooxolanes and perfluorooxanes [5] with perfluoro-*n*-alkyl and perfluoro-*i*-alkyl groups in position 2. This indicates that ring closure is straight forward and that the isomerization of alkyl groups in position 2 occurs after oxolane or oxane ring formation. The content of perfluoro-2-alkyl-oxolanes in the mixture after ECF is particularly high and corresponds to 42 wt.% [5]. Product perfluoro-2-(*n*-butyl)oxolane reflects the intramolecular cyclization during the Simons process via attack of a carbon centered radical on oxygen [5]. The products perfluoro-2-(*s*-butyl)oxolane and perfluoro-2-(*i*-butyl)oxolane are formed similarly but with subsequent isomerization of a *n*-butyl into *s*-butyl or *i*-butyl groups, probably involving intermediate formation of *cyclo*-propane derivatives between the positions 1 and 3, 2 and 4 of the *n*-butyl chain. The formation of a *t*-butyl structure is not possible and it was not found in the reaction mixture [5].

3. Conclusion

Our new model for the mechanism of ECF process (Schemes 1 and 3) is able to explain or to predict:

(i) the isomerization of branched alkyl to linear chains;
(ii) the isomerization of linear to branched alkyl chain;
(iii) ring contraction isomerization.

The key step in the formation of isomeric products during the Simons process is the ring closure reaction via carbocationic or biradical intermediates. A quantitative estimation of product distribution patterns is possible. The influence of bulky groups ($-SO_2F$, $-C(O)F$, etc.) or the nitrogen atom on the isomerization can be rationalized.

4. Experimental

4.1. Apparatus

A stainless steel Simons-type cylindrical cell (total volume 390 cm^3) with an array of nickel anodes (effective anodic area: $S = 4.27\ dm^2$) and cathodes with the same effective area was used for ECF of *i*-butylsulfonyl fluoride and *cyclo*-propane carbonic acid fluoride. The cell was equipped with a stainless steel condenser and two FEP-traps cooled to $-78\ ^\circ C$. ECF of *i*-propylsulfonyl fluoride was carried out in a cell with a total volume of 310 cm^3, effective anodic area, $S = 3.75\ dm^2$. In all experiments the temperature of the cell body was maintained at $0\ ^\circ C$ and the temperature of the condenser was kept at $-30\ ^\circ C$.

4.2. Analytical procedures

^{19}F and ^{1}H NMR spectra were measured on the Brucker WP 80 SY (80.1 MHz for ^{1}H NMR and 75.4 for ^{19}F NMR), Brucker Advance 300 (300.13 MHz for ^{1}H NMR and 282.40 for ^{19}F NMR) and Brucker DRX 500 (500.13 MHz for ^{1}H NMR and 470.59 for ^{19}F NMR) spectrometers from neat liquids obtained in the Simons cell and collected in the traps at −78 °C. Spectra were recorded using FEP sample tubes inside a 5 mm thin walled NMR tube with an acetonitrile-D_3 film as an external lock and CCl_3F as internal reference. For the proton spectra the frequency of the TMS in acetonitrile-D_3 solution was used as a standard frequency. For complete identification of all compounds, the product from the cell and traps after washing with water and drying was separated into several narrow fractions by distillation. High resolution ^{19}F and ^{1}H NMR spectra were measured for every fraction in $CDCl_3$ solution. NMR data are given in the Table 5. Published ^{19}F and ^{1}H NMR data for different partially fluorinated *n*- and *i*-butanes [52,53] were very useful for complete identification of the substances in the ECF experiment with *i*-butylsulfonyl fluoride.

The purity of the starting materials was checked with a Perkin-Elmer gas chromotograph using a column (4% siliconoil DC 2000 on Chromosorb) of length 1.5 m and 2 mm i.d. at 120 °C. The temperature of the injector was 130 °C and the temperature of the FID detector was maintained at 250 °C. The carrier gas was He.

4.3. Calculations

Quantum chemical calculations were performed with the GAUSSIAN 98 software package [46] using the density functional theory (DFT) [54]. All molecule geometries were optimized to standard convergence criteria using a DFT hybrid method with Becke's [55,56] non-local three parameter exchange and the Lee et al. [57] correction (B3LYP) and a 6–31G(d) basis set for the C_4 species and 6–311G(d, p) for the C_3 compounds. The calculations were performed for $C_4H_8SO_2F$ radicals (*n*-, *i*-, and *s*-structures), $[C_4H_8SO_2F]^+$ cations (*n*-, *i*, and five-membered cyclic structures), $[C_3H_6C(O)F]^+$ cations (*n*-, *i*-, cyclopropyl structures), C_2H_4-CHC(O)F biradicals (triplet and singlet state, the last one is spontaneously cyclized into a *cyclo*-propane structure), and the corresponding mono- and bifluorinated compounds as isolated gaseous species.

The resulting relative energies of different isomers and reaction enthalpies do not include any influences from the solvent HF nor the electric field near the anode.

4.4. Chemicals

i-Butylsulfonyl fluoride was synthesized from *i*-butylsulfonyl chloride (obtained by the method [58,59]) in the following manner: 297.5 g (1.9 mol) of *i*-butylsulfonyl chloride were mixed with a saturated solution of potassium bifluoride in water (200 g, 2.56 mol of KHF_2 in 200 cm^3 of H_2O) in a 1 l polyethylene flask. The reaction mixture was intensively stirred at room temperature during three days (after 24 and 48 h 50 cm^3 of H_2O were added) and the organic phase was separated and filtered off from the white deposit. Two hundred and forty grams of the resulting clear liquid (contained 70% of *i*-$BuSO_2F$ and 30% of *i*-$BuSO_2Cl$) were mixed again with 70 g (0.9 mol) of KHF_2 in 150 cm^3 of H_2O and stirred at room temperature additionally during 4 days. The organic phase was separated, washed with water, filtered and dried with Na_2SO_4. One hundred ninety grams of *i*-butylsulfonyl fluoride (purity of 98.6% by GC analysis) were obtained (yield 71.4%). ^{19}F NMR spectrum (solvent: $CDCl_3$; standard internal CCl_3F) δ (ppm): −57.50 t (SO_2F). ^{1}H NMR spectrum (solvent: $CDCl_3$; standard: internal TMS) δ (ppm): 1.15 dd (CH_3), 2.23 t, sep (CH), 3.43 dd (CH_2); $^5J_{H,F} = 0.9$ Hz, $^3J_{H,H} = 6.7$ Hz, $^3J_{H,F} = 4.0$ Hz.

i-Propylsulfonyl fluoride (purity 98.7% by GC analysis) was synthesized in 91% yield from *i*-propylsulfonyl chloride by halogen exchange with KF in water.

cyclo-Propane carboxylic acid fluoride was prepared in situ from the corresponding chloride (Acros Organics) by dissolving in anhydrous HF at −78 °C with following warming up (slowly and carefully by the reason of HCl evolution) to 5 °C. The formation of *cyclo*-propane carboxylic acid fluoride was confirmed by ^{19}F NMR spectra (solvent HF) at −20 °C: 29.03 ppm, d [C(O)F], $J_{H,F} = 8.2$ Hz. The absence of other signals in the spectra confirms that the *cyclo*-propane ring remains untouched by the treatment with HF.

The solution of *cyclo*-propane carboxylic acid fluoride in HF (two different concentrations: 31.9 and 45.7 wt.%), was used for the electrochemical fluorination.

Caution! Anhydrous HF is an extremely hazardous chemical. Good ventilation and proper protecting clothes are required for the work with this substance. For details see [1].

4.5. Electrochemical fluorination of i-butylsulfonyl fluoride

One hundred thirty grams of *i*-butylsulfonyl fluoride were added in 10 equal portions (firstly at the beginning and subsequently after 46.7; 89.4; 135.5; 180.2; 219.6; 264.3; 309.5; 356.5 and 400.9 A h, respectively) to 334 g of liquid hydrogen fluoride previously electrolyzed in the cell for 28 h. The gaseous products from the cell were passed through the condenser at −30 °C and two FEP traps held at −78 °C. The electrolysis, which proceeded at a cell voltage of 4.8–5.2 V and a current density of 0.42–0.47 A/dm^2, was completed after consumption of 534.6 A h (119.3% of the theoretical value calculated for a 18 electron process).

Seventy grams of a transparent liquid were drained from the cell, washed with water and dried over $MgSO_4$. Dilution of the HF solution from the cell with ice-water gave in addition, 58 g of a liquid, which was dried over $MgSO_4$.

Table 4
Added mass of starting material (i-$C_3H_7SO_2F$) vs. electricity consumed

Mass of i-$C_3H_7SO_2F$ (g)	Electricity consumed (A h)
15.00	0
12.05	44.80
11.04	84.72
10.97	122.68
5.43	160.98

Twenty-four grams of a transparent liquid were obtained from the trap after separation from the HF layer. Analyses of all those samples was carried out by means of ^{19}F NMR spectroscopy. Data are given in the Tables 1 and 2.

4.6. Electrochemical fluorination of i-propylsulfonyl fluoride

54.49 g (0.432 mol) of *i*-propylsulfonyl fluoride were added in five portions, Table 4, to 229 g of liquid hydrogen fluoride previously electrolyzed in the cell for 24 h. The gaseous products from the cell were passed through the condenser at −30 °C and two FEP traps held at −78 °C. The electrolysis, which proceeded at a cell voltage of 5.0–5.2 V and a current density of 0.44–0.45 A/dm^2, was completed after consumption of 195.0 A h (120.7% of the theoretical value calculated for a 14 electron process).

18.9 g of a transparent, non-mixable with HF liquid was drained from the cell. Dilution of the HF solution from the cell with ice-water gave in addition 5.5 g of a liquid, which was dried over $MgSO_4$ and combined with the product separated from the cell. This mixture (24.4 g) was subjected to the analysis and fractional distillation. 23.2 g of a transparent liquid were obtained from the trap after separation from the HF layer. Analyses of all those samples was carried out by means of ^{19}F NMR spectroscopy. Data are given in the Tables 2 and 3.

4.7. Electrochemical fluorination of cyclo-propane carboxylic acid fluoride (III)

84.1 g (0.955 mol) of *cyclo*-propane carboxylic acid fluoride (III) dissolved in anhydrous HF (see Section 4.4) were added in six portions, Table 5, to 343 g of liquid hydrogen fluoride previously electrolyzed in the cell for 48 h. The gaseous products from the cell were passed through the condenser at −30 °C and two FEP traps held at −78 °C. The electrolysis, which proceeded at a cell voltage of 4.9–5.2 V and a current density of 0.35–0.47 A/dm^2, was completed after consumption of 312.7 A h (101.9% of the theoretical value calculated for a 12 electron process). 97.8 g of a transparent liquid were obtained from the trap after separation from the HF layer. Analyses of this sample was carried out by means of ^{19}F NMR spectroscopy.

Table 5
Added mass of starting material ($cyclo$-C_3H_5COF) vs. electricity consumed

Mass of $cyclo$-C_3H_5COF (g)	Electricity consumed (A h)
13.7	0
19.1	35.67
13.1	86.55
12.3	139.87
14.1	177.95
11.8	220.65

Acknowledgements

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