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Free radical and isomerisation processes during the electrochemical fluorination of *n*-butyryl chloride, *i*-butyryl chloride and pivaloyl chloride in anhydrous hydrogen fluoride

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Abstract

Electrochemical perfluorination (ECPF) of the title compounds containing primary, secondary and tertiary carbon atoms was carried out in anhydrous hydrofluoric acid (AHF). Detailed analysis of major and minor products suggest that carbon chain isomerisation involving *cyclo*-propane intermediate is more prevalent during ECPF of *i*-butyryl chloride when compared to *n*-butyryl chloride. Simple statistical probability involving free radical intermediates also support this observation. ECPF involving *cyclo*-propane intermediate is even more prevalent in pivaloyl chloride containing three methyl substituents. In this case, perfluorinated *cyclo*-propane intermediates were also observed in the product sample. Distribution of minor perfluorinated and partially fluorinated products also suggest the predominant role of normal free radical pathway involving single-electron transfer.

Keywords: Electrochemical fluorination; *n*-Butyryl chloride; *i*-Butyryl chloride; Pivaloyl chloride; *cyclo*-Propane intermediate

1. Introduction

Electrochemical perfluorination (ECPF) process consists of essentially a number of electron transfer and associated chemical steps. For example, conversion of *i*-butyryl fluoride to perfluoro-*i*-butyryl fluoride involves removal of 14 electrons and 7 protons from the molecule and replacement of 7 fluoride ions (Scheme 1).

In addition to this desired process, additional competitive processes involving C–C bond cleavage, isomerisation and cyclisation process may also occur simultaneously. Hence, comprehensive understanding of the detailed mechanistic pathways has eluded researchers in this field over five decades despite widespread commercial exploitation of the process.

The present state of understanding of the mechanism of electrochemical fluorination [1] involves high valent NiF_3 film mediated free radical process as shown in Scheme 2.

Each hydrogen is replaced by a similar sequential process and the free radical intermediate formed during the overall step (Eq. (1) in Scheme 2) can undergo additional chemical transformations such as cyclisation and isomerisation mentioned above. Systematic analysis of a variety of small and large reactants using mainly NMR data of partially as well as perfluorinated samples were found to be in agreement with free radical pathway [2–7]. There is also reasonable consensus towards this pathway in recent times [8–16].

Carbon chain isomerism is a common phenomena frequently encountered in electrochemical fluorination. Formation of a *cyclo*-propane intermediate through 1,3 coupling of carbon free radicals formed on NiF_3 surface due to preferable orientation was proposed to quantitatively understand the isomerisation process as shown in Scheme 3 [17].

The *cyclo*-propane intermediate containing three C–C bonds α, β and γ can now undergo cleavage and fluorination on all the

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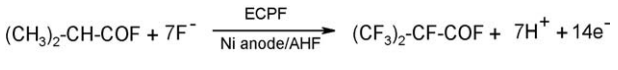
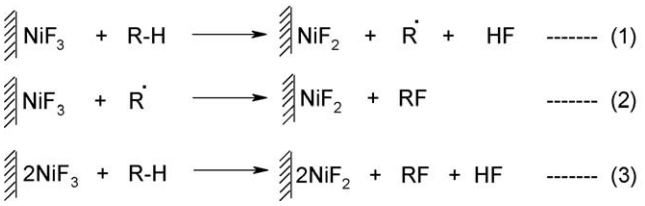


Scheme 1.



Scheme 2.

three bond positions. Cleavage at γ position above will give the fluorinated product with original carbon skeleton. Further cleavage at α or β positions would lead to formation of a new isomer (linear). Thus, there is an overall 2:1 chance of isomerisation for each pair of H atom removal from the $–CH_3$ group leading to *n* and *iso* product respectively. The formation of *n*-perfluoro alkyl derivative from the *i*-alkyl reactant in Scheme 3 would be much higher if the further replacement of two more pairs of H atoms also occur through this *cyclo*-propane intermediate. Statistically this ratio would be as high as 26:1 (see Scheme 7 reported by Ignat'ev et al. [17]).

The above model explains the mechanism of carbon chains isomerism during electrochemical fluorination at least qualitatively. Ignat'ev et al. found some quantitative correlation as well for the formation of higher amounts of perfluoro-*n*-butanesulfonyl fluoride during the electrochemical fluorination of *i*-butanesulfonyl fluoride and the formation of perfluoro-*n*-propanoyl fluoride during the ECPF of *cyclo*-propanoyl fluoride. However, ECPF of *i*-propanesulfonyl fluoride did not show agreement with this mechanism. Many other isomerisation processes reported earlier also are at variance with the predictions of *cyclo*-propane intermediate model [17]. It is apparent that single-free radical pathway (Scheme 1) and diradical/*cyclo*-propane pathway (Scheme 2) operate simultaneously during ECPF process.

Further experimental investigations focusing on the relative predominance of these two pathways would indeed be desirable. Some of the issues that need to be addressed include the following:

(i) Is the diradical/*cyclo*-propane model applicable for conversion of *n*-alkyl group to *i*-alkyl group as well? Is there any preferred direction from branched alkyl chain to linear alkyl chain or vice versa?
(ii) What are the effects of substituents on the three carbons forming the *cyclo*-propane intermediate?
(iii) Does the cyclization model work for reactant molecules containing trialkyl group as well?

The electrochemical fluorination of primary (*n*-butyryl chloride), secondary (*i*-butyryl chloride) and tertiary (pivaloyl chloride) carboxylic acid chlorides were taken up to address some of the issues stated above.

The ECPF of *n*-butyryl chloride (NBC) and *i*-butyryl chloride (IBC) was compared earlier by Gambaretto et al. [6]. The report indicated relatively higher conversion of *i*-butyryl fluoride to perfluoro-*n*-butyryl fluoride when compared to conversion of *n*-butyryl fluoride to perfluoro-*i*-butyryl fluoride. In the present work, a more detailed investigation into these two processes including partially fluorinated and cleavage products was undertaken. To our knowledge, the ECPF of pivaloyl chloride has not been studied in detail so far.

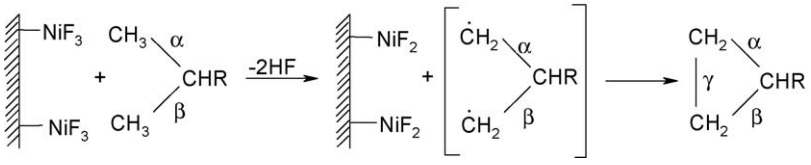
2. Results and discussion

2.1. Formation of perfluoro carboxylic acid and their product distribution

During the ECPF of IBC, NBC and pivaloyl chloride (PC) no perfluorinated product was recovered from the bottom of the electrochemical reactor. The vapor phase products were collected in the cold trap at −70 °C and the weight of total products obtained was taken at the same temperature. Typical experimental results obtained during the ECPF of the above three compounds are shown in Table 1. The current efficiency values are only indicative as these are obtained by assuming that no cleavage products were present in the product mixture.

For one compound namely IBC, the experiments were carried out at current densities ranging from 1.2 to 2.4 A/dm^2 (Table 1, experiment nos. 1–4). Relative decrease in total weight of products formed and hence current efficiency was noticed when the current density increased beyond 2 A/dm^2 (Table 1, experiment no. 4). Increasing the cell temperature to 10 from 5 °C (experiment no. 5) also did not have significant effect on total yield. In general, overall current efficiency of 40–46% could be achieved under optimum conditions. Further improvement in current efficiency up to 51% could be achieved with effective cooling of electrochemical reactor at −10 °C (Table 1, experiment no. 6).

The ECPF of NBC (Table 1, experiment no. 7) and PC (experiment no. 8) were also carried out under such optimum conditions. The perfluorinated products could once again be collected only in the cold trap. As is common in ECPF processes, more cleavage and volatility loss is noticed while



Scheme 3.

Table 1
Results of ECPF of *i*-butyryl chloride (IBC), *n*-butyryl chloride (NBC) and pivaloyl chloride (PC)

Experiment no.	Reactants	Current density (A/dm^2)	Total amount of reactant added (g)	Total charge passed (A h)	Perfluorinated product obtained (g)	Current efficiency (%)	Selectivity (mol%)[a]			
							PFBA (*i*)	PFBA (*n*)	PFPA	TFA
1	IBC	1.2	66.7	237	57.6	42.2	46.3	55.8	2.1	<0.5
2	IBC	1.6	106	376	102.4	47.3	42.7	55.4	1.9	<0.5
3	IBC	2.02	103	364	93.6	44.8	41.8	50.6	1.7	5.7
4	IBC	2.43	167.7	606	94.4	27.1	41.5	54.7	1.4	2.3
5	IBC[b]	1.6	112.1	380	100.8	46.1	45.7	42.8	3.1	8.3
6	NBC	2.02	104	370	80	37.6	6.9	92.0	1.0	<0.1
7	PC	1.6	76.9	215.6	44.8	37.7	7.6	12	21.0	<0.1
8	IBC[c]	1.6	110.1	384	113	51.2	54.4	44.8	0.8	<0.1

Note: Current efficiency was calculated based on the perfluorinated products obtained at the cold trap maintained at −70 °C. ECPF reactor and condenser were maintained at 5 and −30 °C, respectively, except for experiment nos. 5 and 6. Average cell voltage = 5.3 ± 0.2 V. PFBA, perfluorobutyric acid; PFPA, perfluoropropionic acid; TFA, trifluoroacetic acid. Volume of the electrolyte: 200 ml; active anode area: 2.47 dm^2.

[a] Based on ^{19}F NMR data.

[b] ECPF cell temperature maintained at 10 °C.

[c] ECPF cell temperature maintained at −10 °C.

moving from primary to tertiary carboxylic acid chlorides (compare experiment nos. 5, 7 and 8 in Table 1).

The total product from the trap was treated with alkali and then neutralised as described in Section 3. Though many other compounds were also present in trace quantities (Sections 3.2 and 3.3), the main constituents were found to be perfluoro carboxylic acids namely perfluoro-*i*-butyric acid (PFIBA), perfluoro-*n*-butyric acid (PFNBA), perfluoropropionic acid (PFPA) and perfluoroacetic acid (PFAA). The product distribution of these four acids in the eight experiments are summarised in Table 2.

These data clearly indicate that PFNBA is always formed in higher quantities during the ECPF of IBC (Table 1, experiment nos. 1–5) when the ECPF is carried out at a cell temperature of 5 °C. The product distribution between PFIBA and PFNBA is found to be around 45:55 (experiment nos. 1–4). Increase in cell temperature leads to slightly higher levels of cleavage products (experiment no. 5). A higher selectivity of PF *i*-butyric acid (54.4%) was obtained when the reactor temperature was maintained at −10 °C. Even under this condition around 45% of perfluoro-*n*-butyric acid was still obtained. Raising or lowering of the ECPF temperature thus decreases or increases perfluoro-*i*-butyric acid yield only through increase and decrease of cleavage product formation. Formation of significantly higher quantity of PFNBA in all these experiments (experiment nos. 1–6) indeed clearly suggests the diradical/*cyclo*-propane intermediate route of fluorination steps (Scheme 3) at least partially.

Quite interestingly ECPF of NBC leads to 92% yield of PFNBA. The isomer is noticed only to the extent of 6.9% (experiment no. 6, Table 2). This result is also in agreement with the earlier observation by Gambaretto et al. [6]. Two reasons may be attributed for this observation. In general, radical process involving one NiF_3 site and the carbon center of the organic molecule (Scheme 2) has much higher probability than the four centered interaction required for a diradical mechanism (Scheme 3). When the fluorination involves secondary or tertiary carbon atoms, the probability for orientation of 1–3 carbon atoms at the NiF_3 surface would be higher. In linear chain compounds this probability is indeed less and hence lowers isomerism.

Second even if the *cyclo*-propane intermediate is formed there is still a 2:1 possibility of formation of *n*-butyl derivative when compared to *i*-butyl compound during each pair of fluorine addition as in Scheme 4 for example, the cleavage of *cyclo*-propane intermediates at α and γ position would still lead to n-butyric acid intermediates, β cleavage alone would lead to i-butyric acid intermediate. Hence, even if the process proceeds through *cyclo*-propane intermediate, the mole ratio of PFNBA to PFIBA would be only 26:1 (see Scheme 7 in [17]). In general, wherever *cyclo*-propane intermediate pathway is followed, there is higher probability of formation of linear chain from secondary and tertiary carboxylic acids.

In pivaloyl chloride, all the three methyl groups of the compound lie in the same plane and hence there are much higher possibility for diradical pathway. Sterric factors would also lead to cleavage products. Due to this combined effect only small quantity of perfluoropivaloic acid could be identified in the NMR spectra (see Section 3.3). PFIBA and PFNBA are found to be the major products (experiment no. 7, Table 1). The overall yield of perfluorinated products was also lower for this compound.

2.2. Minor constituents of fluorinated products obtained during the ECPF of IBC

Analysis of the minor components using ^{19}F as well as ^{1}H NMR indicated that practically all the minor products obtained from ECPF of *n*-butyryl chloride are invariably observed in the ECPF products obtained from IBC as well. Hence more detailed analysis of minor products obtained during ECPF was confined to products obtained from IBC alone. The complete NMR data covering 22 compounds obtained from the product mixture during ECPF of IBC are listed in Table 2. These compounds are further classified under the four following categories:

Table 2
^{19}F and ^{1}H NMR data of polyfluorinated compounds obtained during the ECPF of *i*-butyryl chloride and *n*-butyryl chloride

No.	Structure	Chemical shift, δ (ppm)	J (Hz)
1	$(CH_3)_2CH\text{-}COOH$	a: 2.46 sept b: 1.07 d	$^3J\ H^a\ H^b = 6.9$ [18]
2	$(CH_3)_2CF\text{-}COOH$	a: −160.4 b: 1.68 d	$^3J\ H^b\ F^a = 22.2$
3	$H_3C\text{-}CF(CF_3)\text{-}COOH$	a: −73.0 b: −180.2 c: 1.71 dm	$^3J\ H^c\ F^b = 21.2$
4	$(CHF_2)_2CF\text{-}COOH$	a: −194 b: −134 d c: 6.52 td	$^2J\ HF = 55$ $^3J\ HF = 11.5$
5	$(CF_3)_2CH\text{-}COOH$	b: −64.3 a: 4.81 sept	$^3J\ HF = 8$
6	$(CF_3)_2CF\text{-}COOH$	a: −179.66 sept b: −74.38 d	$^3J\ FF = 7.8$ [17]
7	$CH_3\text{-}CH_2\text{-}CH_2\text{-}COOH$	a: 2.59 t b: 1.56 qt c: 0.89 t	$^3J\ H^c\ H^b = 7.6$ $^3J\ H^b\ H^a = 2.3$ [18]
8	$CH_3\text{-}CF_2\text{-}CF_2\text{-}COOH$	a: −128.0 b: −120.6 c: 1.78 tt	
9	$CF_3\text{-}CH_2\text{-}CF_2\text{-}COOH$	a: −105.6 c: −63.5 b: 3.17 qt	$^3J\ H^b\ F^c = 9.7$ $^3J\ H^b\ F^a = 5.2$
10	$HCF_2\text{-}CF_2\text{-}CF_2\text{-}COOH$	a: −126.8 b: −119.6 c: −127.5 d: 6.38 tt	$^2J\ HF = 52.5$
11	$CF_3\text{-}CF_2\text{-}CF_2\text{-}COOH$	a: −126.98 s b: −119.37 q c: −80.77 t	[19,20] $^3J\ F^{b,c} = 8.6$
12	$CH_3\text{-}CHF\text{-}COOH$	a: −172.5 b: 4.83 d, b c: 1.79 dd	$^2J\ HF = 47.6$ $^3J\ HF = 4.6$ $^3J\ HH = 2.3$
13	$CH_3\text{-}CF_2\text{-}COOH$	a: −105.5 b: 2.58 t	$^3J\ HF = 2.3$
14	$CF_3\text{-}CH_2\text{-}COOH$	b: −64.4 a: 3.4 q	$^3J\ HF = 10.9$
15	$CF_3\text{-}CHF\text{-}COOH$	a: −215.9 c: −75.4 b: 6.35 dq	$^2J\ H^a\ F^a = 52.5$
16	$CHF_2\text{-}CF_2\text{-}COOH$	a: −127.3 b: −134.3 d c: 6.58 tt	$J^2\ H^b\ F^b = 53$ $^2J\ H^b\ F^b = 53$ $^3J\ H^b\ F^a = 5.4$
17	$CF_3\text{-}CF_2\text{-}COOH$	a: −121.77 b: −83.02	[20]
18	$(CF_3)_2CHF$	a: −215.9 c: −75.6 b: 6.14 d, sept	$^2J\ HF = 41.8$ $^3J\ HF = 5.8$
19	$CF_3\text{-}COOH$	a: −75.5	[21]
20	CF_4	−64.4	[21]
21	$(CF_3)_2CF\text{-}CHF\text{-}COOH$	a: −185.0 c: −179.5 d: −74.4 b: 5.7 d, sept, d	$^2J\ H^a\ F^a = 42.4$ $^4J\ H^a\ F^d = 6.3$
22	$(CF_3)_3C\text{-}F$	a: −186.0 b: −75.6	[21]

(a) reactant IBC and its partially and perfluorinated products without cleavage (**1–6**);
(b) products based on partially and perfluorinated rearranged product, namely NBC (**8–11**);
(c) products based on cleavage of IBC or NBC (**12–20**);
(d) products from intermolecular methyl transfer (**21–22**).

The NMR data for each subgroup are summarised in Table 2. These data clearly suggest that both Schemes 2 and 3 are operative during the ECPF of IBC. Intermediates corresponding to these two pathways in each group are briefly indicated below.

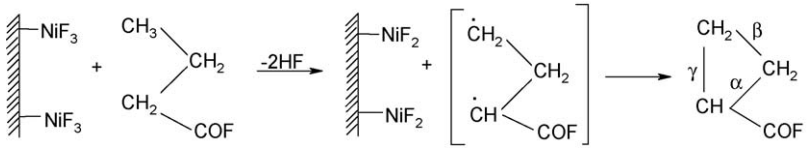
Among the partially fluorinated IBA derivatives (Table 2) compounds **4–6** may be attributed to be formed by *cyclo*-propane intermediate. Compounds **2** and **3** would have come only from free radical pathway. Compound **2** is an interesting intermediate involving first substitution at tertiary carbon.

If partial fluorination along with isomerisation occur during the ECPF of *i*-butyryl fluoride through *cyclo*-propane intermediate, fluorine addition would occur at α and β position of the resulting *n*-butyric acid (see Scheme 3, where R = COF). Compounds **9** and **10** would thus be accounted by *cyclo*-propane intermediate route. Compound **8** can however be formed only through radical pathway without *cyclo*-propane intermediate.

Methyl cleavage during ECPF of IBC leads to fluorine substituted propionic acids. Five such compounds (**12–16**) were identified in the product mixture. Methyl cleavage would normally accompany fluorine substitution at the cleavage position. Compound **14** namely CF_3CH_2COOH appears to be an exception involving methyl cleavage and H atom absorption. Compounds like **18**, which are indeed low boiling are also probably trapped in the perfluorinated liquid, leading to distinct NMR spectral data.

The methyl radical formed during cleavage can combine with intermediate molecules of IBC or NBC leading to the formation of five carbon chains of the type (**21**), four carbon of the type (**22**) could be identified in the product mixture.

All these data suggest that all commonly observed free radical substitution processes also simultaneously occur during the carbon chain isomerisation involving *cyclo*-propane intermediates during the ECPF of IBC. Quiet interestingly no product containing cyclopropyl group was observed among these constituents (Table 2).



Scheme 4.

2.3. Minor constituents of fluorinated products obtained during the ECPF of pivaloyl chloride

The minor compounds characterised by ^{19}F and ^{1}H NMR data from the ECPF product of pivaloyl chloride are presented in Table 3. In addition to perfluoropivaloic acid (**24**) other perfluoro carboxylic acids such as perfluoro(2-methyl)butyric acid (**25**), perfluoro-3-methylbutyricacid (**26**), and perfluoro-*n*-pentanoic acid (**27**) were also obtained as minor products. Formation of such compounds would involve many free radical steps including intra molecular rearrangements.Quite striking support for ECPF process through *cyclo*-propane intermediate comes from the observation of three *cyclo*-propane derivatives (**29**)–(**31**) in the product mixture. As mentioned earlier (Section

Table 3
^{19}F and ^{1}H NMR data of perfluorinated and polyfluorinated compounds obtained during the ECPF of pivaloyl chloride

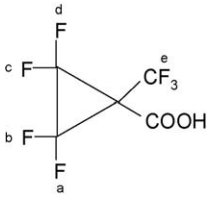
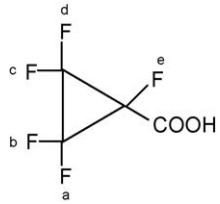
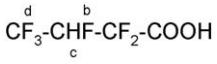
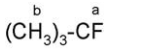
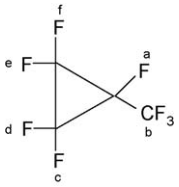
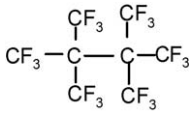
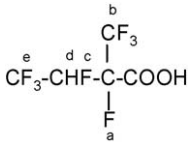
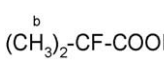
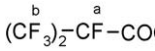
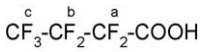
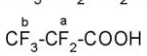
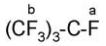
No.	Structure	Chemical shift, δ (ppm)	J (Hz)	Selectivity (mol%)
23	$(CH_3)_3$-C-COOH	a: 1.1 s		
24	$(CF_3)_3$-C-COOH	a: −69.0		3.1
25	CF_3-CF_2-C(F)-COOH	a: −160.0 b: −68.98 c: −118.58, −119.2 d: −80.8	[17] $^2J\ F^{cA,B} = 293$	7.2
26	$(CF_3)_2$-CF-CF_2-COOH	a: −124.6 b: −186.0 c: −72.19		1.0
27	CF_3-CF_2-CF_2-CF_2-COOH	a: −125.68 b: −123.4 c: −118.7 d: −80.8	[22]	12.8
28	$(CF_3)_2$-CF-CF-$(CF_3)_2$	a, d: −72.2 b, c: −178.97	[23]	0.7
29		a, d: −123.4 b −124.0 e −72.5	$^2J\ F^{a,b} = 282$ [23,24]	9.8
30		a, d: −119.83 b, c: −120.56 e: −181.47	$^2J\ F^{a,b} = 278.6$ [23,24]	3.4
31		−150.0 s	[25]	<0.1

Table 3 (*Continued*)

No.	Structure	Chemical shift, δ (ppm)	J (Hz)	Selectivity (mol%)
32		a: −122.07, −122.69 b: −216.22 d: −74.15 c: 6.27 d, m	^{2}J $F^{aA,B}$ = 291 ^{2}JHF = 45.4	4.5
33		a: −142.4 b: 1.66d	^{3}J HF = 22.2	1.3
34		a: −187.1 b: −72.2 c, f: −130.1 d, e: −130.7	^{2}J $F^{aA,B}$ = 282 [23]	6.0
35		−63.4	[23]	0.3
36		a: −181.3 b: −73.3 c: −217.4 e: −73.8 d: 6.35 ddm	^{2}J HF = 40 ^{3}J HF^a = 16	5.3
2				1.8
4	$(CF_2H)_2$–CF–COOH			<0.1
6				7.6
11				12
17				21.0
20	CF_4			<0.1
22				1.0

3.1) pivaloyl chloride contains three methyl groups on the same plane of the tetrahedral molecule. The formation of *cyclo*-propane intermediate for such a trialkyl group is at least three times higher than the dialkyl carbon structure. Hence *cyclo*-propane structures involving C_5 compound itself (**29**), C_4 compounds with methyl group removal (**30**), and even *cyclo*-propane itself (**31**) could be identified in the mixture. Formation of perfluoro *cyclo*-propane and its derivatives are indicated in Scheme 5. ^{19}F NMR data shows that compounds such as **4**, **6**, **9**, **11**, **14**, **17**, **18**, **19** and **22** are also formed during the ECPF of pivaloyl chloride. In all the three cases very small quantities of starting material has been found even after completing the electrolysis (**1**, **7**, **23**).

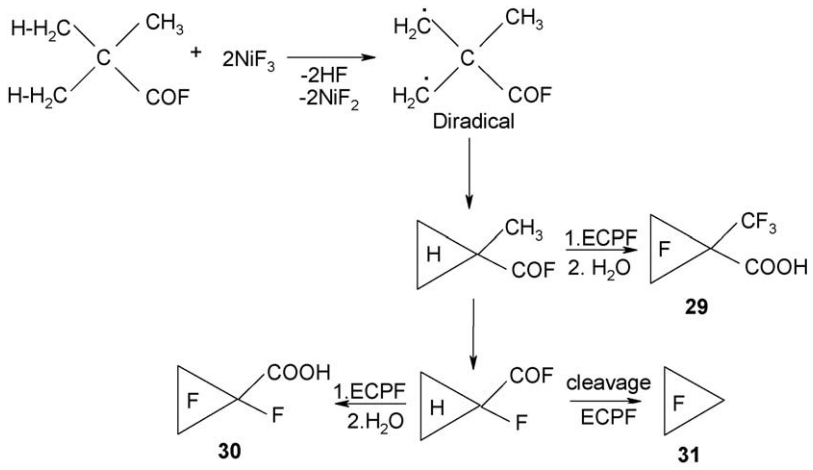
3. Experimental details

3.1. General

A 200 ml stainless steel electrolysis cell with alternate nickel anodes and cathodes (effective anode area = 2.47 dm^2) was employed. Products were collected in FEP traps kept at −70 °C after passage through a condenser kept at −30 °C. Perfluorinated carboxylic acid fluoride obtained was neutralised using 10% aqueous sodium hydroxide in a double walled glass vessel kept at −20 °C. Sodium salt of the perfluoro carboxylate was treated with mineral acid to regenerate perfluoro carboxylic acid. Electrochemical reactor temperature was varied between −10 and +10 °C. No product could be isolated from cell drains. All the products were obtained only at the cold trap kept at −70 °C.

Gas chromatograms were recorded on a Hewlett Packard 6890 plus gas chromatograph. The temperature of the injector, column (HP 1701, 30 m × 0.32 mm × 0.25 μm) and the detector (FID) were held at 130, 90 and 250 °C, respectively. Nitrogen was used as a carrier gas.

^{19}F and ^{1}H NMR spectra were recorded on a JEOL ECA 500 Spectrometer (500 MHz for ^{1}H and 470 MHz for ^{19}F, respectively). Acetone-d_6 (99.5 atom D, Aldrich) was used as solvent. Chemical shifts for ^{19}F and ^{1}H NMR spectra were reported in relative to $CFCl_3$ and TMS, respectively. Negative shifts are up field from the reference ($CFCl_3$ and TMS).



Scheme 5.

Purity of anhydrous hydrogen fluoride (M/s TANFAC Industries Ltd., Cuddalore, Tamil Nadu, India) was more than 99.9%. Reagent grade *i*-butyryl chloride, *n*-butyryl chloride and pivaloyl chloride (M/s Merck Germany) were used.

3.2. GC–MS results

GC–MS of mixture of perfluorinated compounds obtained from the ECPF of *i*-butyryl chloride were measured using Agilent 6890 GC with 5973N mass selective detector (Column HP 5MS; 30 m × 0.25 mm × 0.25 μm) at 70 eV. The following were the prominent products identified from *m/z* values.

Results indicate that heptafluorobutyric acid, pentafluoropropionic acid and trifluoroacetic acid were the main products. In addition to the above, *m/z* peaks due to partially fluorinated products were also obtained. GC–MS results are reproduced below:

(a) *MS of perfluorobutyric acid*. MS *m/z* (rel. int.): 197 $[M - OH]^+$ (3.8), 169 $[C_3F_7]^+$ (39.7), 150 $[C_3F_6]^+$ (73.5), 131 $[C_3F_4]^+$ (14.7), 119 $[C_2F_5]^+$ (83.8), 100 $[C_2F_4]^+$ (70.6), 69 $[CF_3]^+$ (100), 50 $[CF_2]^+$ (8.8), 45 $[CO_2H]^+$ (91.1) and 31 $[CF]^+$ (14.7).

(b) *MS of perfluoropropionic acid*. MS *m/z* (rel. int.): 147 $[M - OH]^+$ (7.0), 119 $[C_2F_3]^+$ (50.4), 100 $[C_2F_4]^+$ (7.0), 69 $[CF_3]^+$ (73.5), 50 $[CF_2]^+$ (14.0), 45 $[CO_2H]^+$ (100) and 31 $[CF]^+$ (33.6).

(c) *MS of trifluoroacetic acid*. MS *m/z* (rel. int.): 97 $[M - OH]^+$ (35.0), 69 $[CF_3]^+$ (73.5), 50 $[CF_2]^+$ (14.0), 45 $[CO_2H]^+$ (100), 31 $[CF]^+$ (33.6) and 28 $[CO]^+$ (28).

(d) *MS of heptafluoropropane*. MS *m/z* (rel. int.): 170 $[M]^+$ (1.5), 151 $[M - F]^+$ (2.3), 120 $[C_2F_5H]^+$ (1.5), 101 $[C_2F_4H]^+$ (1.5), 82 $[C_2F_3H]^+$ (1.5), 70 $[CF_3H]^+$ (1.5), 69 $[CF_3]^+$ (100) and 51 $[CF_2H]^+$ (13).

4. Conclusions

The present investigation suggests that free-radical pathway involving single-electron transfer is the predominant mechanism (Scheme 1) of electrochemical fluorination. The free radical generated in this step can undergo further fluorination, cleavage, cyclisation or intermolecular interactions leading to formation of a wide variety of partially fluorinated and perfluorinated minor products. The second pathway (Scheme 2) involving diradical process and *cyclo*-propane intermediate is prevalent only when branched alkyl groups like *i*-propyl and *t*-butyl groups are present in the reactant molecules. This pathway leads to formation of *n*-alkyl products from starting compounds containing *i*-propyl group. In the case compounds containing *t*-butyl group, *cyclo*-propane intermediate pathway is even more prevalent. Perfluoro *cyclo*-propane and its derivatives are obtained as minor product in this process.

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