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ORIGINAL PAPER

Effect of alkyl chain length on the electrochemical perfluorination of *n*-alkane (C_6–C_{10}) carboxylic acid chlorides

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Abstract Electrochemical perfluorination (ECPF) of *n*-hexanoyl, *n*-heptanoyl, *n*-octanoyl, *n*-nonanoyl and *n*-decanoyl chlorides was carried out under identical experimental conditions in liquid HF. The product distribution among perfluorinated carboxylic acids, perfluoro ethers, perfluoroalkanes, isomerised and fragmented products containing less number of carbon atoms was identified using ^{19}F NMR. The selectivity of C_6–C_{10} perfluoro carboxylic acid varied between 29 and 36%. The alkali insoluble perfluoro cyclic ether and perfluoro alkane fractions increased with increasing chain length. The increase of perfluoroalkane fractions is mainly due to decarboxylation. Cyclic ether fractions also decreased slightly with increase in chain length. Among the cyclic ethers α substituted oxolanes were the predominant products. Six membered cyclic ethers were always found to contain β substitution. The possible pathways for these products are also indicated.

Keywords Electrochemical perfluorination · *n*-Alkane carboxylic acid chlorides · Perfluoro cyclic ethers · Perfluoro alkanes · Perfluoro acids

1 Introduction

Formation of multiple products during the ECPF of alkane carboxylic acid chlorides has remained a serious challenge for the past 5 decades [1–4]. Apart from the main perfluorinated carboxylic acid fluorides, perfluoro cyclic ethers and perfluoro carbons are also formed (Scheme 1). In addition carbon chain isomerisation and C–C bond cleavage products containing less carbon atoms have also been reported [5–11].

Naturally with such a wide possibility of product distribution, prediction of the mechanistic pathway, as well as likely product distribution for an unknown compound, becomes extremely difficult. Some controversy regarding product distribution is also noticed in the literature [1, 3, 12]. For example while perfluoro oxolanes are reported to be the predominant cyclic ethers [12], some reports suggest perfluoro oxane as the predominant product [3, 4]. Abe et al have studied the structure of cyclic ethers formed from ECPF of alcohols and aldehydes [12], α-alkyl substituted carboxylic acids [13] and cyclic ethers [14], with a view to resolving this issue.

Among *n*-alkane carboxylic acid chlorides ECPF of *n*-octanoyl chloride has received special attention due to its importance in industrial production. The effect of anode current density [15], reactant concentration [16], electrolyte flow [17], electrode material [18] and other process parameters [19, 20] on this process have been reported. Partially fluorinated octanoyl chlorides were found to yield a significantly higher proportion of perfluoro octanoyl fluoride [21–23]. Even among these studies specifically related to octanoyl chloride there are different views on the influence of operating parameters on product distribution. For example Comninellis reported an increase in the yield of perfluoro octanoyl fluoride with increase in current density [15] or cell voltage, which is contrary to earlier observations [24–26]. Relatively fewer reports on the electrochemical fluorination of other *n*-alkane carboxylic acid chlorides are available [15, 27, 28].

Recently a mechanistic scheme for carbon chain isomerisation during the electrochemical fluorination of alkane

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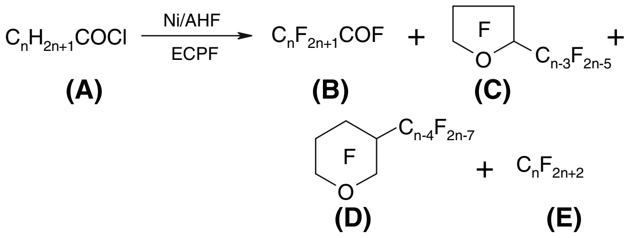


Scheme 1

sulfonyl fluoride was proposed [29]. We have extended this study to *n*-butyryl, iso-butyryl and pivaloyl chlorides and explained the cause for higher conversion from iso-alkane carboxylic acid to *n*-alkane carboxylic acid during electrochemical fluorination [30]. The present work is an extension of this investigation based on the ^{19}F NMR data of the products formed during the ECPF of higher chain length *n*-alkane carboxylic acid chlorides. An attempt is made to ascertain the general product distribution trends and also propose mechanistic schemes wherever possible.

2 Experimental

2.1 Reagents and apparatus

Synthetic grade (>98%) alkane carboxylic acid chlorides were purchased form M/s Merck, Germany and used as such. Anhydrous hydrogen fluoride (AHF) >99.9% was supplied by M/s TANFAC, Cudalore, Tamilnadu, India.

An Aplab (India) DC power supply was used for electrolysis. ^{19}F NMR spectra were recorded with 376.5 MHz (400 MHz for ^{1}H) Bruker NMR Spectrometer with $CDCl_3$ as solvent. $CFCl_3$ and TMS were used as internal reference for ^{19}F and ^{1}H NMR spectra, respectively.

2.2 Electrochemical cell

A double walled 200 mL capacity stainless steel electrolysis cell with a pack of alternate nickel anodes and cathodes was employed (effective anode area = 2.3 dm^2). The temperature of the cell and condenser was maintained at 5 and –30 °C, respectively using cryostats. Volatile products were collected in a PTFE-FEP traps kept at –70 °C using an immersion cooler at the outlet of the cell condenser. Liquid products from the cell were drained through a ball valve at the bottom of the cell.

2.3 Electrochemical fluorination of *n*-alkane carboxylic acid chlorides

Pre-electrolysis was done at the start of each experiment in order to dry AHF and activate electrode surfaces. It was carried out for about 36–48 h until the initial current of 4 A reduced to 0.2 A. Cell voltage was maintained between 5.0 and 5.5 V during this period. A required quantity of acid chloride and AHF mixture was prepared separately before every addition of acid chloride.

ECPF was carried out under galvanostatic conditions at 1.7 A dm^{-2}. An acid chloride concentration of 9% (w v^{-1}) was taken initially and the electrolysis was carried out in a pre-electrolysed AHF medium until the concentration of reactant reached 1%. The required concentration of reactant and AHF were maintained periodically. The electrolysis was stopped after passing of a pre-determined charge.

Crude perfluorinated products obtained both from the cell drain and trap were collected together and neutralized with aqueous KOH solution. The alkali soluble aqueous phase containing potassium perfluoro carboxylate and alkali insoluble phase (perfluoro cyclic ethers and perfluoro alkanes) form two separate layers and were separated. Perfluoro carboxylic acid was obtained by acidifying the aqueous phase using concentrated hydrochloric acid.

2.4 Identification of perfluorinated products

Structural determination of the products was carried out on the basis of ^{19}F NMR spectra. NMR of crude perfluorinated acid was recorded from + 50 to –250 ppm vs $CFCl_3$. Normal and iso perfluoro acids were distinguished by the chemical shift positions of *n*-methyl ($\simeq$ 80 ppm) and iso-methyl groups (70–75 ppm). Perfluoro acids with a lower number of carbon atoms were also identified in these regions.

The alkali insoluble fraction containing perfluoro cyclic ethers and perfluoro alkanes was washed thoroughly with water and dried over anhydrous sodium sulphate. The crude alkali insoluble portion was distilled into fractions. NMR spectra of crude as well as fractioned portions were recorded and compared. Normal and iso perfluoro alkanes obtained due to the cleavage of C–C bonds and isomerisation were distinguished in a manner similar to that of the corresponding acids.

While determining the structure of perfluoro cyclic ethers, the following observations suggested by Abe et al. were taken into account [13].

a. The presence of α-difluoro methylene groups of the perfluoro furan ring (oxolane) appeared at the lower field which consists of AB pattern (J $\simeq$ 130 Hz) as multiplet around –85 ppm.
b. The presence of α-difluoro methylene groups of the perfluoro pyran ring (oxane) observed at the lower field which consists of AB pattern (J = 154–158 Hz) at δ = –78 to –93 ppm.
c. The presence of β and γ fluoro methine groups of perfluoro cyclic ethers (perfluoro furans and pyrans) were observed between –180 and –190 ppm.

d. The presence of trifluoro methyl group attached to the ring carbon was observed at $\delta = -70$ to -80 ppm.

The presence of four multiplets with $J_{AB} = 154.4$ Hz and 158.1 Hz centered around –76 ppm and –89 ppm respectively suggests that there will be no α-substituent in perfluoro oxane structure. The presence of multiplets between –182 and –189 ppm suggests the formation of $-CFR_F$ group at the β-position as reported by Abe et al. [13].

3 Results and discussion

3.1 Influence of reactant chain length and current density

The overall yields and current efficiency obtained during the electrochemical fluorination of *n*-alkane (C_6–C_{10}) carboxylic acid chlorides under identical conditions are summarised in Table 1. The total weight of perfluorinated products obtained per 100 g of the reactant is lowest in the case of hexanoyl chloride due to volatility loss of lower molecular weight perfluorinated compounds. The total product weight increases with chain length. However, in all the cases there is substantial volatility loss due to fragmentation during electrochemical fluorination. The current efficiency was also lower for hexanoyl chloride. Higher current efficiencies above 60% were noticed for octanoyl and nonanoyl chlorides. This observation further confirms that maximum yield, as well as current efficiencies, are obtained for C_8 and C_9 carboxylic acid chlorides.

Among the major perfluorinated products obtained (Scheme 1), perfluoro alkane carboxylic acid fluoride (B) alone is soluble in alkali due to hydrolysis (Scheme 2). This portion is termed the acid fraction. The other components, namely perfluoro oxolane (C), perfluoro oxane (D) and perfluoro carbons (E), are insoluble in alkali. Table 1 again indicates that alkali insoluble portion is significantly higher for all the five reactants studied, and it increases slightly from 66.4% for *n*-hexanoyl chloride to over 71% for *n*-decanoyl chloride.

The effect of current density variation on the overall selectivity between acid fraction and alkali insoluble fraction were investigated for hexanoyl, heptanoyl and octanoyl chlorides (Table 2). In all the cases higher current density leads to lower selectivity towards the acid fraction.

The main effort in the present investigation is to identify as many products as (more than 1% of the total product formed) possible from the acid fraction as well as alkali insoluble fraction using ^{19}F NMR data. During the ECPF of all the five alkane carboxylic acid chlorides, thirty three perfluorinated products were identified. The ^{19}F NMR data for all these compounds are summarised in Table 3. Some interesting observations relating to product distributions in each fraction are discussed below.

3.2 Product distribution in the acid fraction

The results presented in Table 4 indicate that the main product in all these cases is perfluoro *n*-alkane carboxylic acid with the same chain length (B in Scheme 1). This fraction (*n*-acid) is, however, found to decrease with the chain length of acid chlorides from 90.7% for *n*-hexanoyl chloride to 75.4% for *n*-decanoyl chloride. With increase in chain length the possibility of C–C bond cleavage leading

Table 1 Results of ECPF of *n*-alkane carboxylic acid chlorides

Sl. No.	Reactants	Amount of reactant taken (g)	Charge passed (Ah)	Perfluorinated products (g)	wt/100 g of starting (g)	Current efficiency (%)	[b]Selectivity (%)	
							[a]Alkali insoluble	Acid
1.	Hexanoyl chloride	65.6	302	58.0	88.4	35.9	66.4	33.6
2.	Heptanoyl chloride	65.3	308	83.7	128.2	51.7	64.5	35.5
3.	Octanoyl chloride	82.0	383	116.1	141.6	63.2	68.8	31.2
4.	Nonanoyl chloride	58.8	286	91.5	155.6	62.5	70.7	29.3
5.	Decanoyl chloride	54.6	270	73.6	134.8	53.9	71.3	28.7

[a] Alkali insoluble are Perfluoro cyclic ethers and Perfluoro alkanes

[b] Based on the weight of acid obtained

Volume of electrolyte: 200 mL

Current: 4 A

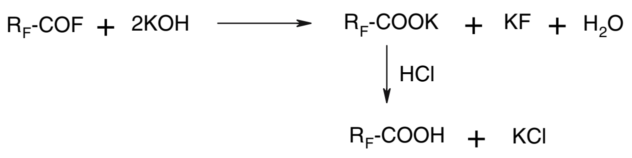
Active anode area: 2.3 dm^2

Current density: 1.7 A dm^{-2}

Cell voltage: 5.5–7.0 V

Cell temperature: 5 °C

Condenser temperature: –30 °C Conc. of acid chlorides: 9–11%/w v^{-1}



$$R_F\text{-COF} + 2KOH \longrightarrow R_F\text{-COOK} + KF + H_2O \xrightarrow{HCl} R_F\text{-COOH} + KCl$$

Scheme 2

to formation of lower chain length carboxylic acids also increases. Data presented in Table 4 relating to other cleavage products mainly consist of lower chain length carboxylic acids confirming the above.

For each reactant NMR data could be quantitatively analysed to identify perfluoro-*n*-alkane carboxylic acids (compounds 1, 3, 5, 7, 9 in Table 3) and perfluoro-iso-alkane carboxylic acids (compounds 2, 4, 6, 8, 10 in Table 3). Interestingly in all these cases perfluoro *n*-alkane carboxyl acids are in substantially large excess (9 to 11 times) when compare to perfluoro-iso-alkane carboxylic acids (Table 4). This observation confirms the earlier trend reported for perfluoro-*n*-butyric acid [30].

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 has been proposed (Scheme 3) to understand this process. The cyclo-propane intermediate containing three C–C bonds α, β and γ can now undergo cleavage and fluorination on all the three bond positions. In this cyclo-propane intermediate route there is a 2:1 possibility of formation of n-derivative when compared to iso compound during each pair of fluorine addition. For example the cleavage of cyclo-propane intermediates at the α and γ position would lead to *n*-acid intermediates. β cleavage alone would lead to iso acid intermediate. Hence, the mole ratio of perfluoro-n-acid to perfluoro-iso-acid would be 26:1 (Scheme 7 in [29]). Recently it was shown that electrochemical perfluorination of *n*-butyric acid leads to the formation of a significantly higher quantity of perfluoro-*n*-butyric acid (PFNBA) 92% compared to perfluoro-iso-butyric acid (PFIBA) 6.9% [30], which also supports the present observation on the ECPF of alkane carboxylic acid chlorides (Scheme 3).

3.3 Product distribution in alkali insoluble fraction

The alkali insoluble portion contains (a) Perfluoro cyclic ethers containing the same carbon chain length, (b) Perfluoro alkanes containing decarboxylated molecules and (c) Other fractions containing fewer carbon atoms (Table 5).

The cyclic ethers primarily contain substituted oxolanes (Furan structure). All the five alkane carboxylic acid chlorides lead to a similar oxolane structure shown in compound 11 in Table 3, where the perfluoro alkyl substituent contains an increasing number of carbon atoms with increase in reactant chain length (compound 11–15 in Table 3). The similarities in this structure indicate that the predominant cyclisation process occurs through oxygen linkage with the γ carbon atom for all the linear alkane carboxylic acid chlorides investigated (Scheme 4).

All the five perfluoro oxanes obtained during the ECPF of different carboxylic acid chlorides once again posses the perfluoro alkyl group in the β position of the perfluorinated oxane ring (compounds 16–20, Scheme 4). This is interesting because these compounds cannot be formed by direct attack of the carbonyl group on any of the linear chain carboxylic acid chloride intermediates. Such an attack would only lead to the perfluoro alkane substitution to the α position of the perfluoro oxane. It appears that the six membered ring compound is formed through a methyl migration process or some isomeric intermediate formed from linear acids during electrochemical fluorination (Scheme 4). Abe et al. have indicated a similar methyl migration process during the electrochemical fluorination

Table 2 Influence of current density on the selectivity of Perfluoro products

Reactants	Current density (A dm^{-2})	Current efficiency (%)	[b]Selectivity (%)	
			[a]Alkali insoluble	Acid
Hexanoyl chloride	1.3	26.2	45.7	54.3
	1.7	35.9	66.4	33.6
	2.2	35.7	80.1	19.9
Heptanoyl chloride	1.7	51.7	64.5	35.5
	2.2	47.4	72.8	27.2
Octanoyl chloride	1.3	54.4	65.4	34.6
	1.7	63.2	68.8	31.2
	2.2	59.0	75.0	25.0

[a] Alkali insoluble portion consists of perfluoro cyclic ethers and perfluoro alkanes. Experimental conditions are same as in Table 1

[b] Based on the weight of acid obtained

Table 3 ^{19}F NMR data of perfluoro carboxylic acids obtained from ECPF of *n*-alkane carboxylic acid chlorides

No.	Perfluoro carboxylic acids	Chemical shift /δ, ppm
1.	$\overset{e}{\mathrm{CF_3}}\text{-}\overset{d}{\mathrm{CF_2}}\text{-}\overset{c}{\mathrm{CF_2}}\text{-}\overset{b}{\mathrm{CF_2}}\text{-}\overset{a}{\mathrm{CF_2}}\text{-COOH}$	–80.81 (t, $3F^e$) $^3J_{FF}$ = 8.8 Hz –117.91 (t, $2F^a$) $^3J_{FF}$ =11.7 Hz –122.78 (br,m $2F^b$) –122.50 (br, $2F^c$) –125.97 (br, $2F^d$)
2.	$(\overset{d}{\mathrm{CF_3}})_2\text{-}\overset{c}{\mathrm{CF}}\text{-}\overset{b}{\mathrm{CF_2}}\text{-}\overset{a}{\mathrm{CF_2}}\text{-COOH}$	–71.79 (m, $6F^d$) –114.70 (sept, $2F^a$) $^4J_{FF}$ =8.8 Hz –117.20 (sept, $2F^b$) $^5J_{FF}$ =5.9 Hz –185.25 (br, $1F^c$)
3.	$\overset{f}{\mathrm{CF_3}}\text{-}\overset{e}{\mathrm{CF_2}}\text{-}\overset{d}{\mathrm{CF_2}}\text{-}\overset{c}{\mathrm{CF_2}}\text{-}\overset{b}{\mathrm{CF_2}}\text{-}\overset{a}{\mathrm{CF_2}}\text{-COOH}$	–80.99 (t, $3F^f$) $^3J_{FF}$ =8.8 Hz –118.78 (t, $2F^a$) $^3J_{FF}$ =11.7 Hz –121.50 (m, $2F^b$) –122.55 (br, $4F^{c,d}$) –125.98 (m, $2F^e$)
4.	$(\overset{e}{\mathrm{CF_3}})_2\text{-}\overset{d}{\mathrm{CF}}\text{-}\overset{c}{\mathrm{CF_2}}\text{-}\overset{b}{\mathrm{CF_2}}\text{-}\overset{a}{\mathrm{CF_2}}\text{-COOH}$	–71.84 (m, $6F^e$) –118.44 (t, $2F^a$) $^3J_{FF}$ =14.6 Hz –121.76 (sept, $2F^b$) $^5J_{FF}$ =11.0 Hz –114.36 (sept, $2F^c$) $^4J_{FF}$ =11.0 Hz –184.30 (br, $1F^d$)
5.	$\overset{g}{\mathrm{CF_3}}\text{-}\overset{f}{\mathrm{CF_2}}\text{-}\overset{e}{\mathrm{CF_2}}\text{-}\overset{d}{\mathrm{CF_2}}\text{-}\overset{c}{\mathrm{CF_2}}\text{-}\overset{b}{\mathrm{CF_2}}\text{-}\overset{a}{\mathrm{CF_2}}\text{-COOH}$	–80.94 (t, $3F^g$) $^3J_{FF}$ =11.0 Hz –118.76 (t, $2F^a$) $^3J_{FF}$ =11.0 Hz –121.29 (br,m $2F^b$) –121.66 (br,m $2F^c$) –122.39 (br,m $2F^d$) –122.51(br,m $2F^e$) –125.95 (br,m $2F^f$)
6.	$(\overset{f}{\mathrm{CF_3}})_2\text{-}\overset{e}{\mathrm{CF}}\text{-}\overset{d}{\mathrm{CF_2}}\text{-}\overset{c}{\mathrm{CF_2}}\text{-}\overset{b}{\mathrm{CF_2}}\text{-}\overset{a}{\mathrm{CF_2}}\text{-COOH}$	–71.82 (m $6F^f$) –118.69 (t, $2F^a$) $^3J_{FF}$ =14.6 Hz –122.07 (m, $2F^b$) –125.78 (m, $2F^c$) –114.57 (sept, $2F^d$) $^4J_{FF}$ =11.0 Hz –185.73br ($1F^e$)
7.	$\overset{h}{\mathrm{CF_3}}\text{-}\overset{g}{\mathrm{CF_2}}\text{-}\overset{f}{\mathrm{CF_2}}\text{-}\overset{e}{\mathrm{CF_2}}\text{-}\overset{d}{\mathrm{CF_2}}\text{-}\overset{c}{\mathrm{CF_2}}\text{-}\overset{b}{\mathrm{CF_2}}\text{-}\overset{a}{\mathrm{CF_2}}\text{-COOH}$	–80.64 (t, $3F^h$) $^3J_{FF}$ =11.0 Hz –117.56 (t, $2F^a$) $^3J_{FF}$ =11.0 Hz –121.18 (br, $2F^b$) –121.45(br, $4F^{c,d}$) –122.12 (m, $2F^e$) –122.29 (br, $2F^f$) –125.75 (m, $2F^g$)
8.	$(\overset{g}{\mathrm{CF_3}})_2\text{-}\overset{f}{\mathrm{CF}}\text{-}\overset{e}{\mathrm{CF_2}}\text{-}\overset{d}{\mathrm{CF_2}}\text{-}\overset{c}{\mathrm{CF_2}}\text{-}\overset{b}{\mathrm{CF_2}}\text{-}\overset{a}{\mathrm{CF_2}}\text{-COOH}$	–71.59 (m, $6F^g$) –117.48 (t, $2F^a$) $^3J_{FF}$ =11.3 Hz –114.46 (br, $2F^e$) –120.28 (br, $2F^b$) –120.77 (br, $2F^c$) –125.90 (m, $2F^d$) –185.5 (br, $1F^f$)

Table 3 continued

No.	Perfluoro carboxylic acids	Chemical shift /δ, ppm
9.	$\overset{i}{\mathrm{CF_3}}\text{-}\overset{h}{\mathrm{CF_2}}\text{-}\overset{g}{\mathrm{CF_2}}\text{-}\overset{f}{\mathrm{CF_2}}\text{-}\overset{e}{\mathrm{CF_2}}\text{-}\overset{d}{\mathrm{CF_2}}\text{-}\overset{c}{\mathrm{CF_2}}\text{-}\overset{b}{\mathrm{CF_2}}\text{-}\overset{a}{\mathrm{CF_2}}\text{-COOH}$	-80.89 (t, 3F^{i}) $^{3}J_{FF}$ =11.0 Hz –118.74 (t, 2F^{a}) $^{3}J_{FF}$ =11.0 Hz –121.30 (br, 2F^{b}) –121.50 (br, 6F^{c,d,e}) –122.38 (br, 2F^{f}) –122.51 (br, 2F^{g}) –125.79 (br, 2F^{h})
10.	$\overset{h}{\mathrm{(CF_3)_2}}\text{-}\overset{g}{\mathrm{CF}}\text{-}\overset{f}{\mathrm{CF_2}}\text{-}\overset{e}{\mathrm{CF_2}}\text{-}\overset{d}{\mathrm{CF_2}}\text{-}\overset{c}{\mathrm{CF_2}}\text{-}\overset{b}{\mathrm{CF_2}}\text{-}\overset{a}{\mathrm{CF_2}}\text{-COOH}$	–71.81 (m, 6F^{h}) –114.5 (m, 2F^{f}) –118.62 (t, 2F^{a}) $^{3}J_{FF}$ =11.0 Hz –120.24 (br, 2F^{b}) –121.05 (br, 2F^{c}) –123.31 (br, 2F^{d}) –125.53 (m, 2F^{e}) –185.74 (br, 1F^{g})

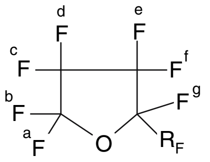
No	Structure	Chemical shift /δ, ppm
11.	 $\mathrm{R_F} = \text{-}\overset{h}{\mathrm{CF_2}}\text{-}\overset{i}{\mathrm{CF_3}}$	–83.77 (d, 1F^{a}) –84.12 (d, 1F^{b}) J_{AB} = 131.8 Hz –125.65 (m, 1F^{c}) –126.35 (m, 1F^{d}) J_{AB} = 263.8 Hz –135.74 (q, 1F^{e}) –136.40 (q, 1F^{f}) J_{AB} = 248.5 Hz –133.34 (quin, 1F^{g}) $^{3}J_{FF}$ =15.4 Hz –79.68 (d, 3F^{i}) $^{4}J_{FF}$ = 7.5 Hz
12.	$\mathrm{R_F} = \text{-}\overset{h}{\mathrm{CF_2}}\text{-}\overset{i}{\mathrm{CF_2}}\text{-}\overset{j}{\mathrm{CF_3}}$	–84.30 (d, 1F^{a}) –84.64 (d, 1F^{b}) J_{AB} = 128.0 Hz –126.15 (m, 1F^{c}) –126.85 (m, 1F^{d}) J_{AB} = 263.5 Hz –136.24 (q, 1F^{e}) –136.91 (q, 1F^{f}) J_{AB} = 252.3 Hz –122.97 (dd, 1F^{g}) $^{3}J_{FF}$ = 27.8Hz, $^{5}J_{FF}$ = 10.5 Hz –125.57 (m, 2F^{h}) –126.42 (t, 2F^{i}) $^{3}J_{FF}$ = 11.3 Hz –80.59 (d, 3F^{j}) $^{5}J_{FF}$ = 15.1 Hz
13.	$\mathrm{R_F} = \text{-}\overset{h}{\mathrm{CF_2}}\text{-}\overset{i}{\mathrm{CF_2}}\text{-}\overset{j}{\mathrm{CF_2}}\text{-}\overset{k}{\mathrm{CF_3}}$	–83.96 (d, 1F^{a}) –84.31 (d, 1F^{b}) J_{AB} = 131.8 Hz –125.22 (m, 1F^{c}) –126.37 (m, 1F^{d}) J_{AB} = 263.6 Hz –135.88 (q, 1F^{e}) –136.55 (q, 1F^{f}) J_{AB} = 252.3 Hz –127.22 (br, 1F^{g}) –120.62 (m, 2F^{h}) –122.57 (m, 2F^{i}) –125.67 (br, 2F^{j}) –80.82 (t, 3F^{k}) $^{3}J_{FF}$ =11.3 Hz

Table 3 continued

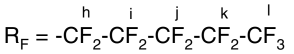
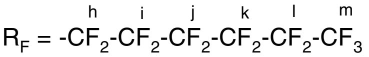
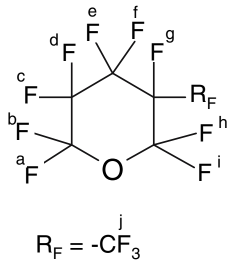
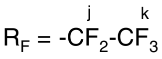
No	Structure	Chemical shift /δ, ppm
14.	 $R_F = -\overset{h}{CF_2}-\overset{i}{CF_2}-\overset{j}{CF_2}-\overset{k}{CF_2}-\overset{l}{CF_3}$	–83.95 (d, $1F^a$) –84.29 (d, $1F^b$) J_{AB} = 128.0 Hz $1F^c$ $1F^d$ –135.85 (q, $1F^e$) –136.52 (q, $1F^f$) J_{AB} = 252.3 Hz –129.7 (br, $1F^g$) –120.44 (br, $2F^h$) –121.45 (br, $2F^i$) –124.78 (br, $2F^j$) –125.70 (br, $2F^k$) –80.8 (t, $3F^l$) $^3J_{FF}$ =15.4 Hz
15.	 $R_F = -\overset{h}{CF_2}-\overset{i}{CF_2}-\overset{j}{CF_2}-\overset{k}{CF_2}-\overset{l}{CF_2}-\overset{m}{CF_3}$	–83.93 (d, $1F^a$) –84.28 (d, $1F^b$) J_{AB} = 131.8 Hz $1F^c$ $1F^d$ –135.84 (q, $1F^e$) –136.50 (q, $1F^f$) J_{AB} = 248.5 Hz –126.50 (m, $1F^g$) –120.45 (m, $2F^h$) –123.02 (br, $2F^i$) –123.64 (br, $4F^{j,\,k}$) –127.15 (br, $2F^l$) –80.83 (t, $3F^m$) $^3J_{FF}$ =9.8 Hz
16.	 $R_F = -\overset{j}{CF_3}$	–77.95 (quin, $1F^a$) –78.37 (quin, $1F^b$) J_{AB} = 158.1 Hz –138.01 (sext, m, $1F^c$) –138.74 (sext, m, $1F^d$) J_{AB} = 274.8 Hz –140.75 (sext, $1F^e$) –141.50 (sext, $1F^f$) J_{AB} = 282.4 Hz –187.02 (m, $1F^g$) –91.50 (m, $1F^h$) –91.92 (m, $1F^i$) J_{AB} = 158.1 Hz –79.64 (d, $3F^j$) $^3J_{FF}$ = 7.5 Hz
17.	 $R_F = -\overset{j}{CF_2}-\overset{k}{CF_3}$	–78.21 (quin, $1F^a$) –78.62 (quin, $1F^b$) J_{AB} = 154.4 Hz –138.40 (sext, m, $1F^c$) –139.14 (sext, m, $1F^d$) J_{AB} = 278.6 Hz –140.70 (sext, $1F^e$) –141.46 (sext, $1F^f$) J_{AB} = 286.1 Hz –185.50 (sext, $1F^g$) –91.64 (m, $1F^h$) –92.06 (m, $1F^i$) J_{AB} = 158.1 Hz –118.56 (m, $2F^j$) –81.3 (t, $3F^k$) $^3J_{FF}$ = 11.3 Hz

Table 3 continued

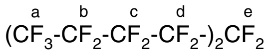
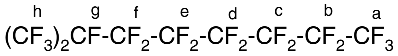
No	Structure	Chemical shift /δ, ppm
18.	$R_F = \text{-}\overset{j}{CF_2}\text{-}\overset{k}{CF_2}\text{-}\overset{l}{CF_3}$	−77.94 (quin, 1F^a) −78.35 (quin, 1F^b) J_{AB} = 154.4 Hz −137.99 (sext, m, 1F^c) −138.71 (sext, m, 1F^d) J_{AB} = 271.1 Hz −140.15 (sext, 1F^e) −140.91 (sext, 1F^f) J_{AB} = 286.1 Hz 1F^g −91.26 (m, 1F^h) −91.68 (m, 1F^i) J_{AB} = 158.1 Hz 2F^j 2F^k −80.61 (t, 3F^l) $^3J_{FF}$ = 11.3 Hz
19.	$R_F = \text{-}\overset{j}{CF_2}\text{-}\overset{k}{CF_2}\text{-}\overset{l}{CF_2}\text{-}\overset{m}{CF_3}$	−77.91 (quin, 1F^a) −78.33 (quin, 1F^b) J_{AB} = 158.1 Hz −137.97 (sext, m, 1F^c) −138.69 (sext, m, 1F^d) J_{AB} = 271.1 Hz −140.10 (sext, 1F^e) −140.86 (sext, 1F^f) J_{AB} = 286.1 Hz 1F^g −91.22 (m, 1F^h) −91.64 (m, 1F^i) J_{AB} = 158.1 Hz 2F^j 2F^k 2F^l 2F^m
20.	$R_F = \text{-}\overset{j}{CF_2}\text{-}\overset{k}{CF_2}\text{-}\overset{l}{CF_2}\text{-}\overset{m}{CF_2}\text{-}\overset{n}{CF_3}$	−77.87 (quin, 1F^a) −78.29 (quin, 1F^b) J_{AB} = 158.1 Hz −137.94 (sext, m, 1F^c) −138.67 (sext, m, 1F^d) J_{AB} = 274.8 Hz −140.07 (sext, 1F^e) −140.82 (sext, 1F^f) J_{AB} = 282.4 Hz 1F^g −91.19 (m, 1F^h) −91.60 (m, 1F^i) J_{AB} = 154.4 Hz 2F^j 2F^k 2F^l 2F^m 2F^n

No.	Perfluoro alkanes	Chemical shift / δ, ppm
21.	$\overset{a}{CF_3}\text{-}\overset{b}{CF_2}\text{-}\overset{a}{CF_3}$	−82.43 (t, 6F^a) $^3J_{FF}$ = 7.5 Hz −130.68 (sept, 2F^b) $^3J_{FF}$ = 11.3 Hz
22.	$\overset{a}{CF_3}\text{-}\overset{b}{CF_2}\text{-}\overset{b}{CF_2}\text{-}\overset{a}{CF_3}$	−83.43 (br, 6F^a) −128.17 (br, 4F^b)

Table 3 continued

No.	Perfluoro alkanes	Chemical shift /δ, ppm
24.	$\overset{a}{CF_3}-\overset{b}{CF_2}-\overset{c}{CF_2}-\overset{b}{CF_2}-\overset{a}{CF_3}$	–80.92 (t, 6F^{a}) $^{4}J_{FF}$ a,c = 10.2 Hz –126.51 (br, s, 4F^{b}) –123.91 (m, 2F^{c})
25.	$\overset{d}{(CF_3)_2}\overset{c}{CF}-\overset{b}{CF_2}-\overset{a}{CF_3}$	–70.67m (6F^{d}) –80.28sept (3F^{a}) $^{5}J_{FF}$=5.8 Hz –111.04br (2F^{b}) –184.0br (1F^{c})
26.	$(\overset{a}{CF_3}-\overset{b}{CF_2}-\overset{c}{CF_2}-)_2$	–81.3 (t, 6F^{a}) $^{3}J_{FF}$ = 11.3 Hz –126.7 (m, 4F^{b}) –123.47 (m, 4F^{c})
27.	$\overset{e}{(CF_3)_2}\overset{d}{CF}-\overset{c}{CF_2}-\overset{b}{CF_2}-\overset{a}{CF_3}$	–70.54m (6F^{e}) –80.6t (3F^{a}) $^{3}J_{FF}$ = 7.5 Hz –124.64m (2F^{b}) –115.35sept (2F^{c}) –183.90br (1F^{d})
28.	$(\overset{a}{CF_3}-\overset{b}{CF_2}-\overset{c}{CF_2}-)_2\overset{d}{CF_2}$	–80.9 (t, 6F^{a}) $^{3}J_{FF}$ = 11.3 Hz –126.26 (m, 4F^{b}) –128. 7 (br, s, 4F^{c}) –121.94 (m, 2F^{d})
29.	$\overset{f}{(CF_3)_2}\overset{e}{CF}-\overset{d}{CF_2}-\overset{c}{CF_2}-\overset{b}{CF_2}-\overset{a}{CF_3}$	–72.44m (6F^{f}) –80.65t (3F^{a}) $^{3}J_{FF}$ = 7.5 Hz –119.60br (2F^{d}) –123.95br (2F^{c}) –125.47br (2F^{b}) –179.54br (1F^{e})
30.	$(\overset{a}{CF_3}-\overset{b}{CF_2}-\overset{c}{CF_2}-\overset{d}{CF_2}-)_2$	–80.86 (t, 6F^{a}) $^{3}J_{FF}$ = 9.9 Hz –126.22 (m, 4F^{b}) –123.65 (m, 4F^{c}) –122.04 (m, 4F^{d})
31.	$\overset{g}{(CF_3)_2}\overset{f}{CF}-\overset{e}{CF_2}-\overset{d}{CF_2}-\overset{c}{CF_2}-\overset{b}{CF_2}-\overset{a}{CF_3}$	–73.6m (6F^{g}) –80.56t (3F^{a}) $^{3}J_{FF}$ = 7.5 Hz –116.0br (2F^{e}) –120.28br (2F^{d}) –120.77br (2F^{c}) –125.37br (2F^{b}) –182.60br (1F^{f})

Table 3 continued

No.	Perfluoro alkanes	Chemical shift /δ, ppm
32.	 $(\overset{a}{CF_3}\text{-}\overset{b}{CF_2}\text{-}\overset{c}{CF_2}\text{-}\overset{d}{CF_2}\text{-})_2\overset{e}{CF_2}$	–80.83 (t, 6F^a) $^3J_{FF}$ = 7.5 Hz –126.19 (br, 4F^b) –122.77 (br, 4F^c) –121.97 (br, 4F^d) –121.17 (br, 2F^e)
33.	 $\overset{h}{(CF_3)_2}\overset{g}{CF}\text{-}\overset{f}{CF_2}\text{-}\overset{e}{CF_2}\text{-}\overset{d}{CF_2}\text{-}\overset{c}{CF_2}\text{-}\overset{b}{CF_2}\text{-}\overset{a}{CF_3}$	–71.93 m (6F^h) –182.6 br (1F^g) –120.4 br (2F^f) –12.78 br (2F^e) –123.02 br (2F^d) –126.07 br (2F^c) –127.15 br (2F^b) –80.58 t (3F^a) $^3J_{FF}$ = 7.5 Hz

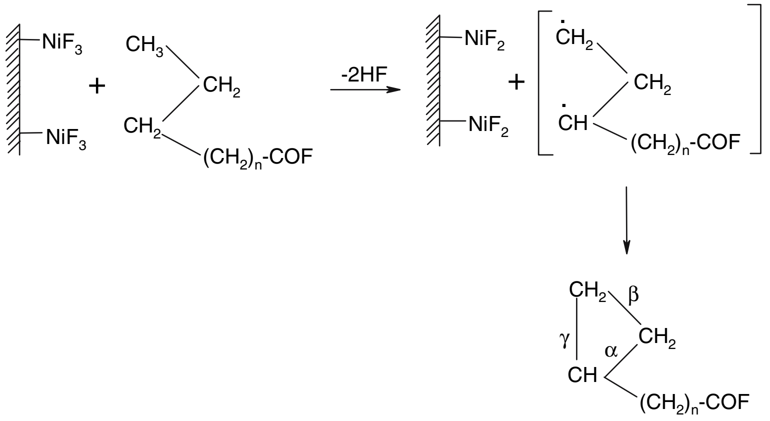
s—Single, d—doublet, t—triplet, q—quartet, quin—quintet, sext—sextet, sept—septet, m—multiplet

Table 4 Selectivity of perfluoro carboxylic acids obtained from ECPF of *n*-alkane carboxylic acid chlorides

No.	Reactants	[a]Perfluorinated carboxylic acids obtained/mole %		
		n	iso	Other cleavage products
1.	*n*-hexanoyl chloride	90.7	8.1	1.2
2.	*n*-heptanoyl chloride	84.5	8.7	6.8
3.	*n*-octanoyl chloride	72.1	9.2	18.7
4.	*n*-nonanoyl chloride	71.0	8.7	19.0
5.	*n*-decanoyl chloride	75.4	8.0	16.5

Experimental conditions are same as in Table 1

[a] Based on ^{19}F NMR



Scheme 3

of α-substituted carboxylic acid chlorides [13]. The present study suggests that such six membered rings can be formed, even in the absence of α substitution provided a favourable intermediate containing a methyl group in the γ position is available.

Apart from cyclic ethers, the alkali insoluble portion also contains decarboxylated perfluoro alkane as the other major component. Both perfluoro-*n*-alkanes and perfluoro-iso-alkanes are obtained (compound 21–33). For all the five acid chlorides, the perfluoro-*n*-alkane

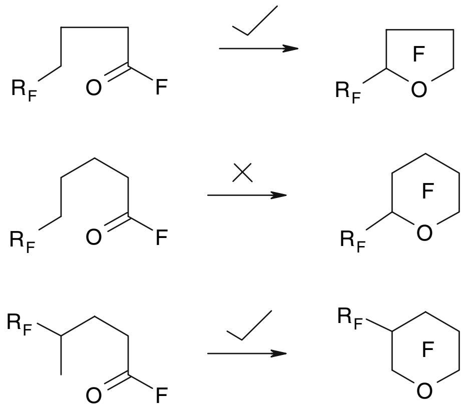
Table 5 Selectivity of alkali insoluble perfluoro products obtained from ECPF of *n*-alkane carboxylic acid chlorides

No.	Reactants	[b]Perfluorinated products obtained from alkali insoluble fraction/mole %				
		Perfluoro -*n*-alkane	Perfluoro -iso-alkane	Perfluoro oxolane	Perfluoro oxane	[a]Other cleavage products
1.	*n*-hexanoyl chloride	40.4	4.7	23.4	5.9	26.4
2.	*n*-heptanoyl chloride	8.9	3.4	25.0	6.2	26.5
3.	*n*-octanoyl chloride	3.6	9.8	22.2	3.7	20.7
4.	*n*-nonanoyl chloride	1.3	10.9	20.9	3.4	23.5
5.	*n*-decanoyl chloride	9.5	11.5	18.2	4.2	26.7

Note. Perfluoro oxolane (Five membered cyclic ether) is more than Perfluoro oxane (six membered cyclic ether)

[a] Other cleavage products are mainly lower alkanes

[b] Based on ^{19}F NMR



Scheme 4

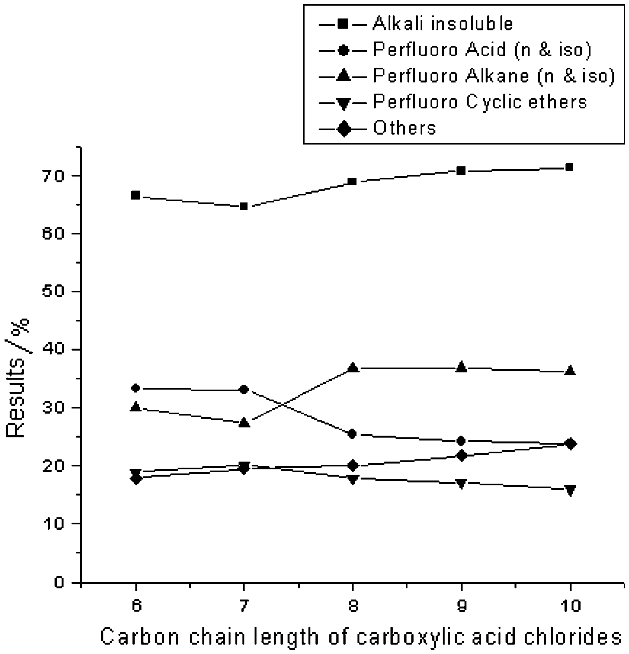


Fig. 1 A plot of experimental results vs alkyl chain length of *n*-alkane carboxylic acid chlorides

content was found to be in the range 38–44%. The perfluoro-iso-alkane fraction increases noticeably with increasing reactant chain length. The alkali insoluble fraction also contained perfluoro alkanes with lower chain length.

3.4 Overall product distribution

The overall product distributions obtained from the acid fraction, as well as the alkali insoluble fraction, are compiled in Fig. 1. The alkali insoluble fraction remains at a high level of around 65–70% for all the *n*-alkane carboxylic acid chlorides investigated. The yield of perfluoro carboxylic acids with the same chain length decreases slightly with increasing alkane carboxylic acid chloride chain length. A similar decrease is also noticed for perfluorinated cyclic ethers. The yields of decarboxylated perfluoro alkanes as well as fragmented components increase with increasing reactant chain length accounting for this variation. Table 6 summarises the distribution of all the identified products including n and iso perfluoro acids, n and iso perfluoro carbons, oxolane and oxanes and fragmented acids and perfluoro alkanes. The overall similarity in the product distribution for all the five *n*-alkane carboxylic acid chloride reactants is striking. Among the isomerised products (Perfluoro-iso-alkane carboxylic acid and perfluoro-iso-alkane) only the percentage yields of perfluoro-iso-alkane increase with alkane reactant chain length. This is understandable because both ends of the decarboxylated fluoro alkane intermediate can undergo isomerisation leading to the formation of identical isomeric product. The present investigation thus suggest that a similar reaction mechanism and similar isomerisation, cyclisation, decarboxylation and fragmentation patterns operate during the electrochemical fluorination of all the carboxylic acid chlorides investigated.

Table 6 Overall product distributions obtained during ECPF of *n*-alkane carboxylic acid chlorides/mole %

Sl.	Reactants	[a]Acid					[b]Alkali insoluble		
		n	iso	others-*n*-alkane	Perfluoro-iso-alkane	Perfluoro oxolane	Perfluoro oxane	Perfluoro	Others
1.	Hexanoyl chloride	0.5	2.7	0.4	26.8	.2	15.5	3.4	17.5
2.	Heptanoyl chloride	30.0	3.1	2.4	25.1	2.2	16.1	4.0	17.1
3.	Octanoyl chloride	22.5	2.9	5.8	30.0	6.7	15.3	2.6	14.2
4.	Nonanoyl chloride	21.0	3.2	5.1	29.2	7.7	14.7	2.4	16.7
5.	Decanoyl chloride	21.6	2.3	4.7	28.1	8.2	13.0	3.0	19.0

[a] Based on ^{19}F NMR

4 Conclusion

This study indicates that similar mechanistic pathways and product distribution patterns exist for the ECPF of *n*-alkyl carboxylic acid chlorides. The product distribution among perfluoro acids, ethers and alkanes does not vary significantly with alkane chain length. Cyclisation leading to formation of cyclic ethers proceed by coupling with γ carbon or the methyl group attached to γ carbon, which may be formed as an intermediate during the free radical fluorination processes. Decarboxylation, isomerisation and C–C bond cleavage processes also occur which increase with increasing chain length. All these observation lend further support to the view that the ECPF process on a nickel fluoride anode surface is essentially a free radical process for a wide variety of organic compounds, which are soluble in liquid HF medium.

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