Products formed at intermediate stages of electrochemical perfluorination of propionyl and n-butyryl chlorides. Further evidence in support of NiF$_3$ mediated free radical pathway

T.M. Rangarajan [a], S. Sathyamoorthi [a], D. Velayutham [a,*], M. Noel [a,1], R.P. Singh [b], Raju Brahma [b]

[a] CSIR-Central ElectroChemical Research Institute, Karaikudi 630 006, India
[b] Centre for Fire Explosives and Environmental Safety, DRDO, NewDelhi 54, India

ABSTRACT

The partially fluorinated HF soluble intermediates formed during the electrochemical perfluorination of propionyl chloride (PC) and n-butyryl chloride (n-BC) were analyzed after passing 0%, 25%, 50%, 75% and 100% of theoretical charge required for the fluorination of PC and n-BC. The acid fluorides formed were converted to their corresponding sodium salt by alkali treatment and were separated by methanol extraction. The methanol was subsequently removed from the extract by vacuum distillation and the residue containing partially fluorinated sodium carboxylates was analyzed using ^{19}F and ^{1}H NMR spectra. Initial perfluorination on activated electrode surface indicates the operation of 'zipper-mechanism'. Formation of partially fluorinated product mixture, initial selectivity towards primary and secondary carbon, carbon chain isomerization and formation of cleaved and coupled products support the general operation of free radical pathway in the overall electrochemical process.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Electrochemical perfluorination of propionyl and n-butyryl fluorides is well known for many decades [1,2]. Gambaretto et al. [2], suggested EC$_b$EC$_N$ mechanism for electrochemical fluorination process. Dimitrov and co-workers in a fairly detailed investigation mainly involving electrochemical perfluorination (ECPF) of trialkylamine have established formation of many partially fluorinated intermediates in this process [3–7]. The HF soluble partially fluorinated intermediates were isolated at different stages of ECPF [3,6,7]. Many studies by Dimitrov et al. [5–8], Sartori et al. [9–11], and Velayutham et al. [12] also confirmed the free radical pathway. Since anodically activated nickel is the only electrode in ECPF process, the involvement of high valent nickel fluoride species such as NiF$_3$ and NiF$_4$ in ECPF process has been suggested by Ignat'ev et al. [9,11,13]. In an interesting experiment, fluorinated products were obtained under open circuit conditions on an anodically polarized NiF$_3$ surface [9]. Free radical pathway involving a cyclopropane intermediate was also suggested to explain the carbon chain isomerization during ECPF of alkane sulphonic acid [13] and alkane carboxylic acid fluorides [12,14].

Partially fluorinated compounds were found as minor constituents in the perfluorination products during ECPF in a number of investigations cited above. However, analysis of partially fluorinated compounds dissolved in the HF phase at different stages of electrolysis is not quite commonly attempted. The ECPF of triethylamine reported by Dimitrov et al. [7] and Hollitzer and Sartori [15] appears to be the only study of this kind. This approach is adapted here for the ECPF of propionyl (PC) and n-butyryl chloride (n-BC) by systematically analyzing the HF phase at different stages of electrolysis. Since the perfluorinated products such as perfluoropropionyl fluoride (bp = −30 °C) and perfluoro-n-butyryl fluoride (bp = 5 °C) are highly volatile [16], they do not remain in the HF phase. This allows convenient draining of HF phase and comprehensive analysis of even trace levels of fluorinated compounds in the HF phase.

2. Results and discussion

Typical partially fluorinated and perfluorinated carboxylic acid salts obtained at different stages of ECPF of PC are presented in Table 1. The product selectivity values presented in this table are calculated based on the ^{19}F NMR signal intensities obtained at each

Table 1
Selectivity (mol%) of products obtained from ECPF of propionyl chloride after passing pre-determined electricity.

Compound	Selectivity (mol%) of products after passing pre-determined electricity					
	0%	25%	50%	75%	100%	[a]Immersion cooler
CH_3-CHFCOONa (I)	–	18.0	16.1	9.83	<0.01	–
CH_2F-CH_2COONa (II)	–	–	–	32.71	<0.01	–
CH_3CF_2COONa (III)	–	<0.01	15.1	<0.01	<0.01	0.53
CHF_2-CH_2COONa (IV)	–	–	–	18.9	–	–
CH_2F-CHFCOONa (V)	–	–	–	12.71	–	–
CF_3-CH_2COONa (VI)	–	–	–	6.68	–	–
CH_2F-CF_2COONa (VII)	–	–	10.0	–	–	0.33
CHF_2-CF_2-COONa (VIII)	–	–	5.7	–	–	1.0
CF_3CF_2COONa (X)	10.5	18.0	9.45	0.39	7.5	92.7
CF_3COONa (XIII)	14.3	–	2.2	1.1	23.0	2.1
F_2C=C(CH_3)COONa (XIV)	75.2	9.3	8.5	3.76	57.5	<0.01
Others		54.7	32.95	13.9	12.0	4.0

CF_3CHFCOONa (IX), CH_2FCOONa (XI), CF_2HCOONa (XII), and $CF_3CF_2CF_2$COONa (XXI) are traces in immersion cooler trap.
[a] At the end of the completion of electrolysis (after 100% of theoretical charge passed).

Table 2
Selectivity (mol%) of products obtained from ECPF of n-butyryl chloride after passing pre-determined electricity.

Compound	Selectivity (mol%) of products after passing pre-determined electricity					
	0%	25%	50%	75%	100%	[a]Immersion cooler
CH_3CHFCH$_2$COONa (XV)	<0.01	47.63	8.69	17.23	–	–
$CH_3CF_2CH_2$COONa (XVI)	–	16.62	17.08	19.35	2.88	–
$CF_3CH_2CH_2$COONa (XVII)	–	3.19	3.60	3.34	1.73	–
CF_2HCF_2CH_2COONa (XVIII)	–	–	0.13	–	–	0.18
$CF_3CF_2CF_2$COONa (XXI)	–	0.29	0.59	0.95	19.65	81.5
$(CF_3)_2$CHCOONa (XXII)	–	0.41	1.26	0.82	0.82	0.21
CF_3CF_2COONa (X)	9.83	0.51	0.12	0.18	5.50	4.45
CF_3COONa (XIII)	2.87	0.386	1.06	1.14	6.18	5.50
F_2C=C(CH3)COONa (XIV)	87.3	4.06	4.68	6.0	6.46	–
H_3CFC=CHCOONa (XXIV)	–	1.64	9.98	5.04	<0.01	–
Others		25.25	52.81	45.95	56.78	8.16

$CF_3CH_2CF_2$COONa (XIX), $CF_3CF_2CH_2$COONa (XX), $(CF_3)_2$CFCOONa (XXIII), CH_2FCOONa (XI), and CF_2HCOONa (XII), are found less than 1% in immersion cooler trap.
[a] At the end of the completion of electrolysis (after 100% of theoretical charge passed).

stage and hence they are not directly connected to the overall yield. Similar data for the ECPF of nBC are summarized in Table 2.

The ^1H and ^{19}F NMR data obtained from ECPF of PC as well as nBC are also summarized in Table 3. Some of the salient features connected with the mechanism of ECPF are discussed below.
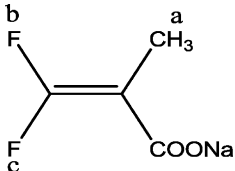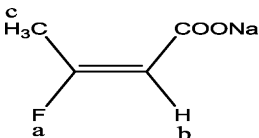
2.1. Zipper-mechanism

Electrochemical fluorination occurs on the active electrode surface even under open circuit potential (OCP) conditions. The nickel electrode during activation phase (before adding the organic

Table 3
^{19}F and ^1H NMR data of polyfluorinated and perfluorinated compounds obtained from ECPF of propionyl chloride and n-butyryl chloride.

Compound	^{19}F, δ (ppm)[a]	^1H, δ (ppm)	J (Hz)	Refs.
$\overset{b}{CH_3}\overset{a}{CH_2}$COONa		a: 2.085q b: 0.961t	$^3J_{H^aH^b}$ = 7.6	
$\overset{c}{CH_3}$-$\overset{b\ a}{CHF}$COONa(I)	a: −172.57quin (s)	b: 5.13dq c: 1.39dd	$^2J_{H^bF^a}$ = 48.9 $^3J_{H^cF^a}$ = 22.6 $^3J_{H^bH^c}$ = 7.6	[12,17,19]
$\overset{c}{CH_2}\overset{b}{F}$ − $\overset{a}{CH_2}$COONa(II)	b: −215.43tt (s)	a: 2.49dt c: 3.70dt	$^2J_{H^cF^b}$ = 48.9 $^3J_{H^aF^b}$ = 26.3 $^3J_{H^aH^c}$ = 8.0	[17,19]
$\overset{b}{CH_3}\overset{a}{CF_2}$COONa(III)	a: −96.77q (s)	b: 1.63t	$^3J_{H^bF^a}$ = 18.8	[12,17,19]
$\overset{c\ b}{CHF_2}$ − $\overset{a}{CH_2}$COONa(IV)	b: −115.08dt (s)	a: 2.66td c: –[d]	$^2J_{H^cF}$ = 56.5 $^3J_{H^aF^b}$ = 18.8 $^3J_{H^aH^c}$ = 4.8	
$\overset{d\ c}{CH_2F}$ − $\overset{b\ a}{CHF}$COONa(V)	a: −188.01m (d) c: −229.39m (d)	b: –[d] d: –[d]	$^2J_{H^dF^c}$ = 45.2 $^3J_{H^aF^a}$ = 15.1 $^3J_{H^dF^a}$ = 26.3	[17]
$\overset{b}{CF_3}\overset{a}{CH_2}$COONa(VI)	b: −62.68t (s)	a: 2.99q	$^3J_{H^aF^b}$ = 11.3	[12,19]
$\overset{c\ b}{CH_2F}$ − $\overset{a}{CF_2}$COONa(VII)	a: −114.55q (d) b: −237.45tt(t)	c: –[d]	$^2J_{H^cF^b}$ = 48.9 $^3J_{H^cF^a}$ = 15.1 $^3J_{F^bF^a}$ = 15.1	[19]
$\overset{c\ b}{CHF_2}$ − $\overset{a}{CF_2}$ − COONa(VIII)	a: −121.68q(t) b: −136.42dt(t)	c: 6.252tt	$^2J_{H^cF}$ = 52.7 $^3J_{H^cF^a}$ = 3.76 $^3J_{F^bF^a}$ = 4.80	[19]

Table 3 (*Continued*)

Compound	^{19}F, δ (ppm)[a]	^{1}H, δ (ppm)	J (Hz)	Refs.
$\overset{c}{C}F_3 - \overset{b\,a}{C}HFCOONa$(IX)	a: −194.46dq(q) c: −74.60dd	b: 5.39dm	$^{2}J_{H}{}^{b}{}_{F}{}^{a}$ = 48.9 $^{3}J_{F}{}^{a}{}_{F}{}^{c}$ = 11.3 $^{3}J_{H}{}^{b}{}_{F}{}^{c}$ = 7.5	[19]
$\overset{b}{C}F_3\overset{a}{C}F_2COONa$(X)	a: −119.92s (s) b: −82.17s (s)			
$\overset{b}{C}H_2\overset{a}{F}COONa$(XI)	a: −216.19t (s)	b: 5.07d	$^{2}J_{H}{}^{b}{}_{F}{}^{a}$ = 48.9	
$\overset{b}{C}F_2\overset{a}{H}COONa$(XII)	b: −123.63d (s)	a: −[d]	$^{2}J_{H}{}^{a}{}_{F}{}^{b}$ = 56.5	[17]
$\overset{a}{C}F_3COONa$(XIII)	a: −74.50 (s)			[12,18]
(XIV) — structure: b-F and a-CH₃ on C=C; c-F and COONa	[b]b: −72.10s (s) [b]c: −70.21s (s)	a: 1.881s		[17]
$\overset{c}{C}H_3\overset{b}{C}H_2\overset{a}{C}H_2COONa$		a: 2.106t b: 1.510sext c: 0.844t	$^{3}J_{H}{}^{a}{}_{H}{}^{b}$ = 7.2 $^{3}J_{H}{}^{b}{}_{H}{}^{c}$ = 7.2	
$\overset{d}{C}H_3 - \overset{c\,b}{C}HF - \overset{a}{C}H_2COONa$(XV)	b: −168.8oct.t (s)	a: −[d] c: −[d] d: 1.341dd	$^{2}J_{H}{}^{c}{}_{F}{}^{b}$ = 48.9 $^{3}J_{H}{}^{d}{}_{F}{}^{b}$ = 22.5 $^{3}J_{H}{}^{a}{}_{F}{}^{b}$ = 7.5 $^{3}J_{H}{}^{c}{}_{H}{}^{d}$ = 6.0	[17]
$\overset{c}{C}H_3\text{-}\overset{b}{C}F_2\text{-}\overset{a}{C}H_2COONa$(XVI)	b: −83.26sext (s)	a: 2.796t c: 1.688t	$^{3}J_{H}{}^{a}{}_{F}{}^{b}$ = 18.8 $^{3}J_{H}{}^{c}{}_{F}{}^{b}$ = 18.8	
$\overset{c}{C}F_3\text{-}\overset{b}{C}H_2\text{-}\overset{a}{C}H_2COONa$(XVII)	c: −65.44t (s)	a: 2.401t b: −[d]	$^{3}J_{H}{}^{b}{}_{F}{}^{c}$ = 11.3	
$\overset{d}{C}F_2H\text{-}\overset{c\,b}{C}F_2\text{-}\overset{a}{C}H_2COONa$(XVIII)	b: −118.06t (s) d: −136.78dqin (t)	a: 3.561t c: −[d]	$^{2}J_{H}{}^{c}{}_{F}{}^{d}$ = 52.7 $^{3}J_{H}{}^{b}{}_{F}{}^{d}$ = 7.5 $^{4}J_{F}{}^{a}{}_{F}{}^{d}$ = 7.5	
$\overset{c}{C}F_3\overset{b}{C}H_2\overset{a}{C}F_2COONa$(XIX)	a: −115.63t (s) c: −67.53t (s)	b: −[d]	$^{3}J_{H}{}^{b}{}_{F}{}^{c}$ = 11.3 $^{3}J_{H}{}^{b}{}_{F}{}^{a}$ = 11.3	
$\overset{c}{C}F_3\overset{b}{C}F_2\overset{a}{C}H_2COONa$(XX)	b: −117.98q c: −79.78t (t)	a: −[d]	$^{3}J_{H}{}^{a}{}_{F}{}^{b}$ = 7.5 $^{3}J_{F}{}^{b}{}_{F}{}^{c}$ = 7.5	
$\overset{c}{C}F_3\text{-}\overset{b}{C}F_2\text{-}\overset{a}{C}F_2COONa$(XXI)	a: −117.43q b: −126.47s c: −79.93t		$^{4}J_{F}{}^{a}{}_{F}{}^{c}$ = 11.3	
$(\overset{b}{C}F_3)_2\text{-}\overset{a}{C}HCOONa$(XXII)	b: −63.48d (s)	a: 4.968m	$^{3}J_{H}{}^{a}{}_{F}{}^{b}$ = 7.5	[12]
$(\overset{b}{C}F_3)_2\overset{a}{C}FCOONa$(XXIII)	a: −173.11sept b: −73.51d		$^{3}J_{F}{}^{a}{}_{F}{}^{b}$ = 7.5	[12]
(XXIV) — structure: c-H₃C and COONa on C=C; a-F and b-H	a: −79.64quin (s)	b: 5.544d c: 1.932d	$^{3}J_{H}{}^{b}{}_{F}{}^{a}$ = 18.8 $^{3}J_{H}{}^{c}{}_{F}{}^{a}$ = 18.8	[17]

[a] Multiplicity in parentheses is due to proton decoupled spectra.
[b] Splitting observed in some cases with coupling constant of 3.75 Hz.
[c] s-singlet; d-doublet; t-triplet; q-quartet; quin-quintet; sext-sextet; sept-septet; oct-octet; m-multiplet.
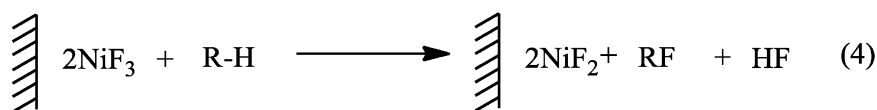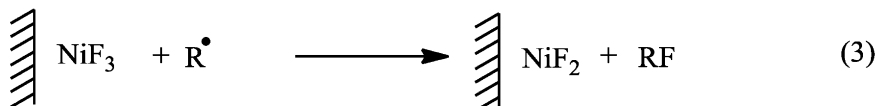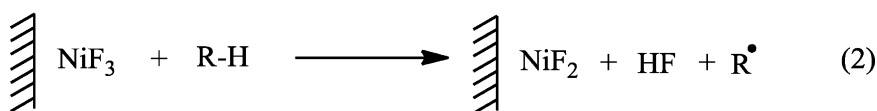[d] Some of the proton signals are merged with other signals. Wherever possible proton signals have been identified and reported.

reactant) is indeed converted to high valent nickel fluoride (Eq. (1) in Scheme 1). This active surface fluorinates the organic molecule even in the absence of electric current (Scheme 1). Quite interestingly perfluorinated products (X) and (XIII) are the major components in this process. Compound (XIV) is also due to the coupling of electro generated CF_3 radical with propionyl fluoride (Scheme 2). The unsaturated double bond is formed during the subsequent neutralization and evaporation steps.
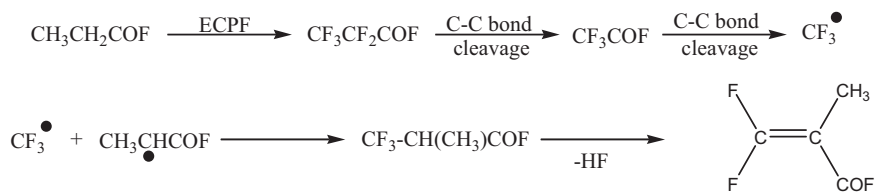
It is interesting to note that under open circuit potential (OCP) conditions, hydrogen gas evolution does not occur at the cathode surface and hence no stirring of the electrolyte due to gas evolution occurs. This would enable the organic reactants near the NiF_3 anode surface to undergo complete fluorination even if they are not strongly held by adsorption on the electrode surface. Thus the 'zipper-mechanism' may indeed be due to absence of mass transport.

Direct perfluorination of organic molecules on the electrode surface was termed as 'zipper-mechanism' [5] by earlier workers. At least this mechanism appears to operate under the zero current conditions. This type of fluorination under OCP was also observed earlier by Ignat'ev et al. [9]. In the case of n-BC, perfluorobutyryl derivative (XXI) is not at all obtained under open circuit conditions. C-3 (X) and C-2 (XIII) acid salts and CF_3 based compound (XIV) are the major products in this case. It appears that during perfluorination under OCP condition C–C bond cleavage predominates in the case of n-BC.

$$2NiF_2 + 2HF \longrightarrow 2NiF_3 + 2H^+ + 2e^- \qquad (1)$$

$$NiF_3 + R\text{-}H \longrightarrow NiF_2 + HF + R^\bullet \qquad (2)$$

$$NiF_3 + R^\bullet \longrightarrow NiF_2 + RF \qquad (3)$$

$$2NiF_3 + R\text{-}H \longrightarrow 2NiF_2 + RF + HF \qquad (4)$$

Scheme 1. Schematic diagram shows the fluorination reaction on active nickel electrode surfaces.

$$CH_3CH_2COF \xrightarrow{ECPF} CF_3CF_2COF \xrightarrow[\text{cleavage}]{\text{C-C bond}} CF_3COF \xrightarrow[\text{cleavage}]{\text{C-C bond}} CF_3^\bullet$$

$$CF_3^\bullet + CH_3\overset{\bullet}{C}HCOF \longrightarrow CF_3\text{-}CH(CH_3)COF \xrightarrow{-HF} \quad$$
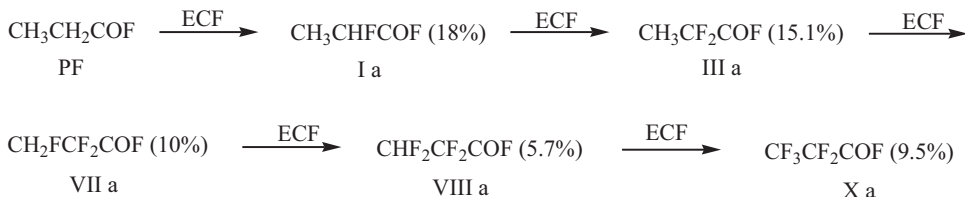
Scheme 2. Schematic diagram shows the formation of unsaturated fluoro compound (XIV) from propionyl chloride.

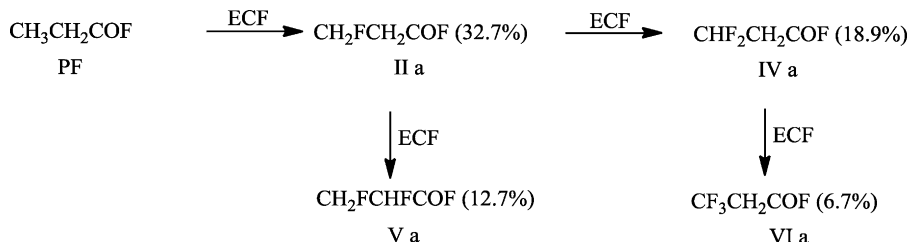## 2.2. Primary vs. secondary radical

During the initial stages of fluorination, number of partially fluorinated products are formed as indicated by NMR data (Fig. 1) of ECPF of n-BC after passage of 25% of theoretical charge. In the case of PC, α-fluorinated acid salt (I) constitutes about 18% of the total fluorinated molecules. In the case of n-BC, β-mono-fluoro (XV) and di-fluoro (XVI) compounds account for almost 64% of the total fluorinated molecule, and α-fluorinated butyryl derivatives are not noticed in the NMR signals. It appears that the initial free radical fluorination prefers a secondary carbon atom away from the carboxyl group wherever possible. Hence β-carbon fluorination for n-BC and α-carbon fluorination for PC are observed as indicated above. The more difficult α-carbon fluorination has been noticed earlier for many other compounds like trialkylamine [3,5–7].

2.3. Random fluorination

The wide distribution of partially fluorinated products at different stages of fluorination indicates that there are no major selectivity rules favoring any particular fluorination site. The number of partially fluorinated products increase with increasing the percentage of theoretical charge passed. The minor constituents and unidentified fluorine signals reach almost 33% of the total signals for C-3 acid salt (Table 1) and about 50% of the total signals for C-4 acid salt (Table 2). One can also observe stepwise fluorination in both cases. In the case of PC, for example, the following sequence of fluorinated products are observed after passage of 50% of theoretical charge as shown in Scheme 3. Stepwise fluorination of end methyl group is also noticed in the identified partially fluorinated compounds for PC after passage of 75% of theoretical charge as shown in Scheme 4. All these

$$CH_3CH_2COF \xrightarrow{ECF} CH_3CHFCOF\ (18\%) \xrightarrow{ECF} CH_3CF_2COF\ (15.1\%) \xrightarrow{ECF}$$
$$\text{PF} \qquad\qquad\qquad \text{I a} \qquad\qquad\qquad\qquad \text{III a}$$

$$CH_2FCF_2COF\ (10\%) \xrightarrow{ECF} CHF_2CF_2COF\ (5.7\%) \xrightarrow{ECF} CF_3CF_2COF\ (9.5\%)$$
$$\text{VII a} \qquad\qquad\qquad \text{VIII a} \qquad\qquad\qquad\qquad \text{X a}$$

Scheme 3. Schematic diagram shows the formation of polyfluoro compounds from propionyl chloride after the passage of 50% of theoretical charge.

$$CH_3CH_2COF \xrightarrow{ECF} CH_2FCH_2COF\ (32.7\%) \xrightarrow{ECF} CHF_2CH_2COF\ (18.9\%)$$
$$\text{PF} \qquad\qquad\qquad\quad \text{II a} \qquad\qquad\qquad\qquad\quad \text{IV a}$$
$$\downarrow \text{ECF} \qquad\qquad\qquad\qquad\qquad\quad \downarrow \text{ECF}$$
$$CH_2FCHFCOF\ (12.7\%) \qquad\qquad CF_3CH_2COF\ (6.7\%)$$
$$\text{V a} \qquad\qquad\qquad\qquad\qquad \text{VI a}$$

Scheme 4. Schematic diagram shows the formation of polyfluoro compounds from propionyl chloride after the passage of 75% of theoretical charge.
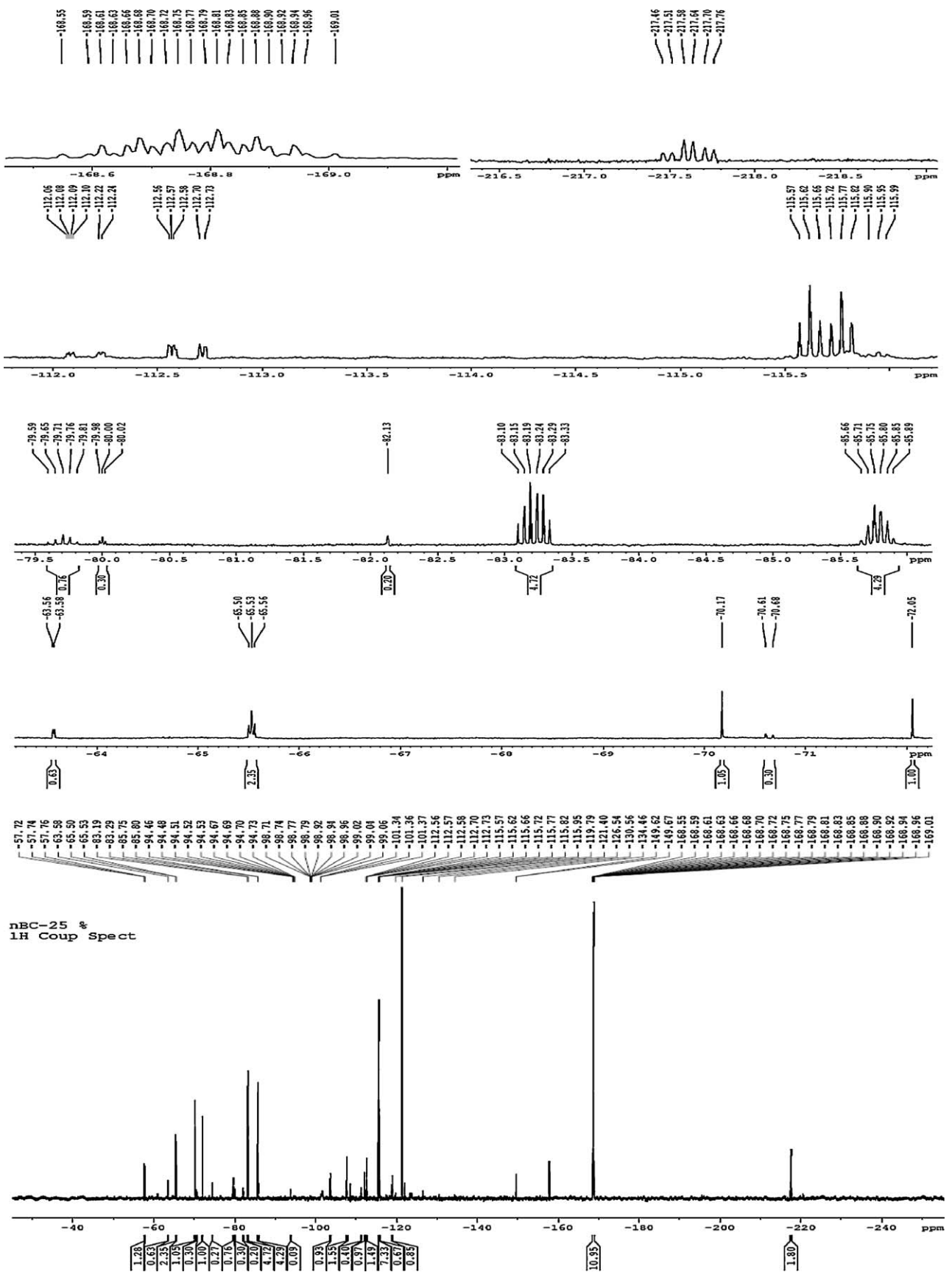
Fig. 1. Proton coupled ^{19}F NMR spectrum of fluorinated carboxylates obtained after 25% of the charge passed in the ECPF of n-BC.

observations indicate random free radical fluorination of all the C–H bonds.

2.4. Carbon chain isomerization

Carbon chain isomerization is not possible in the case of PC. Even in the case of n-BC isomerized products (XXII) and (XXIII) are formed only with very low selectivity. Conversion of linear molecule into isomerized product is quite difficult according to the cyclopropane intermediate mechanism suggested earlier [12–14].

2.5. Cleavage and coupling

In the free radical pathway C–C bond cleavage leading to compounds with less number of carbon atoms as well as radical–radical coupling or radical–reactant coupling leading to molecules containing more number of carbon atoms should be possible. This is indeed observed in the case of fluorination of PC, for example, compound (XIII) with one carbon atom less and compounds (XIV) and (XXI) with one carbon atom more are formed. In the case of n-BC, compound (X) with one carbon atom less and compound (XIII) with two carbon atoms less are noticed. Compound with one carbon more was also observed during ECF of n-BC with less than 1%.

The overall selectivity of perfluorinated compounds generally decreases slightly with increasing chain length [13,14]. This type of behaviour is noticed here as well. The overall selectivity of perfluoro compound (X) was 92% while the selectivity of perfluoro compound (XXI) was 81.5% obtained from immersion cooler trap (after 100% of theoretical charge passed).

3. Conclusions

The present study provides further evidence for the direct involvement of high valent nickel fluorides on the electrode surface at least during the initial stages of electrochemical perfluorination. Free radical mechanism appears to be the major pathway as indicated by formation of large number of partially fluorinated compounds at every stage of electrochemical fluorination. For both PC and nBC this mechanism also explains radical coupling, C–C bond cleavage and carbon chain isomerization. At least in the initial phases fluorination proceeds at the secondary carbon atom. Fluorination at the α-carbon atom may slightly be more difficult due to steric effect and electronic effect. Carbocation pathway or EC_bEC_N mechanism is not absolutely necessary for explaining the last two factors. It is thus, safe to conclude that free radical pathway with the involvement of high valent nickel fluorides is the overall mechanistic pathway of electrochemical perfluorination.

4. Experimental details

4.1. Reagents and apparatus

Synthetic grade (>98%) alkane carboxylic acid chlorides were purchased from M/s SRL, India 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 D_2O as solvent. $CFCl_3$ and TMS were used as internal reference for ^{19}F and ^{1}H NMR spectra respectively.

4.2. Electrochemical perfluorination of acid chlorides

A double walled 200 ml stainless steel electrolytic cell with alternate nickel anodes and cathodes (effective anode area = 2.47 dm^2) was employed. The cell and condenser temperature were maintained at 5 and −30 °C, respectively. Volatile products were collected in a FEP (Fluorinated Ethylene Propylene) trap kept at −80 °C using an immersion cooler at the outlet of the cell condenser.

Pre-electrolysis was carried out for 48 h in order to dry AHF and activate the electrode surfaces. Cell voltage was maintained between 5.0 and 5.5 V during this period until the initial current of 4 A reduced to 0.2 A. A mixture of acid chloride (40 g of PC) and AHF was prepared separately and added to the ECF cell after the completion of pre-electrolysis. Cell current was switched off for 30 min and about 20 ml of electrolyte mixture was drained off from the cell to analyze the fluorinated product with out passing current to the cell (0% charge). Electrolysis was then continued at constant current of 4.0 A (cell voltage 5–6.5 V) until theoretical charge was passed. About 20 ml of electrolyte was drained at every 25% of theoretical charge passed. Drained electrolytes at every stage and the condensate from the immersion cooler trap at the end of complete electrolysis were immediately neutralized with aqueous sodium hydroxide solution and water was evaporated using rotary evaporator at 60 °C until complete dryness. Dry salt obtained contains sodium salt of poly fluorinated acids and sodium fluoride. The fluoro organic product was extracted using anhydrous methanol. The methanol insoluble NaF was filtered off. Methanol extract was evaporated to dryness under vacuum to get sodium polyfluoro propionate. Similar procedure was followed for the ECPF of n-butyryl chloride.

4.3. Identification of fluorinated products

Identification of partially fluorinated products was carried out by recording ^{19}F (both ^{1}H coupled and decoupled spectra) and ^{1}H NMR of crude products. Assignment of molecular structure and the identification of fluorinated products are based on,

a. chemical shifts exhibited by various fluoro groups (mono, di, tri, etc.);
b. integral values;
c. splitting pattern obtained from both ^{1}H coupled and decoupled spectra; and
d. coupling constant values.

References

[1] H.M. Scholberg, H.G. Bryee, US Patent 2,717,871 (1955).
[2] G.P. Gambaretto, M. Napoli, L. Conte, A. Scipioni, R. Armelli, J. Fluorine Chem. 27 (1985) 149–155.
[3] A. Dimitrov, S. Rudiger, J. Fluorine Chem. 47 (1990) 23–33.
[4] A. Dimitrov, H. Stewig, S. Rudiger, L. Kolditz, J. Fluorine Chem. 47 (1990) 13–22.
[5] S. Rudiger, A. Dimitrov, K. Hottmann, J. Fluorine Chem. 76 (1996) 155–160.
[6] A. Dimitrov, D. Pfeifer, U. Jonethal, S. Rudiger, K. Seppelt, J. Fluorine Chem. 82 (1977) 143–150.
[7] A. Dimitrov, S. Rudiger, K. Seppelt, T. Peplinski, J. Fluorine Chem. 68 (1994) 15–19.
[8] G. Udo, S. Rudiger, A. Dimitrov, J. Fluorine Chem. 76 (1996) 139–144.
[9] P. Sartori, N. Ignat'ev, S. Datsenko, J. Fluorine Chem. 75 (1995) 157–161.
[10] P. Sartori, D. Velayutham, N. Ignat'ev, M. Noel, J. Fluorine Chem. 83 (1997) 1–8.
[11] P. Sartori, N. Ignat'ev, J. Fluorine Chem. 87 (1998) 157–162.
[12] D. Velayutham, K. Jayaraman, K. Kulangiappar, N. Ilayaraja, Y. Rambabu, P. Santhan Rao, S. Narayana Reddy, K. Victor Babu, M. Noel, J. Fluorine Chem. 127 (2006) 1111–1118.
[13] N.V. Ignat'ev, U.W. Biermann, U. Heider, A. Kucheryna, S.V. Ahsen, W. Habel, P. Sartori, H. Willner, J. Fluorine Chem. 124 (2003) 21–37.

[14] N. Ilayaraja, A. Manivel, D. Velayutham, M. Noel, J. Appl. Electrochem. 38 (2008) 175–186.
[15] E. Hollitzer, P. Sartori, J. Fluorine Chem. 35 (1987) 329–341.
[16] G.G. Totir, G.S. Chottiner, C.L. Gross, D.A. Scherson, J. Electrochem. Soc. 148 (2001) 262–266.
[17] R. Dolbier (Ed.), Guide to Fluorine NMR for Organic Chemists, John Wiley & Sons, New York, 2009.
[18] H. Gunther (Ed.), NMR Spectroscopy, An Introduction, John Wiley & Sons, New York, 1980.
[19] R. Fields, Annu. Rep. NMR Spectrosc. 5 (Part 1) (1972) 99–304.