Prevention of anode fouling during the electrochemical perfluorination of aromatic carboxylic acid chlorides

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ARTICLE INFO

ABSTRACT

The electrochemical perfluorination of benzoyl chloride, *p*-substituted benzoyl chlorides and *cyclo*-hexane carboxylic acid chloride in anhydrous hydrogen fluoride (AHF) medium on nickel electrode is reported. Experimental conditions suppressing polymeric film formation on the electrode are optimized. Addition of 1 wt.% dimethyl sulfide based on the volume of AHF in the initial stage of electrochemical fluorination and maintenance of the reactant and intermediate concentrations below a critical level ensured electrochemical fluorination of all the reactants without fouling of the electrode surface. Presence of *p*-substituents in the benzene ring improved the selectivity of alicyclic perfluoro carboxylic acid. GC/MS and ^{19}F NMR data for the major perfluorinated products are reported.

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1. Introduction

Electrochemical perfluorination (ECPF) of aliphatic carboxylic acid chlorides, a well known industrial process, has received considerable attention from time to time [1–4]. However, publications relating to the ECPF of aromatic carboxylic acid chlorides are scarce. An aromatic compound like pyridine with a heteroatom in the nucleus has not undergone any polymerisation and fouling on the electrode and hence facile perfluorination of such compounds is possible [5]. ECPF of alkyl-substituted benzoyl chlorides has been achieved with electrode polarity reversal according to an early US patent [6]. This is the only report cited by Abe and Nagase in their comprehensive review in 1982 [7]. ECPF of dimethyl isophthalate [8] and alkoxy benzoyl chlorides [9] in the presence of about 10% dimethyl sulfide (DMS) has also been reported. Neither the optimum operating conditions nor the product distribution obtained during the ECPF of these compounds is available in the literature.

It is well known that aromatic hydrocarbons undergo oxidative polymerisation leading to electrode fouling [10]. Some preliminary ECPF experiments of benzoyl chloride and related compounds carried out earlier in this laboratory also indicated similar effects. The primary objective of the present work is to overcome such effects by optimizing the reactant and additive (DMS) concentration, reversing the electrode polarity and minimizing the residual

reactant in the electrolytic cell. The effect of substituents in the benzene ring on the yield and product distribution are discussed.

2. Results and discussion

2.1. Electrochemical perfluorination of 4-methylbenzoyl chloride

Preliminary optimization studies were carried out using 4-methylbenzoyl chloride (**1b**) and the results are summarized in Table 1. During initial experiment at a current density of 13.0 mA/cm^2, darkening of the electrolyte solution was observed and the cell voltage increased gradually from the initial value of 5 to 6 V. Beyond 6 V, the current density decreased to 4.5 mA/cm^2 with a sharp rise in the cell voltage. It was observed that the blackening of electrolyte and sharp rise in cell voltage always lead to black tar like film formation on the electrode surface, which is referred to as electrode fouling. The total yield of perfluorinated products based on reactant taken was only around 25% (Table 1, Run 1). When the ECPF experiment was carried out at 8.7 mA/cm^2, around 40.5 g of reactant could be fluorinated. However, the electrode fouling effects became visible after 62 h. The conversion yield was improved to 34% (Table 1, Run 2).

The effect of polarity reversed was studied when the cell reached 6 V while employing a current density of 8.7 mA/cm^2 (Table 1, Run 3). The anode surface became cathodic and vice versa during polarity reversal. This procedure delayed the electrode fouling process to some extent and the theoretical electric charge required for the electrolysis could be passed. However, the electrode fouling could not be prevented by this procedure. Post-electrolysis observation revealed that, both the electrodes

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Table 1
Optimization studies on 4-methylbenzoyl chloride.

Run	Quantity of reactant (g)	Additive[a] (g)	Current density (mA/cm^2)	Electric charge (Ah)	Product obtained (g)	Yield (%)	Current efficiency (%)
1	21.1	–	13.0	77	13.2	25.5	24.3
2	40.4	–	8.7	142	32.2	34.0	33.5
[b]3	29.5	–	8.7	122	37.3	53.7	45.0
[b]4	42.1	0.2	8.7	166	56.3	56.7	49.8
[b]5	29.6	2.1	8.7	125	44.7	64.1	52.8
[c]6	38.5	2.1	8.7	166	66.9	73.7	59.6
[c]7	52.7	2.1	13.0	219	70.1	54.4	45.8

[a] Dimethyl sulfide (DMS) as additive.
[b] Experiment with polarity reversal.
[c] 10% excess current during each reactant addition.

contained black film after electrolysis. Interestingly, the yield was improved to 54% (Table 1, Run 3) under these conditions.

It has been reported in the literature that, inorganic metal fluorides can be used as additives during electrochemical fluorination of bicyclic aromatic compounds [11]. Sulfur containing compounds such as dimethylsulfoxide [12], mercaptan [13], and sulfolane [14] are known to inhibit anode fouling. Of all these additives, DMS has been reported to be efficient during the electrochemical fluorination of aromatic compounds [8].

Efforts were made in this study to find out the minimum concentration of DMS required to prevent the electrode fouling. In the initial experiment, 0.2 g of DMS in 210 ml of electrolyte (around 0.1%, w/v) was added along with the first batch of the reactant (4-methylbenzoyl chloride). The polarity reversal was also found to be necessary together with the DMS addition and the conversion yield was improved to 57% as indicated in Table 1 (Run 4). Further improvement in the conversion yield was observed when employing 2.1 g of DMS (1%, w/v).

During electrolysis, polymerisation and electrode fouling were noticed especially during subsequent reactant addition. In all the above experiments, around 5% reactant was added (10 g per 210 ml electrolyte) in each step. Further additions were made as soon as the theoretical electric charge was passed. Since the overall current efficiency is ~60% or less (Table 1), presence of partially fluorinated intermediates in the solution is inevitable. To ensure complete fluorination of these intermediates, 10% excess electric charge was passed during the electrolysis of each batch before introducing the next batch of reactant. This procedure was found to be very effective, since the cell voltage remained within the range of 5.0–5.5 V throughout the electrolysis and hence no polarity reversal was required. The yield was calculated to be around 74% (Table 1, Run 6). After electrolysis, no fouling on the electrode surface was noticed and the electrodes could be used for prolonged periods of time. Even at slightly higher current densities, the ECPF proceeded with no fouling effect (Table 1, Run 7). It may be noted that, under these experimental conditions, DMS was added only once in the beginning of the electrolysis and only around 1.0% (w/v) was required. In contrast, early patent literatures indicated addition of larger quantities of DMS (~10.0% DMS, w/v) along with the reactants [8,9].

Recent investigations of ECPF mechanism have suggested the involvement of electro-generated NiF$_3$ film in the overall process according to the following reaction sequences [15–17]:

$$2NiF_2 + 2F^- \rightleftharpoons 2NiF_3 + 2e^- \tag{1}$$

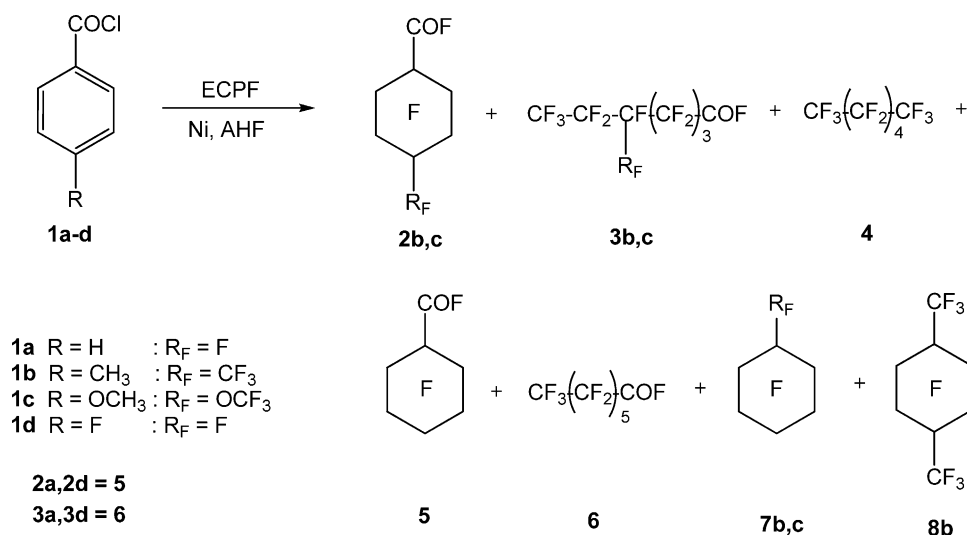$$2NiF_3 + RH \rightleftharpoons 2NiF_2 + RF + HF \tag{2}$$

The availability of NiF$_3$ active sites is thus a pre-requisite for efficient ECPF process. The formation of aromatic cation radicals and their polymerisation on the nickel anode is believed to partial or complete blocking of such active sites.

Sulfur containing compounds may preferably be adsorbed on the electrode surface and subsequently undergo partial or complete electrochemical fluorination. These adsorbed molecules probably form a dispersed fluoro organic layer which prevents the polymerisation of aromatic compounds at the electrode surface. In a recent investigation on the interaction between organic molecules and nickel fluoride films, it was shown that sulfur containing compounds, e.g., sulfolane, formed a thin uniform composite layer on nickel fluoride surface [18]. This film probably prevents dissolution of nickel and simultaneously retains the electro-catalytic activity of the nickel fluoride surface. As long as the total concentration of polymerisable reactants and intermediates is kept below a critical level, the nickel electrode is active and the total cell voltage remains in the range from 5.0 to 5.5 V.

2.2. Substituent effects

The validity of electrolysis conditions optimized during the perfluorination of 4-methylbenzoyl chloride was examined for three other aromatic compounds and cyclo-hexane carboxylic acid chloride (**1e**). These experiments were carried out by adding 5% (w/v) of acid chloride in each batch, electrolysing the solution at a current density of 13.0 mA/cm^2 and passing 10% excess electric charge before the addition of subsequent batches of the reactant. 2.1 g of DMS was also added along with the first batch of the reactant. Under these conditions, the cell voltage varied between 5.0 and 5.5 V for all the five compounds and the electrolyte did not turn black. The results obtained for the five carboxylic acid

Table 2
Camparison of yield and current efficiency of different acid chlorides.

Run	Compound	Quantity of reactant (g)	Electric charge (Ah)	Product obtained (g)	Yield (%)	Current efficiency (%)
1	**1a**	59.0	201	56.2	40.8	36.5
2	**1b**	52.7	219	70.1	54.4	45.8
3	**1c**	53.0	201	44.6	36.4	30.2
4	**1d**	79.2	215	80.1	48.9	42.5
5	**1e**	45.9	183	41.1	40.0	40.4

Current density = 13.0 mA/cm^2.
Additive (DMS) = 2.1 g.

Scheme 1. Products obtained during electrochemical perfluorination of different aromatic carboxylic acid chlorides in AHF medium.
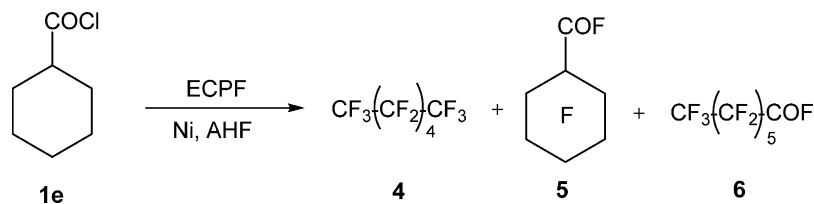
Scheme 2. Electrochemical perfluorination of *cyclo*-hexane carboxylic acid chloride in AHF medium.

chlorides under identical conditions are summarized in Table 2. The total yield was found to be around 40% for benzene (Table 2, Run 1) and *cyclo*-hexane carboxylic acid chlorides (Table 2, Run 5). Of all the acid chlorides, 4-methoxybenzoyl chloride exhibited the lowest overall yield of 36.4% (Table 2, Run 3). The ether linkage in this molecule may probably be more susceptible to bond cleavage. Both 4-methyl (Table 2, Run 2) and 4-fluoro (Table 2, Run 4) benzoyl chlorides containing electron donating and electron withdrawing groups, respectively, showed maximum yields (54 and 49%, respectively). Absence of any substituents in the *para*-position probably enhances the possibility of cationic center in this position. This may lead to nucleophilic attack and formation of quinon like intermediates which results in polymerisation [22]. It appears that the presence of a stable *p*-substitution in the benzene ring, irrespective of its electron donating or electron withdrawing nature, enhances the efficiency of perfluorination process.

Perfluoro carboxylic acids present in the product mixtures from each experiments were isolated by treating the product mixture with excess alkali and the alkali insoluble perfluorocarbons were separated. The alkaline phase was treated with excess hydrochloric acid to isolate the water insoluble perfluoro carboxylic acids. The overall volatility loss during the isolation process was ~20%.

2.3. Distribution of perfluorinated compounds in the product mixture

The crude products obtained from the electrochemical fluorination of each reactant (1a–e) were treated with NaF to remove traces of HF followed by fractional distillation. The middle fraction (93% of the total weight taken) obtained in the boiling range 56–70 °C was subjected to GC/MS and ^{19}F NMR analysis to determine the product distribution pattern and to characterise the products, respectively.

The product distribution pattern for the perfluorination of aromatic carboxylic acid chlorides (1a–d) is indicated in Scheme 1. Similar product distribution pattern was observed for compound 1e as shown in Scheme 2. As can be seen from Schemes 1 and 2, major products identified were alicyclic (2,5) and aliphatic (3,6) carboxylic acid fluorides. The amount of perfluorocarbons obtained (4,7,8) were relatively lower than the perfluoro acids. The product distribution pattern specifying the selectivity towards acid fluorides (2,3,5,6) are indicated in Table 3. The major alicyclic and aliphatic perfluorinated products indicated in Schemes 1 and 2 which were identified by using GC/MS and ^{19}F NMR are summarized in Tables 4 and 5. The NMR results were also compared with available literature data [19–21] wherever possible.

The product distribution obtained for benzoyl chloride (1a), 4-fluorobenzoyl chloride (1d) and *cyclo*-hexane carboxylic acid chloride (1e) was quite similar. In the case of aromatic starting materials, the yield of main perfluorinated product (5) was found to be over 50% and the *p*-fluoro substitution improved the

Table 3
Selectivity of alkali soluble perfluoro products obtained from ECPF of aromatic and cyclic carboxylic acid chlorides.

Reactants	Perfluorinated products obtained from alkali soluble fraction (mol%)				
	2	**3**	**5**	**6**	Other[a]
1a	–	–	50.5	25.5	24.0
1b	45.5	20.7	10.4	7.5	15.9
1c	42.5	19.9	12.9	6.6	19.1
1d	–	–	60.5	22.7	16.8
1e	–	–	35.8	30.8	33.4

[a] Based on GC/MS data.

Table 4
^{19}F and GC/MS data of perfluoro products obtained during ECPF of aromatic and cyclic carboxylic acid chlorides [15–21].
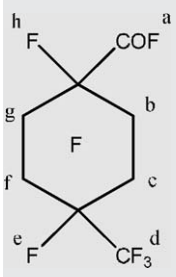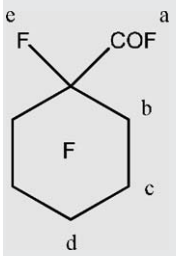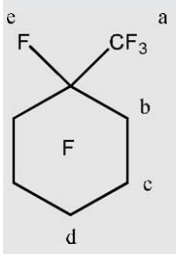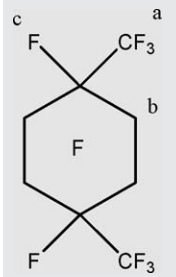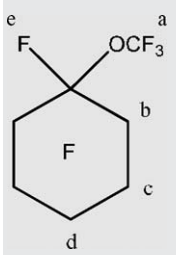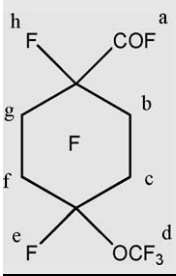
Compound	^{19}F Chemical shift (δ, ppm)	MS m/z (rel. int.)
(structure: h F, COF a, g, b, f, F, c, e F, CF$_3$ d)	$a = +39.45$ (1F, m) $b = -118.84, -119.55, J_{AB} = 267$ Hz $c = -128.40, -129.10, J_{AB} = 264$ Hz $d = -69.98$ (3F, m) $e = -188.70$ (1F, m) $f = -129.92, -129.22, J_{AB} = 264$ Hz $g = -119.11, -119.81, J_{AB} = 264$ Hz $h = -180.10$ (1F, m)	378 ([M]$^+$, C$_8$F$_{14}$O, 0.5%); 359 ([M−F]$^+$, C$_8$F$_{13}$O, 3.0%); 331 ([M−COF]$^+$, C$_7$F$_{13}$, 2.0%); 309 ([M−CF$_3$]$^+$, C$_7$F$_{11}$O, 1.5%); 293 ([M−OCF$_3$]$^+$, C$_7$F$_{11}$, 0.5%); 150 ([C$_3$F$_6$]$^{.+}$, 5.0%); 128 ([C$_3$F$_4$O]$^{.+}$, 2.0%); 100 ([C$_2$F$_4$]$^+$, 18.0%); 69 ([CF$_3$]$^+$, 100%); 50 ([CF$_2$]$^+$, 4.0%); 47 ([COF]$^+$, 21.0%); 31 ([CF]$^+$, 15.0%)
(structure: e F, COF a, b, c, F, d)	$a = +35.08$ (1F, m) $b = -116.93, -117.69, J_{AB} = 286$ Hz $c = -122.60, -123.34, J_{AB} = 278$ Hz $d = -129.94, -130.61, J_{AB} = 252$ Hz $e = -184.30$ (1F, m)	328 ([M]$^{.+}$, C$_7$F$_{12}$O, 2.1%); 312 ([M−O]$^+$, C$_7$F$_{12}$, 4.1%); 309 ([M−F]$^+$, C$_7$F$_{11}$O, 2.1%); 293 ([M−(O)F]$^+$, C$_7$F$_{11}$, 12.3%); 281 ([M−COF]$^+$, C$_6$F$_{11}$, 2.0%); 100 ([C$_2$F$_4$]$^+$, 100%); 50 ([CF$_2$]$^+$, 4.0%); 47 ([COF]$^+$, 20.1%); 31 ([CF]$^+$, 16.2%)
(structure: e F, CF$_3$ a, b, c, F, d)	$a = -72.57$ (3F, m) $b = -120.15, -120.94, J_{AB} = 297$ Hz $c = -124.14, -124.93, J_{AB} = 297$ Hz $d = -131.87, -132.61, J_{AB} = 278$ Hz $e = -187.15$ (1F, m)	350 ([M]$^+$, C$_7$F$_{14}$, 0.01%); 331 ([M−F]$^+$, C$_7$F$_{14}$, 1.5%); 312 ([C$_7$F$_{12}$]$^+$, 1.5%); 281 ([C$_6$F$_{11}$]$^+$, 2.4%); 150 ([C$_3$F$_6$]$^+$, 11.0%); 100 ([C$_2$F$_4$]$^+$, 18.0%); 69 ([CF$_3$]$^+$, 100%); 50 ([CF$_2$]$^+$, 3.0%)
(structure: c F, CF$_3$ a, b, F, F, CF$_3$)	$a = -70.25$ (6F, m) $b = -118.78, -119.55, J_{AB} = 290$ Hz $c = -187.27$ (2F, m)	400 ([M]$^{.+}$, C$_8$F$_{16}$, 0.01%); 381 ([M−F]$^+$, C$_8$F$_{15}$, 0.1%); 331 ([M−CF$_3$]$^+$, C$_7$F$_{13}$, 1.5%); 312 ([C$_7$F$_{12}$]$^+$, 1.5%); 262 ([C$_6$F$_{10}$]$^+$, 0.7%); 200 ([C$_4$F$_8$]$^+$, 8.0%); 100 ([C$_2$F$_4$]$^+$, 18.0%); 69 ([CF$_3$]$^+$, 100%); 50 ([CF$_2$]$^+$, 3.5%);
(structure: e F, OCF$_3$ a, b, c, F, d)	$a = -54.96$ (3F, m) $b = -119.53, -120.31, J_{AB} = 293$ Hz $c = -129.38, -130.16, J_{AB} = 293$ Hz $d = -134.96, -135.70, J_{AB} = 278$ Hz $e = -179.06$ (1F, m)	366 ([M]$^{.+}$, C$_7$F$_{14}$O, 0.1%); 347 ([M−F]$^+$, C$_7$F$_{13}$O, 3.1%); 297 ([M−CF$_3$]$^+$, C$_6$F$_{11}$O, 1.9%); 281 ([C$_6$F$_{11}$]$^+$, 2.5%); 150 ([C$_3$F$_6$]$^+$, 3.7%); 100 ([C$_2$F$_4$]$^+$, 21.9%); 85 ([OCF$_3$]$^+$, 0.4%); 69 ([CF$_3$]$^+$, 100%); 50 ([CF$_2$]$^+$, 3.7%)
(structure: h F, COF a, g, b, f, F, c, e F, OCF$_3$ d)	$a = +35.14$ (1F, m) $b = -117.09, -117.82, J_{AB} = 275$ Hz $c = -129.36, -130.07, J_{AB} = 267$ Hz $d = -54.97$ (3F, m) $e = -179.70$ (1F, m) $f = -130.07, -130.84, J_{AB} = 289$ Hz $g = -119.50, -120.26, J_{AB} = 286$ Hz $h = -179.06$ (1F, m)	394 ([M]$^{.+}$, C$_8$F$_{14}$O$_2$, 0.1%); 375 ([M−F]$^+$, C$_8$F$_{13}$O$_2$, 0.6%); 347 ([M−COF]$^+$, C$_7$F$_{13}$O, 0.6%); 328 ([C$_7$F$_{12}$O]$^+$, 0.3%); 309 ([C$_7$F$_{11}$O]$^+$, 9.7%); 294 ([C$_6$F$_{10}$O$_2$]$^+$, 28.2%); 175 ([C$_4$F$_6$O]$^+$, 11.8%); 100 ([C$_2$F$_4$]$^+$, 35.3%); 85 ([OCF$_3$]$^+$, 2.4%); 69 ([CF$_3$]$^+$, 100%); 50 ([CF$_2$]$^+$, 2.4%); 47 ([COF]$^+$, 11.8%); 31 ([CF]$^+$, 4.7%); 28 ([CO]$^+$, 11.8%)

Table 5
^{19}F and GC/MS data of cleaved perfluoro products obtained during ECPF of aromatic and cyclic carboxylic acid chlorides [15–21].

Compound	^{19}F Chemical shift (δ, ppm)	MS m/z (rel. int.)
$\overset{g\ \ f\ \ e\ \ d\ \ c\ \ b\ \ a}{CF_3\text{-}CF_2\text{-}CF\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}COF}$ $\underset{CF_3}{\overset{h}{\mid}}$	$a = +39.76$ (1F, m) $b = -115.39$ (2F, m) $c = -118.75$ (2F, m) $d = -120.94$ (2F, m) $e = -180.13$ (1F, m) $f = -125.64$ (2F, m) $g = -81.42$ (3F, m) $h = -71.73$ (3F, m)	416 ($[M]^+$, $C_8F_{16}O$, 0.7%); 397 ($[M-F]^+$, $C_8F_{15}O$, 3.5%); 331($[M-O-CF_3]^+$, C_7F_{13}, 3.5%); 281 ($[C_6F_{11}]^+$, 7.1%); 269 ($[C_5F_{11}]^+$, 1.8%); 219 ($[C_4F_9]^+$, 14.3%); 200 ($[C_4F_8].^+$, 10.7%); 197 ($[C_4F_7O]^+$, 3.6%); 181 ($[C_4F_7]^+$, 57.1%); 150 ($[C_3F_6]^+$, 14.3%); 131 ($[C_3F_5]^+$, 71.4%); 119 ($[C_2F_5]^+$, 21.4%); 100 ($[C_2F_4].^+$, 27.1%); 97 ($[C_2F_3O]^+$, 2.8%); 69 ($[CF_3]^+$, 100%); 50 ($[CF_2]^+$, 4.3%); 47 ($[COF]^+$, 10.7%); 31 ($[CF]^+$, 7.1%)
$\overset{a\qquad b\qquad c}{CF_3\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_3}$	$a = -80.36$ (6F, m) $b = -120.31$ (4F, m) $c = -117.81$ (4F, m)	338 ($[M]^+$, C_6F_{14}, 0.1%); 319 ($[M-F]^+$, C_6F_{13}, 1.1%); 269 ($[M-CF_3]^+$, C_5F_{11}, 4.8%); 219 ($[C_4F_9]^+$, 7.1%); 169 ($[C_3F_7]^+$, 35.7%); 119 ($[C_2F_5]^+$, 76.1%); 100 ($[C_2F_4]^+$, 45.2%); 69 ($[CF_3]^+$, 100%); 50 ($[CF_2]^+$, 7.1%)
$\overset{g\ \ f\ \ e\ \ d\ \ c\ \ b\ \ a}{CF_3\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}COF}$	$a = +40.15$ (1F, m) $b = -115.71$ (2F, m) $c = -117.03$ (2F, m) $d,e = -117.63$ (4F, m) $f = -119.53$ (2F, m) $g = -85.17$ (3F, m)	366 ($[M]^+$, $C_7F_{14}O$, 0.1%); 347 ($[M-F]^+$, $C_7F_{13}O$, 2.5%); 297 ($[M-CF_3]^+$, $C_6F_{11}O$, 1.3%); 281 ($[C_6F_{11}]^+$, 1.9%); 269 ($[C_5F_{11}]^+$, 1.2%); 247 ($[C_5F_9O]^+$, 2.5%); 231 ($[C_5F_9]^+$, 6.3%); 219 ($[C_4F_9]^+$, 3.1%); 181 ($[C_4F_7]^+$, 18.7%); 131 ($[C_3F_5]^+$, 41.2%); 119 ($[C_2F_5]^+$, 21.2%); 100 ($[C_2F_4]^+$, 22.5%); 69 ($[CF_3]^+$, 100%); 50 ($[CF_2]^+$, 3.1%); 47 ($[COF]^+$, 12.5%); 31 ($[CF]^+$, 8.7%); 28 ($[CO]^+$, 1.9%)
$\overset{g\ \ f\ \ e\ \ d\ \ c\ \ b\ \ a}{CF_3\text{-}CF_2\text{-}CF\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}COF}$ $\underset{OCF_3}{\overset{h}{\mid}}$	$a = +40.24$ (1F, m) $b = -115.65$ (2F, m) $c = -119.50$ (2F, m) $d = -122.87$ (2F, m) $e = -179.70$ (1F, m) $f = -123.21$ (2F, m) $g = -84.76$ (3F, m) $h = -53.69$ (3F, m)	432 ($[M]^+$, $C_8F_{16}O_2$, 0.1%); 413 ($[M-F]^+$, $C_8F_{15}O_2$, 0.1%); 347 ($[M-OCF_3]^+$, $C_7F_{13}O$, 2.1%); 297 ($[C_6F_{11}O]^+$, 1.4%); 278 ($[C_6F_{10}O]^+$, 1.5%); 197 ($[C_4F_7O]^+$, 2.2%); 181 ($[C_4F_7]^+$, 14.1%); 147 ($[C_3F_5O]^+$, 2.8%); 131 ($[C_3F_5]^+$, 29.6%); 119 ($[C_2F_5]^+$, 16.9%); 100 ($[C_2F_4]^+$, 21.1%); 97 ($[C_2F_3O]^+$, 2.1%); 81 ($[C_2F_3]^+$, 2.3%); 69 ($[CF_3]^+$, 100%); 50 ($[CF_2]^+$, 4.2%); 47 ($[COF]^+$, 15.5%); 28 ($[CO]^+$, 1.5%)

selectivity to 60%. The proportion of aliphatic acid fluoride (**6**) formed by α cleavage of the ring was found to be in the range of 25%. In the case of (**1e**), the cleavage was more significant and compounds **5** and **6** were formed in almost equal proportion.

In the case of compounds **1b** and **1c** which contained –CH₃ and –OCH₃ groups in the p-position, the major products still contained –CF₃ and –OCF₃ groups. The selectivity of **2b** and **2c** was found to be around 40–45%. The aliphatic analogue with COF group obtained by α cleavage (compounds **3b** and **3c**) and the alicyclic analogue without R_F substitution (compound **5**) were the other major products. The perfluorocarbons (**4,7,8**) obtained in all these experiments due to the cleavage of –COF group was relatively lower especially in the case of aromatic starting materials. During the ECPF of **1b**, a small fraction of compound (**8a**) was obtained. This may be due to the conversion of –COF group in **1a** to –CF₃ group.

3. Conclusion

Oxidative polymerisation of aromatic compounds on the anode surface leads to the electrode fouling during electrochemical perfluorination of aromatic carboxylic acid chlorides. This can be prevented by adding 1% dimethyl sulfide (w/v) in the initial stage of electrochemical fluorination. The perfluorinated sulfur compounds adsorbed on the electrode surface sustain the electrode activity by preventing polymeric film formation. It is important to ensure that the total concentration of reactants and partially fluorinated intermediates should not be too high. This is to ensure that these reactants and intermediates do not couple among themselves leading to the formation of oligomers and polymers. Under these conditions, the perfluorinated alicyclic and aliphatic carboxylic acids are the main products. Substituents in the p-position of the benzene ring improve the selectivity of acid fluorides. The exact nature of the product formed from the DMS additive on the electrode surface and the influence of this product requires further investigation.

4. Experiments

4.1. General experimental procedures

An Aplab (India) DC power supply was used for the electrolysis. ^{19}F NMR spectra were recorded with 376.5 MHz (400 MHz for ^1H) Bruker NMR Spectrometer using CDCl₃ as solvent. CFCl₃ was used as internal reference for ^{19}F NMR spectra, respectively. The products were subjected to GC/MS analysis using Agilent 5975C GC/MSD (70 eV) coupled with Triple-Axis HED-EM detector and 7890A GC.

Synthetic grade (>98%) benzoyl chloride (**1a**), 4-methylbenzoyl chloride (**1b**), 4-methoxybenzoyl chloride (**1c**), 4-fluorobenzoyl chloride (**1d**) and cyclo-hexane carboxylic acid chloride (**1e**) were purchased from M/s Merck, Germany and used as received. Anhydrous hydrogen fluoride (AHF) >99.9% was supplied by M/s TANFAC, Cudalore, Tamilnadu, India.

4.2. Electrochemical cell

A double walled 200 ml capacity stainless steel cell with alternate nickel anodes and cathodes was employed (effective anode area = 230 cm²) for the electrolysis. The temperature of the cell and the condenser was maintained at 5 and −30 °C, respectively, using cryostats. Liquid products from the cell were drained through a ball valve fixed at the bottom of the electrolysis cell.

4.3. ECPF of substituted aromatic and cyclo-hexane carboxylic acid chlorides

Prior to each galvanostatic experiments, the electrolyte (AHF) was initially subjected to pre-electrolysis in the same electrochemical cell setup at a constant cell voltage V to ensure removal of trace level of moisture present in the AHF. During pre-electrolysis the nickel electrode is also anodically polarized and electrochemically activated. Pre-electrolysis was carried out for about 36–48 h until initial current of 4 A was reduced to 0.2 A (current drop

indicates the removal of moisture from AHF), the cell voltage was maintained between 5.0 and 5.5 V. A pre-determined quantity of respective acid chloride and AHF mixture was prepared separately before every addition. This is to ensure chemical conversion of aromatic acid chlorides into acid fluorides with the liberation of HCl gas, which is insoluble in AHF. This procedure ensures that the overall electrochemical process is free from the influence of chloride ions.

$$Ar-COCl + HF \rightarrow Ar-COF + HCl\uparrow$$
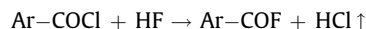
ECPF was carried out galvanostatically at a current density of 8.7 and 13 mA/cm^2. An acid chloride concentration of $\leq$5% (w/v) was taken initially and the electrolysis was carried out in a pre-electrolysed AHF medium. The required concentration of reactant and AHF was maintained periodically. The electrolysis was stopped after passing a pre-determined quantity of electric charge.

Crude perfluorinated products obtained from the cell drain were neutralized using aqueous KOH solution. The alkali soluble aqueous phase containing potassium perfluoro carboxylate and alkali insoluble phase (cyclic perfluoro carbons and perfluoro alkanes) were separated. Perfluoro carboxylic acid was obtained by acidifying the aqueous phase using concentrated hydrochloric acid. Other experimental details and product analysis methods employed in the present studies are described elsewhere [4,5].

Acknowledgements

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