Chapter 5

Prevention of anode fouling during the Electrochemical perfluorination of aromatic carboxylic acid chlorides.

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5.1.0 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 substituents in the benzene ring on the yield and product distribution are discussed.

5.2.0 Experiments

5.2.1 General Experimental Procedures
An Aplab (India) DC power supply was used for the electrolysis. $^{19}\text{F}$ NMR spectra were recorded with 376.5 MHz (400 MHz for $^{1}\text{H}$) Bruker NMR Spectrometer using CDCl$_3$ as solvent. CFCl$_3$ was used as internal reference for $^{19}\text{F}$ 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.

5.2.2 Electrochemical cell

A double walled 200 ml capacity stainless steel cell with alternate nickel anodes and cathodes were employed (effective anode area = 230 cm$^2$) 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.

5.2.3 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) and 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.

\[ \text{Ar-COCI} + \text{HF} \rightarrow \text{Ar-COF} + \text{HCl} \]  

ECPF was carried out galvanostatically at a current density of 8.7 and 13.0 mA/cm². An acid chloride concentration of ≤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].

**5.3.0 Results and discussion**

**5.3.1 Electrochemical perfluorination of 4-methylbenzoyl chloride**
Preliminary optimization studies were carried out using 4-methylbenzoyl chloride (1b) and the results are summarized in Table 5.1. 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 5.0 to 6.0 V. Beyond 6.0 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 5.1, Run 1). When the ECPF experiment was carried out at 8.7 mA/cm$^2$, around 40.5 g of reactant could be fluorinated. The conversion yield was improved to 34% (Table 5.1, Run 2).

**Table 5.1 Optimisation studies on 4-methylbenzoyl chloride**

<table>
<thead>
<tr>
<th>Run</th>
<th>Quantity of reactant (g)</th>
<th>Additive $^c$ (g)</th>
<th>Current density (mA/cm$^2$)</th>
<th>Electric charge (Ah)</th>
<th>Product obtained (g)</th>
<th>Yield (%)</th>
<th>Current efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.1</td>
<td>--</td>
<td>13.0</td>
<td>77</td>
<td>13.2</td>
<td>25.5</td>
<td>24.3</td>
</tr>
<tr>
<td>2</td>
<td>40.4</td>
<td>--</td>
<td>8.7</td>
<td>142</td>
<td>32.2</td>
<td>34.0</td>
<td>33.5</td>
</tr>
<tr>
<td>a3</td>
<td>29.5</td>
<td>--</td>
<td>8.7</td>
<td>122</td>
<td>37.3</td>
<td>53.7</td>
<td>45.0</td>
</tr>
<tr>
<td>a4</td>
<td>42.1</td>
<td>0.2</td>
<td>8.7</td>
<td>166</td>
<td>56.3</td>
<td>56.7</td>
<td>49.8</td>
</tr>
<tr>
<td>a5</td>
<td>29.6</td>
<td>2.1</td>
<td>8.7</td>
<td>125</td>
<td>44.7</td>
<td>64.1</td>
<td>52.8</td>
</tr>
<tr>
<td>b6</td>
<td>38.5</td>
<td>2.1</td>
<td>8.7</td>
<td>166</td>
<td>66.9</td>
<td>73.7</td>
<td>59.6</td>
</tr>
<tr>
<td>b7</td>
<td>52.7</td>
<td>2.1</td>
<td>13.0</td>
<td>219</td>
<td>70.1</td>
<td>54.4</td>
<td>45.8</td>
</tr>
</tbody>
</table>

$^a$ Experiment with polarity reversal

$^b$ 10% excess current during each reactant addition

$^c$ Dimethyl sulfide (DMS) as additive
The effect of polarity reversed was studied when the cell reached 6 V while employing a current density of 8.7 mA/cm² (Table 5.1, 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 contained black film after electrolysis. Interestingly, the yield was improved to 54% (Table 5.1, 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 5.1 (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 5.1), 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 5.1, 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 5.1, 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].

\[
\begin{align*}
2\text{NiF}_2 + 2\text{F}^- & \rightleftharpoons 2\text{NiF}_3 + 2e^- \quad (2) \\
2\text{NiF}_3 + \text{RH} & \rightleftharpoons 2\text{NiF}_2 + \text{RF} + \text{HF} \quad (3)
\end{align*}
\]

The availability of NiF\(_3\) active sites are thus a pre-requisite for efficient ECPF process. The formation of aromatic cation radicals and their polymerisation on the nickel anode is believed to be 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.

5.3.2 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/cm² 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 chlorides under identical conditions are summarised in Table 5.2. The total yield was found to be around 40% for benzene (Table 5.2, Run 1) and cyclo-hexane
carboxylic acid chlorides (Table 5.2, Run 5). Of all the acid chlorides, 4-methoxybenzoyl chloride exhibited the lowest overall yield of 36.4% (Table 5.2, Run 3). The ether linkage in this molecule may probably be more susceptible to bond cleavage. Both 4-methyl (Table 5.2, Run 2) and 4-fluoro (Table 5.2, 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.

**Table 5.2** Comparison of yield and current efficiency of different acid chlorides

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

Current density = 13.0 mA/cm²

Additive (DMS) = 2.1 g
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 \( \sim 20\% \).

5.3.3 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 \(^{19}\text{F} \) 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 5.3. The major alicyclic and aliphatic perfluorinated products indicated in Schemes 1 and 2 which were identified by using GC/MS and \(^{19}\text{F} \) NMR are summarised in Table 5.4 and 5.5. The NMR results were also compared with available literature data [19-21] wherever possible.
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.

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 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.

**Table 5.3** Selectivity of alkali soluble perfluoro products obtained from ECPF of aromatic and cyclic carboxylic acid chlorides

<table>
<thead>
<tr>
<th>Reactants</th>
<th>*Perfluorinated products obtained from alkali soluble fraction (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td>1a</td>
<td>--</td>
</tr>
<tr>
<td>1b</td>
<td>45.5</td>
</tr>
<tr>
<td>1c</td>
<td>42.5</td>
</tr>
<tr>
<td>1d</td>
<td>--</td>
</tr>
<tr>
<td>1e</td>
<td>--</td>
</tr>
</tbody>
</table>

<sup>a</sup>Based on GC/MS data

In the case of compounds 1b and 1c which contained -CH<sub>3</sub> and -OCH<sub>3</sub> groups in the <i>p</i>-position, the major products still contained -CF<sub>3</sub> and -OCF<sub>3</sub> 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<sub>F</sub> 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 -CF<sub>3</sub> group. The <sup>19</sup>F NMR spectra for perfluoro-4-methyl benzoyl fluoride, perfluoro benzoyl fluoride and perfluoro <i>cyclo</i>-hexane carboxylic acid fluoride are shown in Figs. 5.1-5.3 respectively.
Table 5.4 $^{19}$F and GC/MS data of perfluoro products obtained during ECPF of aromatic and cyclic carboxylic acid chlorides [15-21]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{19}$F Chemical shift ($\delta$, ppm)</th>
<th>MS m/z (rel. int.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a = +39.45 (1F, m)</td>
<td>378 ([M]$^{+}$, C$<em>8$F$</em>{14}$O, 0.5%); 359 ([M-F]$^{+}$, C$<em>8$F$</em>{13}$O, 3.0%); 331 ([M-COF]$^{+}$, C$<em>7$F$</em>{13}$, 2.0%); 309 ([M-CF$_3$]$^{+}$, C$<em>7$F$</em>{11}$O, 1.5%); 293 ([M-OCF$_3$]$^{+}$, C$<em>7$F$</em>{11}$, 0.5%); 150 ([C$_3$F$_6$]$^{+}$, 5.0%); 128 ([C$_3$F$_4$O]$^{+}$, 2.0%); 100 ([C$_2$F$_4$]$^{+}$, C$_3$F$_7$, 15.0%);</td>
</tr>
<tr>
<td></td>
<td>b = -118.84, -119.55 J$_{AB}$= 267 Hz</td>
<td>69 ([CF] +, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>c = -128.40, -129.10 J$_{AB}$= 264 Hz</td>
<td>18.0%); 69 ([CF$_3$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>d = -69.98 (3F, m)</td>
<td>18.0%); 69 ([CF$_3$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>e = -188.70 (1F, m)</td>
<td>18.0%); 69 ([CF$_3$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>f = -129.92, -129.22 J$_{AB}$= 264 Hz</td>
<td>18.0%); 69 ([CF$_3$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>g = -119.11, -119.81 J$_{AB}$= 264 Hz</td>
<td>18.0%); 69 ([CF$_3$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>h = -180.10 (1F, m)</td>
<td>18.0%); 69 ([CF$_3$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>a = +35.08 (1F, m)</td>
<td>328 ([M]$^{+}$, C$<em>7$F$</em>{12}$O, 2.1%); 312 ([M-O]$^{+}$, C$<em>7$F$</em>{12}$, 4.1%); 309 ([M-F]$^{+}$, C$<em>7$F$</em>{11}$O, 2.1%); 293 ([M-OH]$^{+}$, C$<em>7$F$</em>{11}$, 12.3%); 281 ([M-COF]$^{+}$, C$<em>6$F$</em>{11}$, 0.5%); 150 ([C$_3$F$_6$]$^{+}$, 5.0%); 128 ([C$_3$F$_4$O]$^{+}$, 2.0%); 100 ([C$_2$F$_4$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>b = -116.93, -117.69 J$_{AB}$= 286 Hz</td>
<td>328 ([M]$^{+}$, C$<em>7$F$</em>{12}$O, 2.1%); 312 ([M-O]$^{+}$, C$<em>7$F$</em>{12}$, 4.1%); 309 ([M-F]$^{+}$, C$<em>7$F$</em>{11}$O, 2.1%); 293 ([M-OH]$^{+}$, C$<em>7$F$</em>{11}$, 12.3%); 281 ([M-COF]$^{+}$, C$<em>6$F$</em>{11}$, 0.5%); 150 ([C$_3$F$_6$]$^{+}$, 5.0%); 128 ([C$_3$F$_4$O]$^{+}$, 2.0%); 100 ([C$_2$F$_4$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>c = -122.60, -123.34 J$_{AB}$= 278 Hz</td>
<td>328 ([M]$^{+}$, C$<em>7$F$</em>{12}$O, 2.1%); 312 ([M-O]$^{+}$, C$<em>7$F$</em>{12}$, 4.1%); 309 ([M-F]$^{+}$, C$<em>7$F$</em>{11}$O, 2.1%); 293 ([M-OH]$^{+}$, C$<em>7$F$</em>{11}$, 12.3%); 281 ([M-COF]$^{+}$, C$<em>6$F$</em>{11}$, 0.5%); 150 ([C$_3$F$_6$]$^{+}$, 5.0%); 128 ([C$_3$F$_4$O]$^{+}$, 2.0%); 100 ([C$_2$F$_4$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>d = -129.94, -130.61 J$_{AB}$= 252 Hz</td>
<td>328 ([M]$^{+}$, C$<em>7$F$</em>{12}$O, 2.1%); 312 ([M-O]$^{+}$, C$<em>7$F$</em>{12}$, 4.1%); 309 ([M-F]$^{+}$, C$<em>7$F$</em>{11}$O, 2.1%); 293 ([M-OH]$^{+}$, C$<em>7$F$</em>{11}$, 12.3%); 281 ([M-COF]$^{+}$, C$<em>6$F$</em>{11}$, 0.5%); 150 ([C$_3$F$_6$]$^{+}$, 5.0%); 128 ([C$_3$F$_4$O]$^{+}$, 2.0%); 100 ([C$_2$F$_4$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
<tr>
<td></td>
<td>e = -184.30 (1F, m)</td>
<td>328 ([M]$^{+}$, C$<em>7$F$</em>{12}$O, 2.1%); 312 ([M-O]$^{+}$, C$<em>7$F$</em>{12}$, 4.1%); 309 ([M-F]$^{+}$, C$<em>7$F$</em>{11}$O, 2.1%); 293 ([M-OH]$^{+}$, C$<em>7$F$</em>{11}$, 12.3%); 281 ([M-COF]$^{+}$, C$<em>6$F$</em>{11}$, 0.5%); 150 ([C$_3$F$_6$]$^{+}$, 5.0%); 128 ([C$_3$F$_4$O]$^{+}$, 2.0%); 100 ([C$_2$F$_4$]$^{+}$, 100%); 50 ([CF$_2$]$^{+}$, 4.0%); 47 ([COF]$^{+}$, 21.0%); 31</td>
</tr>
</tbody>
</table>
a = -72.57 (3F, m) 350 ([M]+, C7F14, 0.01%); 331 ([M-F]+, C7F14, 1.5%); 312 ([C7F12]+, 1.5%); 281 ([C6F11]+, 2.4%); 150 ([C3F6]+, 11.0%); 100 ([C2F4]+, 18.0%); 69 ([CF3]+, 100%); 50 ([CF2]+, 3.0%);
b = -120.15, -20.94 J AB= 297 Hz 69 ([CF3]+, 100%); 50 ([CF2]+, 3.0%);
c = -124.14, -124.93 J AB= 297 Hz 50 ([CF2]+, 3.0%);
d = -131.87, -132.61 J AB= 278 Hz 50 ([CF2]+, 3.0%);
e = -187.15 (1F, m)

a = -70.25 (6F, m) 400 ([M]+, C8F16, 0.01%); 381 ([M-F]+, C8F15, 0.1%); 331 ([M-CF3]+, 1.5%); 312 ([C7F12]+, 1.5%); 262 ([C6F10]+, 0.7%); 200 ([C4F8]+, 8.0%); 100 ([C2F4]+, 18.0%); 69 ([CF3]+, 100%); 50 ([CF2]+, 3.5%);
b = -118.78, -119.55 J AB= 290 Hz 69 ([CF3]+, 100%); 50 ([CF2]+, 3.5%);
c = -187.27 (2F, m) 85 ([OCF3]+, 0.4%); 69 ([CF3]+, 100%); 50 ([CF2]+, 3.7%);
d = -129.38, -130.16 J AB= 293 Hz 85 ([OCF3]+, 0.4%); 69 ([CF3]+, 100%); 50 ([CF2]+, 3.7%);
e = -179.06 (1F, m)
Table 5.5 $^{19}$F and GC/MS data of cleaved perfluoro products obtained during ECPF of aromatic and cyclic carboxylic acid chlorides [15-21]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{19}$F Chemical shift($\delta$, ppm)</th>
<th>MS m/z (rel. int.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a = +35.14 (1F, m)</td>
<td>394 ([M]$^+$, C$<em>8$F$</em>{14}$O$<em>2$, 0.1%); 375 ([M-F]$^+$, C$</em>{8}$F$<em>{13}$O$<em>2$, 0.6%); 347 ([M-COF]$^+$, C$</em>{7}$F$</em>{13}$O, 0.6%); 328 ([C$<em>7$F$</em>{12}$O]$^+$, 7.1%); 309 ([C$<em>7$F$</em>{11}$O]$^+$, 7.1%); 309 ([C$<em>7$F$</em>{11}$O]$^+$, 9.7%); 294 ([C$<em>7$F$</em>{10}$O$_2$]$^+$, 7.1%); 281 ([C$<em>6$F$</em>{11}$]$^+$, 7.1%); 269 ([C$<em>5$F$</em>{11}$]$^+$, 1.8%); 219 ([C$_4$F$_9$]$^+$, 7.1%); 197 ([C$<em>4$F$</em>{11}$O]$^+$, 3.6%); 181 ([C$<em>4$F$</em>{11}$]$^+$, 1.8%); 150 ([C$_3$F$_6$]$^+$, 14.3%); 131 ([C$_3$F$_5$]$^+$, 71.4%); 119 ([C$_2$F$_5$]$^+$, 71.4%); 100 ([C$_2$F$_4$]$^+$, 3.6%); 97 ([C$_2$F$_3$O]$^+$, 2.8%); 69 ([CF$_3$]$^+$, 100%); 50 ([CF$_2$]$^+$, 2.4%); 47 ([COF]$^+$, 11.8%); 31 ([CF]$^+$, 4.7%); 28 ([CO]$^+$, 11.8%);</td>
<td></td>
</tr>
</tbody>
</table>
a = -80.36 (6F, m)

b = -120.31 (4F, m)
c = -117.81 (4F, m)
d = -117.63 (4F, m)
e = -119.53 (2F, m)
f = -119.53 (2F, m)
g = -85.17 (3F, m)
h = -53.69 (3F, m)

CF₃-CF₂-CF₂-CF₂-CF₂-CF₃

338 ([M]+, C₆F₁₄, 0.1%); 319 ([M-F]+, C₄F₁₃, 1.1%); 269 ([M-CF₃]+, C₅F₁₁, 4.8%); 219 ([C₄F₉]+, 7.1%); 169 ([C₃F₇]+, 35.7%); 119 ([C₂F₅]+, 76.1%); 100 ([C₂F₄]+, 45.2%); 69 ([CF₃]+, 100%); 50 ([CF₂]+, 7.1%);

CF₃-CF₂-CF₂-CF₂-CF₂-CF₂-COF

366 ([M]+, C₇F₁₄O, 0.1%); 347 ([M-F]+, C₇F₁₃O, 2.5%); 297 ([M-CF₃]+, C₆F₁₁O, 1.3%); 281 ([C₆F₁₁]+, 1.9%); 269 ([C₅F₁₁]+, 1.2%); 247 ([C₅F₉O]+, 2.5%); 231 ([C₅F₉]+, 6.3%); 219 ([C₄F₉]+, 3.1%); 181 ([C₄F₇]+, 18.7%);

g = -84.76 (3F, m)  

CF₃-CF₂-CF₂-CF₂-CF₂-CF₂-COF

432 ([M]+, C₈F₁₆O₂, 0.1%); 413 ([M-F]+, C₈F₁₅O₂, 0.1%); 347 ([M-OCF₃]+, C₇F₁₃O, 2.1%); 297 ([C₆F₁₁]+, 1.4%); 278 ([C₆F₁₀]+, 1.5%); 197 ([C₄F₇]+, 2.2%); 181 ([C₄F₅]+, 14.1%); 147 ([C₃F₅O]+, 2.8%); 131 ([C₃F₅]+, 29.6%); 119 ([C₂F₅]+, 16.9%); 100 ([C₂F₄]+, 21.1%);

d = -122.87 (2F, m)

c = -179.70 (1F, m)

CF₃-CF₂-CF₂-CF₂-CF₂-CF₂-COF

97 ([C₂F₃O]+, 2.1%); 81 ([C₂F₃]+, 2.3%); 69 ([CF₃]+, 100%); 50 ([CF₂]+, 4.2%); 47 ([COF]+, 15.5%); 28 ([CO]+, 1.5%);
Fig. 5.1 $^{19}$F NMR spectra of Perfluoro 4-methyl benzoyl fluoride
Fig. 5.2 $^{19}\text{F}$ NMR spectra of Perfluoro benzoyl fluoride
Fig. 5.3 $^{19}$F NMR spectra of Perfluoro cyclo-hexane carboxylic acid fluoride
5.4.0 Conclusions

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.

References


17. D. Velayutham, K. Jayaraman, K. Kulangiappar, N. Ilayaraja, Y. Rambabu, P.


