Review on
RECENT DEVELOPMENTS IN THE SYNTHESIS OF PERFLUORO ORGANIC COMPOUNDS BY SIMONS PROCESS OF ELECTROCHEMICAL PERFLUORINATION

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INTRODUCTION

Three principal electrochemical methods are known for introducing fluorine directly into organic compounds, namely electrolysis in anhydrous hydrogen fluoride at nickel anode (Simons Process), electrolysis in molten potassium fluoride/hydrogen fluoride melts at porous carbon anodes (Phillips Process) and electrolysis in fluoride ion solution at platinum anodes (Mild or Selective Flurination). Among the three methods, Simons process of electrochemical perfluorination (ECPF) is the widely adopted industrial process for the production of fluoro organic chemicals used for diverse applications. In this review, an attempt will be made to present a general picture of the three different methods and to focus on the recent developments on synthetic and technical aspects of Simons process.

Electrochemical methods of fluorination of organic compounds — Simons process

Simons Process of electrochemical perfluorination was developed during the 1940s by John Simons as part of the Manhattan Project during Second World War. The process comprises of the electrolysis of a solution or dispersion of organic compounds in anhydrous hydrofluoric acid (AHF) using nickel anodes and nickel or steel cathodes in undivided cells under conditions where evolution of gaseous fluorine does not normally occur. The process yields fully fluorinated products with certain important functional groups such as carboxylic acid, sulphonic acid and amines etc.

being retained in the perfluorinated product. The process is widely adopted by leading chemical manufacturing companies such as 3M Company of USA, Air Products Inc., Asahi Glass Co., BASF AG, Bayer AG, Daikin Industries, Green Cross Corporation, Tokuyama Soda KK and Rimas S.p.A. Research and Development work. These companies are often focussed towards expansion of the synthetic utility of the process, improvement of the production and energy efficiencies etc. The developments in the process have been periodically reviewed [1-13]. There are also several other active research groups in the Universities & Research Labs pursuing Simon process for the synthesis of fluoro organic chemicals such as, Prof. Sartori & group at Duisburg University, Germany, Prof. Gambaretto & group at Italy and several research groups at Japan, both in the Universities and Corporate sector.

Phillips process

It is well known that fluorine gas itself is manufactured electrochemically using carbon anode in KF-2HF melts at around 353 K. Using this type of melt electrolyte and porous electrode materials, a new method of electrochemical fluorination was developed by Phillips Petroleum Company of USA during the 1970s [14]. The process is also known as CAVE Process (Carbon Anode Vapor Phase Electrochemical Fluorination Process).

Phillips or CAVE process is characterised by the electro fluorination of volatile organic substrates

within the matrix of the pores of carbon anode kept immersed in KF.2HF as electrolyte (as in a mild temperature fluorine generator cell) and fluorination probably takes place at the three phase interface of organic vapour, solid carbon and liquid electrolyte in close proximity to or at the sites where fluorine evolves.

Products from Phillips process range from partially fluorinated to fully fluorinated compounds. Certain functional groups such as acyl fluorides, esters and some cyclic structures are retained after fluorination. However this process is hampered by technical complexities such as use of porous electrode, evolution of hazardous fluorine gas, exothermic reactions of fluorine with organic vapours, anode surface effects, etc. and hence the process is not reported to be utilised commercially except by a few companies (3M company and Phillips Petroleum Company) and there are not many reported R & D activities using this method.

Mild or selective fluorination

Electrochemical fluorination can also be carried out in a wide variety of aprotic solvents such as acetonitrile [15], triethyl amine dissolved in acetonitrile [16], $Et_3N.nHF$ and $Et_4NF.nHF$ [17], pyridine HF [18], etc. This process is potentially a unique route for the synthesis of partially fluorinated fluorochemicals which find wide application as speciality chemicals in Pharmaceuticals, Agrochemicals, Pesticides etc. But the process though widely studied remains to be a laboratory curiosity.

R & D work on mild fluorination is pursued by research workers in Japan [19-23]. Focus of research appears to have shifted from aromatic nuclear fluorination to the fluorination of side chains containing active methylene groups and heterocyclic compounds. Platinum is the electrode of choice but use of other anodes such as graphite has also been reported. The developments in this method has been reviewed recently [24]. This method is actively pursued by research workers in CECRI, India [25-27] and the method promises to be an elegant route for synthesis of partially fluorinated organics if the technical problems and process limitations are solved.
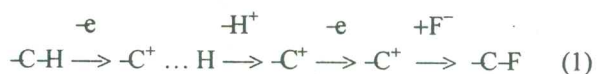
Mechanistic aspects --- Cave process

Among the three fluorination processes outlined above, there is little controversy, over the mechanism of fluorination by CAVE's process as well as selective fluorination process. The experimental conditions namely KF.2HF melt, the carbon anode and the operating temperature of CAVE's process are quite similar to those of fluorine generation processes [14,15]. Hence it is highly probable that the F2 gas itself or the active fluorine free radical intermediate formed on porous carbon anode / molten electrolyte interface is the species that fluorinates the organic molecules in CAVE's process.

Selective ECF

In selective electrochemical fluorination on platinum or compact non-porous carbon anodes, the efficiency of fluorination depends predominently on the oxidation potential of the substrate involved. Hence the two electron overall oxidation process occurs through successive electrochemical (E) and Chemical (C) sequence in an EC_B EC_B mechanism [28].

$$-C-H \xrightarrow{-e} -C^+ \dots H \xrightarrow{-H^+} -C^+ \xrightarrow{-e} -C^+ \xrightarrow{+F^-} -C-F \quad (1)$$

Inside chain fluorination reaction involving active methylene group attached to activating groups like sulfur, the initial electron transfer itslef is assisted by such activating groups. This mechanism is termed as Ponnrar Mechanism [25-27].

Simons process

However the reaction mechanism for Simon's process still remains a highly controversial and unsettled issue. Quite briefly, three mechanisms are proposed by different groups working in this area.

A carbocation mechanism was proposed as reported in [29-31]. This mechanism is very similar to the EC_B EC_B mechanism proposed

above for selective electrochemical fluorination in presence of solvents. In liquid HF, it is suggested that the strong HF media would assist the proton removal. With increasing fluorine substitution, the remaining hydrogen atoms would become more acidic and hence more easily removable according to these authors. This mechanism was supported by some evidences such as isomerisation products and cyclization during electrochemical fluorination. However, this mechanism contradicts the general fact that the oxidation potential of organic compounds increases with increasing fluorine or electron-withdrawing substituents. This is why, in selective fluorination, the substitution stops with mono or difluoro derivative. Even in Et4NF.nHF media [32-33], one cannot achieve replacement of more than 4 hydrogen atoms by fluorine atoms. This should be contrasted with Simon's process of octanoyl chloride for example where as many as 15 hydrogen atoms are completely substituted by fluorine atoms.

It should also be noted that electrochemical perfluorination occurs effectively only on nickel electrodes. It is well- established in recent studies in this laboratory that nickel is always covered by a compact nickel fluoride film which allows further electron transfer and oxidation only in the fluorine evolution region [34-36]. Even simple redox couples like ferrocene and quinhydrone which show well-defined redox behaviour on carbon and platinum electrodes [37] do not show any oxidation peak on nickel anodes upto 3 V. Hence the extrapolation of EC_B EC_B mechanism observed on platinum electrodes for one or two fluorine substitution to the perfluorination on NiF_2 film covered nickel electrode appears not justifiable.

A second popular mechanism for perfluorination is the well-known 'Zipper mechanism' which proposes that the reactant is adsorbed on the electrode surface and remain on it, until all the hydrogen atoms are substituted by fluorine atoms. This mechanism explains how the complete replacement of all the hydrogen atoms indeed becomes possible. However, it is well-known that many polyfluorinated species and even polymeric species always remain in solution during and even at the completion stages of electrochemical fluorination. Some recent analysis of the products in the HF phase have a large variety of partially fluorinated products are indeed formed, a fact which contradicts the operation of zipper mechanism as described in [38-39].

The third mechanism, namely free radical mechanism is gaining current in recent times with many evidences supporting it. In fact, Simons himself, during the very initial phase of development of the process suggested that electrogenerated active fluorine free radical acts as the fluorinating agent for the organic compounds. This mechanism certainly explains the wide product distribution, the potential independent fluorination for a number of substrates and other observations [40]. Watanabe provided some supporting evidence for the presence of active free radicals of fluorine on the anode surface [40]. Extensive product distribution studies during and at the end of fluorination process especially as reported in [38-39] supports the involvement of this free radical pathway. In our detailed investigation of product distribution during the electrochemical fluorination of N, N, N^1, N^1 tetramethyl ethylene diamine [41] and 2-fluoro pyridine [42] also, we observed the free radical pathway very useful in explaining the range of fragmented products.

However, a simple free radical mechanism cannot explain why nickel alone should be an effective anode for the process. The catalytic role played by the NiF2 film in the electrochemical perfluorination process is quite obvious. The retention of fluorine free radicals reported in [40] may in fact be due to its stabilisation as high-valent nickel fluoride such as NiF_3. Quite recently Zemwa and co-workers have synthesised such high valent nickel fluoride complexes in liquid HF. The oxidation reactions of high valent nickel fluorides were found to be similar to those of nickel anodes during electrochemical fluorination [43-44]. Sartori and his co-workers, have also 'electrogenerated' such high valent nickel fluorides on the nickel anodes by prolonged electrolysis and established their fluorinating

capabilities in their recent study [45]. These studies indeed require further confirmation. However, it appears safe to conclude that this is the most likely mechanistic pathway of electrochemical fluorination.

Synthetic Aspects and commercial applications of Simons Process

As discussed earlier, Simons Process dominates the other two ECF methods with regard to synthetic scope and commercial applications. This method has been used for the perfluorination of hydrocarbons, fluorohydrocarbons, chlorohydro carbons, amines, N-heteroaromatics, ethers, carboxylic acids and their derivatives, alkane sulphonyl chlorides and thiols. Products obtained are generally completely fluorinated. Thus all hydrogen is replaced with fluorine, carbon-carbon multiple bonds are saturated with fluorine and S=O bonds in sulfones and alkane sulphonyl chlorides and C=O bonds in carboxylic acids and their derivatives remain in tact to a useful degree. A high proportion of the published information on Simons process has been targetted at the synthesis of inert fluids, for applications in the fields of biomedical, medicine, electronics, hydraulics as well as in the more established fields of premium surfactants, emulsifying agents in polymerisation processes and synthetic building blocks. Recent developments in synthetic and other technical aspects of Simons process are reviewed in this section.

Perfluoro amines

Perfluoro amines are among the class of compounds that are commercially produced by Simons process. These form a part of perfluoro carbons (PFCs) which are used for biomedical purposes and comprise of perfluoro carbons or analogs containing other atoms such as oxygen, nitrogen and bromine in addition to carbon and fluorine. These PFC liquids have good solubilities for oxygen and are used as vehicles for respiratory gas transport primarily as O_2 carrying resuscitation fluids designed to supplement conventional blood transfusion. PFC emulsions are also referred to as "Blood substitutes". R and D

efforts on synthesis of perfluoro amines have been pursued by several groups all over the world for developing "Artificial Blood formulations".

Electrochemical fluorination of morpholine [45] and piperidine (1a) were among the earliest compounds studied. Research group in the University of Padua, Italy have studied the electrochemical fluorination of cyclic amines such as N-N diethyl cyclo hexyl amine and N-ethyl dicyclo hexyl amine [46]. These compounds are fluorinated with poor yields and form a mixture of fragmented products.

Green Cross Corporation, USA have been very active in the field of artificial blood substitutes and have studied e.c.f of several amines such as N-methyl decahydro quinoline and N-methyl decahydroisoquinoline [47], tripropylamine [48], bridge head nitrogen compounds such as quinolizidine and methyl substituted quinolizidine [49], N-cycloalkyl pyrrolidines and piperidene [50] etc. They have observed that ring opening reactions occur only at cyclo alkane rings, and bond scission occurred predominantly at a tertiary carbon. They were able to explain the products formation by either a ring contraction or ring opening reaction. Important factor in these processes appeared to be that of steric hindrance.

Electrochemical perfluorination of piperidene carbazole and morpholine derivatives were studied as described in [51-52]. Yields of perfluoro derivatives were of the order of 40-45% with the fluorination of N-carbazoles representing a new class of compounds. They have also emphasised the importance of ring contractions, fragmentations and rearrangements in these types of reactions.

Moldavsky and co-workers have conducted a detailed study of the electrochemical fluorination of commercially important amines such as tripropylamine, tributylamine and triamylamine and also a series of enamines formed by the reaction of hexafluoropropene, its dimers and trimers with secondary amines [53]. Their studies had again confirmed the advantage of using

partially fluorinated starting material for getting enhanced yields and higher current efficiencies.

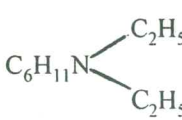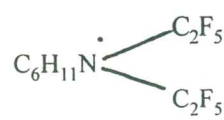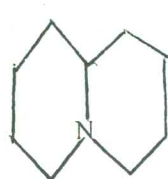Some of the other important perfluoro amines synthesised by ECF process are tabulated in Table I.
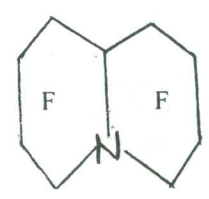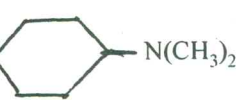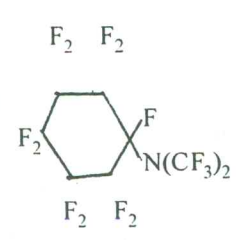
Amino ethers

Tertiary perfluoro amino ethers which can be obtained by electrochemical fluorination of tertiary hexafluoro proproxy alkylamines are another class of inert liquids which are highly suitable for uses such as heat transfer media or dielectrics in electrical systems. They can also be used as low temperature lubricants down to a temperature of

373 K. A range of these compounds can be synthesised with varying physical properties such as boiling points and viscosities for different applications such as hydraulic fluids, inert solvents for chemical reactions, superior oxygen carrier in blood substitute formulations etc. These fluids possess extraordinary chemical resistance to aggressive chemicals such as concentrated mineral acids, alkaline lyes, oxidants, reducing agents, elemental fluorine and fluorinating agents.

In view of the commercial utility of these compounds, companies such as 3M Co. of USA and HOECHST of Germany have been active in the fluorination of amino alkyl ethers. Moore et al. of 3M Co. [57] have reported methods for the electrofluorination of amino alkyl ethers of interest to them.

HOECHST of Germany have patented the electrofluorination of tertiary amino ethers containing perfluoro alkylene/perfluoro alkyl groups for applications as mentioned earlier [58]. HOECHST have also patented the electrochemical fluorination of the products formed by the reaction of hexafluoropropene with amino alcohols and have synthesised perfluorinated amines having side chains containing ether bonds [59]. All these perfluoro compounds were developed for applications as inert reaction media, hydraulic fluids, heat transfer fluids etc.

Dimitrov et al. have studied the electrochemical fluorination of a series of cyclic amino ethers for preparing possible candidates for blood substitutes [60]. The compounds synthesised by them are tabulated in Table II.

Dimitrov and his group have also reported the electrochemical fluorination of 2-phenyl-3,4-dimethylmorpholine [61], another possible candidate for blood substitute formulation.

Efforts to develop and test blood substitute formulations with different perfluoramines are in progress.

TABLE I: Perfluoro amines synthesis by ECF process

Starting material	Main product	Yield (%)	Reference
		26.9	46
		16-23	49
$(C_3H_7)_3N$	$(C_3F_7)_3N$	13	53
$(C_5H_{11})_3N$	$(C_5F_{11})_3N$	23	53
$(CH_3)_2NCOCl$	$(CF_3)_2NCOF$	37	54,55
		—	56

Nitrogen containing carboxylic acids

Nitrogen containing carboxylic acids are a new class of compounds which have been studied by scientists at the National Industrial Research institute of Nagoya, Japan. Nitrogen containing perfluorocarboxylic acids synthesised, were accessed for use as building blocks in biodegradable surfactants and chiral synthesis of biologically active compounds. Hayashi et al have studied the ECF reactions of a series of dialkyl amino acetic, propionic and butyric acid methyl esters where the dialkyl amino groups included dimethyl, diethyl, pyrrolino, morpholino, piperidino and N-methylpiperazino as substituents [62-67]. Typical of these reactions and yields are reported below.

$$(R)_2NCH_2CH_2C(O)OMe \longrightarrow (R)_2NCF_2CF_2C(O)F \quad (2)$$

where

R =	R_f =	Yield
CH_3	CF_3	11%
C_2H_5	C_2F_5	30%
C_3H_7	C_3F_7	26%
C_4H_9	C_4F_9	14%

Perfluoro carboxylic acids containing nitrogen and/or oxygen in the chain are regarded as soft type (degradable materials) in terms of environmental impact compared with those containing saturated perfluoro alkyl groups which are characteristically strong (non degradable). Thus perfluoro carboxylic acids containing nitrogen in the alkyl group are prospective key intermediates for the production of newer degradable fluorochemicals such as surfactants, water/oil repellants etc.

There are not many reports on the synthesis of this class of compounds and the area holds promise for further research in the synthesis of newer molecules.
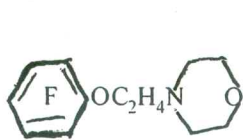
Sulphur compounds

Fluorinated organic sulphur compounds have potential applications in such diverse fields such as fuel cell electrolyte, ion exchange resins, high value surfactants and insecticides. Synthesis of sulphonyl and disulphonyl fluorides has hence engaged the attention of Researchers both in the Corporate Sector and Academic Institutions.

3M company of USA have patented the synthesis of a range of fluoro carbon sulfonic acids starting from trifluoromethanesulphonic acid [CF_3SO_3H] to perfluoro to n-octane sulphonic acid [$C_8F_{17}SO_3H$] [68]. Trifluoro methane sulphonic acid finds applications as esterification catalyst and its lithium salt is used as battery electrolyte. Derivatives of octane sulphonic acid and other $C_5 - C_6$ sulphonic acids find applications in fire fighting formulation, surfactants for imparting oil, water and soil resistant finishes to textiles, leather and paper etc. Perfluoro sulphonamides are used as plant growth regulators and herbicides.

E.C.F of disulphonyl fluorides have also been studied. O'Sullivan et al. [69] and Sartori et al. [70] have synthesised difluoro methyl disulphonyl fluoride with good yields. Gard and co- workers

TABLE II: Electrochemical fluorination of a series of cyclic amino ethers for preparing possible candidates for blood substituted

Starting material	Main product	Yield (%)	Reference
		76	60
$C_2H_5OC_2H_4N$ O	$C_2F_5OC_2F_4N$ F O	35	60

have reported the electrochemical fluorination of partially fluorinated ether containing disulphonyl fluoride CH_2 $(OCF_2 CF_2 SO_2F$ and synthesised fluorinated ether salt derivatives of the product e.g. $Ca [CF_2 (OCF_2 CF_2 SO_3)_2)]$ and characterised the new product [71]. Ignat'ev et al. have reported the electrochemical fluorination of a number of N,N- dialkylamido sulphonyl halides [72] and have made a comparative study of Simons process with cobalt trifluoride fluorination process. They have reported that the yield of fully fluorinated product in the product mixture was around 31% with ECF and 5.9% with the chemical process.

BAYER AG is another leading company which has reported the preparation of sulphonyl fluorides $C_3F_7CHSO_2F$ and $C_3F_7CH_2SO_2F$ in the electrochemical fluorination of sulpholene [73]. The company is also reported to have patented the preparation of perfluoro butyl sulphonyl fluoride.
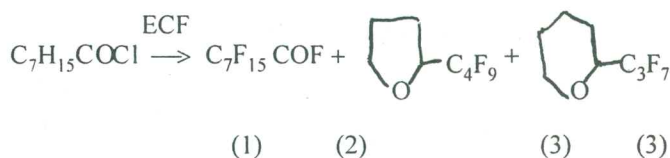
CIBA-Geigy of Switzerland have patented the synthesis of perfluoro octyl sulphonic acid fluoride [74] and Dow Corning Corporation have taken a patent on the electrochemical perfluorination of sulphones for synthesising perfluoro alkyl sulphonyl fluorides [75].

Electrochemical fluorination of a few other cyclic sulphones and miscellaneous sulphonyl chlorides are reported in Table III.

Carboxylic acids

Apart from sulphonic acids and amines, e.c.f. of carboxylic acids is in active area of research and process development studies for commercial product oriented application. Perfluoro carboxylic acids of the general formula C_nF_{2n+1} COOH are produced by the electrochemical perfluorination of the acid chlorides or fluorides (C_nH_{2n+1}COCl). Higher perfluoocarboxylic acids and their derivatives [C_3 onwards] have excellent surface poperties and find wide applications as premium surfactants in Textiles, Paper and Leather indutries. Trifluoro acetic acid is used as a catalyst in alkylation reaction. The yield and selectivity for perfluorcarboxylic acids decrease with increase in chain length of the acid

precursor. ECF of higher carboxylic acid chlorides is often accompanied by skeletal fragmentation, rearrangement and cyclisation processes. A typical example is the electrochemical perfluorination of octanoyl chloride, an important industrial process.

$$C_7H_{15}COCl \xrightarrow{ECF} C_7F_{15}COF + \underset{(2)}{\boxed{O}-C_4F_9} + \underset{(3)}{\boxed{O}-C_3F_7}$$

$$(1) \qquad (2) \qquad (3) \qquad (3)$$

As indicated in (1) above, acid chloride is the preferred precursor for the reaction. The products obtained in the e.c.f. reaction comprise of the perfluoro acid (1) and mixture of cyclic ethers (2) and (3) apart from small quantities of perfluoro heptane. The selectivity for perfluoro ethers was around 55-60% in the product mixture while that of the perfluoro acid fluoride was 30-35%. While perfluoro octanoic acid and its derivatives find applications such as emulsifier in teflon production

TABLE III: Electrochemical fluorination of few other cyclic sulphones and miscellaneous sulphonyl chlorides

Starting material	Main product	Yield (%)	Reference
[cyclohexyl]SO_2	n–$C_6F_{13}SO_2F$	—	76
CH_2ClSO_2Cl	CF_2ClSO_2F	57	77
[cyclopentyl]SO_2	n–$C_4F_9SO_2F$	40-48	76

and as premium surfactant, perfluoro ethers obtained as the major by- product find applications as heat transfer liquids and testing fluids for electronic components. The e.c.f. of octanoyl chloride has been well studied [78-83] relating to optimisation of process conditions, product distribution, cell design aspects etc.
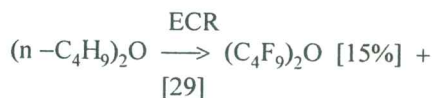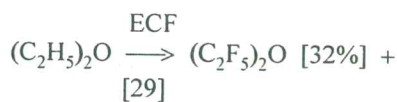
Electro synthesis of trifluoro acetic acid is another important commercial process and was one of the earliest compounds studied. 3M company of USA have studied the electrosynthesis of a series of perfluoro carboxylic acids from $C_1 - C_8$ for different applications [84,85]. There are also reports of the synthesis of perfluoro pentanoic and hexanoic acids [86] etc. Indian research workers at CECRI, Karaikudi have reported about the electrochemical perfluorination of octanoyl, hexanoyl and decanoyl chlorides to the respective acids [83].

Along with perfluoro amines and sulphonic acids, e.c.f of carboxylic acid remains to be an active area of research both in the academic and corporate sector. Many of the reviewers on Simons process cited earlier [1-4] have reported about the electrosynthesis of perfluoro carboxylic acids and their derivatives.

Electrosynthesis of perfluoro ethers

Saturated perfluoro ethers possess a unique combination of physical and chemical properties that have led to their applications in the electronic industry and medical fields. Perfluoro ethers are non polar, colourless, practically non toxic with excellent thermal stabilities.
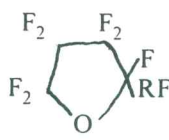
In general E.C.F of dialkyl ethers gives only poor yields of the corresponding perfluoro dialkyl ethers, due to the fission of C - O bond [88].

$$(C_2H_5)_2O \xrightarrow[\text{[29]}]{\text{ECF}} (C_2F_5)_2O \ [32\%] \ +$$

$$CF_3COF\,(36\%) \ + \ C_2F_6$$

$$(n-C_4H_9)_2O \xrightarrow[\text{[29]}]{\text{ECR}} (C_4F_9)_2O \ [15\%] \ +$$

$$n\text{-}C_3F_7COF\,(20\%) \ + \ C_2F_5COF\,(3\%) \ + \ CF_3COF \quad (4)$$

ECF of cyclic ethers proceed with better yields compared to perfluoro dialkyl ethers as given in reaction schemes tabulated in Table IV.

Cyclic ethers also obtained as the major product in the e.c.f. of carboxylic acid chlorides, by the formation of cyclised products [Ref. ECF of

TABLE IV: ECF of cyclic ethers proceed with beter yields compared to perfluoro dialkyl ethers

Starting material	Main product	Yield (%)	Reference
R = H	R_F = F	42	96
$n-C_4H_9$	$n\text{-}C_4F_9$	41	91
$CH_2O\ C_2H_5$	$CF_2O\ C_2F_5$	42	91
$CH_2O\ C_6F_5$	$CF_2O\ C_6F_{11}$ –cyclo	75	92
R = H	R_F = F	35	
$C_n\ H_{2n+1}$	$C_n\ F_{2n+1}$		
n = 1	n = 1	28	88
n = 2, 3, 4	n = 2, 3, 4	23	88
n = 5	n = 5	18	88

octanoyl chloride in section 4.1.5]. Advantage of the preparation of cyclic perfluoro ethers by the ECF of carboxylic acid chlorides or their derivatives lies in the alternate choice of starting material when the hydrocarbon analogue of the desired product is not easily accessible.

Cell design aspects and process improvement studies

Simons cell is basically an unstirred undivided cell with nickel electrodes with provision for cooling of cell contents and for condensing the vapours thorugh reflux condensor. There have been several modifications made to basic Simons cell to improve thr productivity of the cell in terms of higher operating current densities and to achieve better mixing conditions in the cell.

Drakesmith and Hughes have carried out extensive studies using the fluorination of propene and octanoyl chloride as the mdoel compounds and investigated the effect of parameters such as anode potential, current density, reactant concentration, temperature of electrolysis etc. on reproducibility, product yield and product distributiion in novel cell designs of capacities ranging from 100 ml to 100 litres [29]. They have shown that the use of porous nickel and nickel foam anodes provide high specific surface areas, excellent heat dissipation and good mixing.

Lin et al. have designed a novel microprocessor controlled modified Simon reactor system [93]. The reactor employs batch mixer design criteria to enhance mass transfer in the reactor.

3M company of USA have patented a bipolar electrode stack cell for carrying out electrochemical fluorination, which enables the reaction to be conducted with lower energy consumption [94].

Bayer AG [95] Germany have patented the deisgn of electrodes fabricated from nickel or coated with nickel, having a columnar structure. They claim the electrodes to be more stable and operating with lower cell voltages.

Watanabe of Central Glass Co. Japan has reported the development of anodes coated with composite layer of nickel containing a dispersed eutectoid of PTFE particles or fluorinated graphite particles [96].

There are continuing efforts by the R and D groups in the Corporate Sector to improve the cell design of Simons process for achieving better productivities in terms of space time yields, improve product selectivities, solve problems relating to anode corrosion and electrode surface effects, achieve continuous operation by electrolyte circulation, improve heat transfer and to make the Simons process adaptable for a range of substrates and also gaseous reactants. There are also reports of patents to study the use of additives to improve the efficiency of electro fluorination of alkyl sulphonyl chlorides [97] and electrosynthesis of perfluoro bicyclic compounds [98].

Studies have also been reported about the use of partially fluorinated reactants in Simons cell to improve the conversion and selectivities for the desired product in the e.c.f of carboxylic acid halides by blocking cyclisation process and improving the yield of perfluoro carboxylic acid fluorides [99- 102].

CONCLUSION

Simons process remains to be the most versatile electrochemical fluorination process while mild fluorination method appears to be promising. A wealth of literature is available on the synthetic aspects of Simons process. Several leading companies in the world are utilising Simons process for the production of commercially imporant fluoro organic chemicals. R and D groups in both academic and corporate sector are active in pursuing efforts to increase the synthetic scope of Simons process.

With the advantage of the use of simple equipments, mild reaction conditions, use of the 'clean' electrical power as the reagent for effecting chemical transformation, Simons process of electrochemical perfluorination process is and will remain to be a useful industrial method for electrochemical perfluorination of organics. Future research in this process should be directed towards further understanding of the role of nickel

electrodes in e.c.f, enhancing the synthetic scope of the process, improving the product selectivities by controlling the reaction parameters, introducing improved cell designs and examining the possibilities of synthesis of partially fluorinated products using this process.

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