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ELECTROCHEMICAL FLUORINATION USING POROUS NICKEL AND FOAM NICKEL ANODES

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SUMMARY

This work set out to examine the reasons behind some of the problems associated with ECF, namely, lack of reproducibility, low chemical yields, poor selectivity and low current densities, with a view to ameliorating these shortcomings and making the process more attractive to the chemical industry.

The approach was to study the chemistry under controlled conditions of potential, reactant concentration, temperature, etc., and to analyse the results in terms of product structure, distribution and yield.

Two distinct stages in the process were identified, i) the conditioning of the electrode, and, ii) the fluorination of the organic substrate.

These stages are described in detail in relation to two model systems investigated, the fluorination of propene using porous and foam nickel anodes, and the fluorination of the octanoyl chloride using nickel foam anodes. The scales of experiments ranged from 100ml to 100 l cell capacities.

General conclusions are derived and recommendations made for the more efficient operation of the process.

INTRODUCTION

Since the discovery of electrochemical fluorination (E.C.F.) by J.H. Simons[1] in the early 1940s, the scope of the method has been expanded to cover the fluorination of liquid, solid and, more recently, gaseous starting materials. In spite of the large number of compounds which have been studied using this technique there is still no clear

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understanding of the mechanism of fluorination, and indeed even the precise nature of the fluorinating agent (the presence of nickel appears to be essential) is not known, although several credible mechanistic hypotheses have been proposed[2]. The subject has been reviewed at regular intervals during the last few decades[3].

The Chemical Industry has shown interest in electrochemical fluorination over a number of years, principally because it yields, with the following advantages high value products.

(1) The process uses cheap raw materials. Anhydrous hydrogen fluoride and hydrocarbon feedstocks are of low cost relative to the expensive fluorocarbon products.

(2) Because the process is an electrochemical reaction the parameters (e.g. voltage, current) are controllable with precision, therefore precedent would suggest that the product should be, theoretically at least, controllable.

(3) The process requires relatively simple equipment compared with other types of chemical hardware, e.g. high pressure vessels, resulting in lower capital costs.

(4) E.C.F. allows one to prepare in a single step process certain highly fluorinated compounds containing functional groups, e.g. ethers, carboxylic - and sulphonic - acids, which are difficult to prepare by other methods.

(5) Electrical power is a relatively cheap 'reagent'. The power costs for the preparation of heptafluoropropane, a possible precursor for hexafluoropropene, are calculated below.

Chemical step:

$$CH_3 - CH = CH_2 \xrightarrow{HF} CH_3CHFCH_3$$

Electrochemical step:

$$CH_3CHFCH_3 \xrightarrow[6v]{E.C.F.} C_3HF_7$$

i.e. 12 electron process.

$$\text{Energy for 1 Kg product} = \frac{12 \times 26.8 \times 6}{170}$$

$$= 11.35 \text{ kWh}$$

Unfortunately, as Dresdner and Young remark in one of their papers[4], electrochemical fluorination is still an art in many respects and is often thwarted by problems of poor reproducibility, poor chemical yields, low current efficiencies, poor selectivity and low operating current densities.

Typical of these problems are those reported by Kazakov et al.[5] where 500 fluorination experiments are described and 'in practically none of the series of experiments was an acceptable reproducibility of results obtained'.

In order to make the process more attractive to the Chemical Industry it was our aim to investigate these problems in some detail. Towards this end, it was decided to study the reactions of propene as a model compound, as it had a number of different hydrogen atoms, and a double bond. If selectivity of fluorination were to be achieved, it ought to be seen with a molecule of this sort. Most work had been concerned with the electrochemical fluorination of liquids and solids, because these are technically easier to add to a typical Simons' cell with its conventional plate electrode package. Sartori[6] and, later, Nagase[3] reported the fluorination of organic gases by passing them through a P.T.F.E. frit in the base of a Simons' cell and allowing the stream of bubbles to percolate past the standard electrode assembly. Also, workers at Philips Corp., have reported high chemical and current yields from fluorination within a porous carbon anode[7].

We were interested to observe reaction using porous and foam anode materials with a view to performing the reaction at the three phase interface. Figures 1 and 2 show typical samples of porous nickel and nickel foam used as anodes. The porous nickel used was prepared in a collaborative venture between ECRC, Capenhurst and INCO Limited, using sintered powder technology. The nickel foam was prepared by Dunlop Limited, Aviation Division, and marketed under the trade name 'Retimet'. Several advantages were expected to accrue from these materials, for example, high specific surface area per unit volume (typically, 80 mesh - 5600:1 m^2/m^3), allowing lower current densities and higher space/time yields; built-in turbulence promotors, resulting in improved mass transfer and thermal dissipation[8]. The apparatus and the experiments described in this paper were designed to study the electrochemical fluorination by careful control of the reaction parameters, e.g. electrode potentials, temperature, concentration of reactants, contact time, etc., in an attempt to gain a clearer understanding of the process in general.

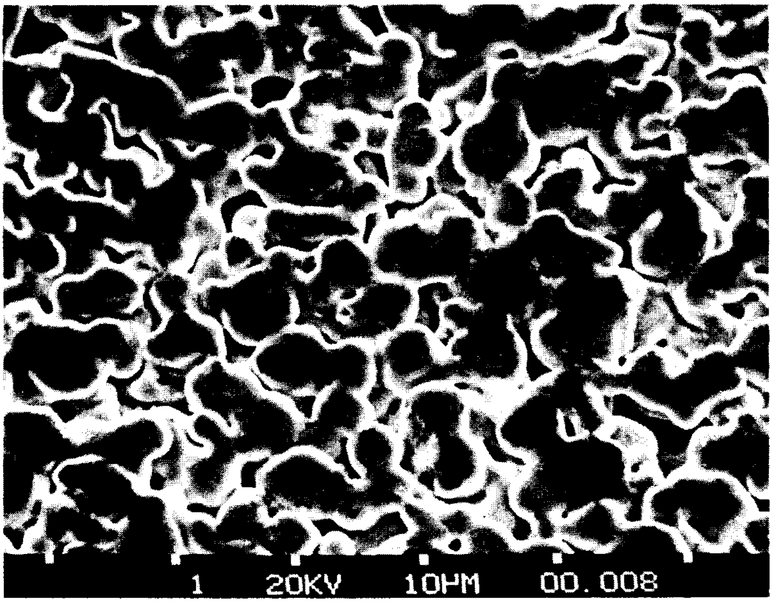


Fig. 1. Porous nickel anode. (approx. 1500x mag.)

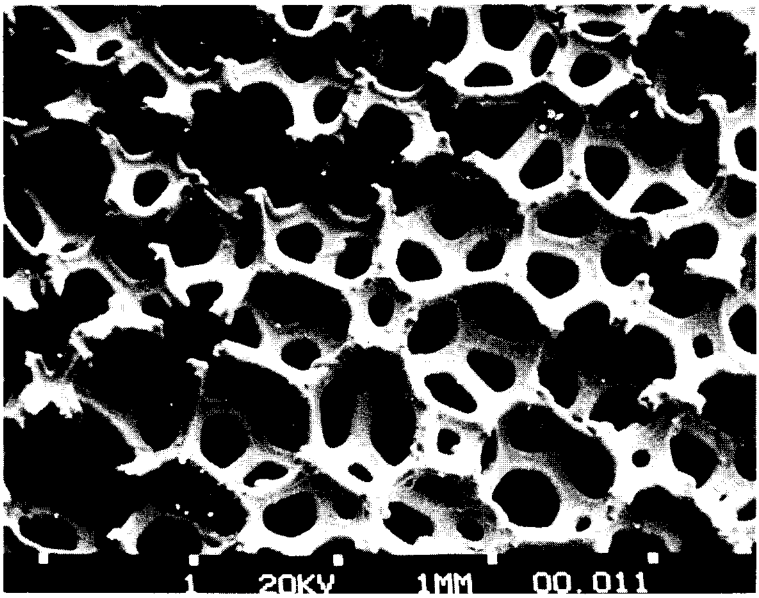


Fig. 2. Nickel foam anode. (approx. 20x mag.)

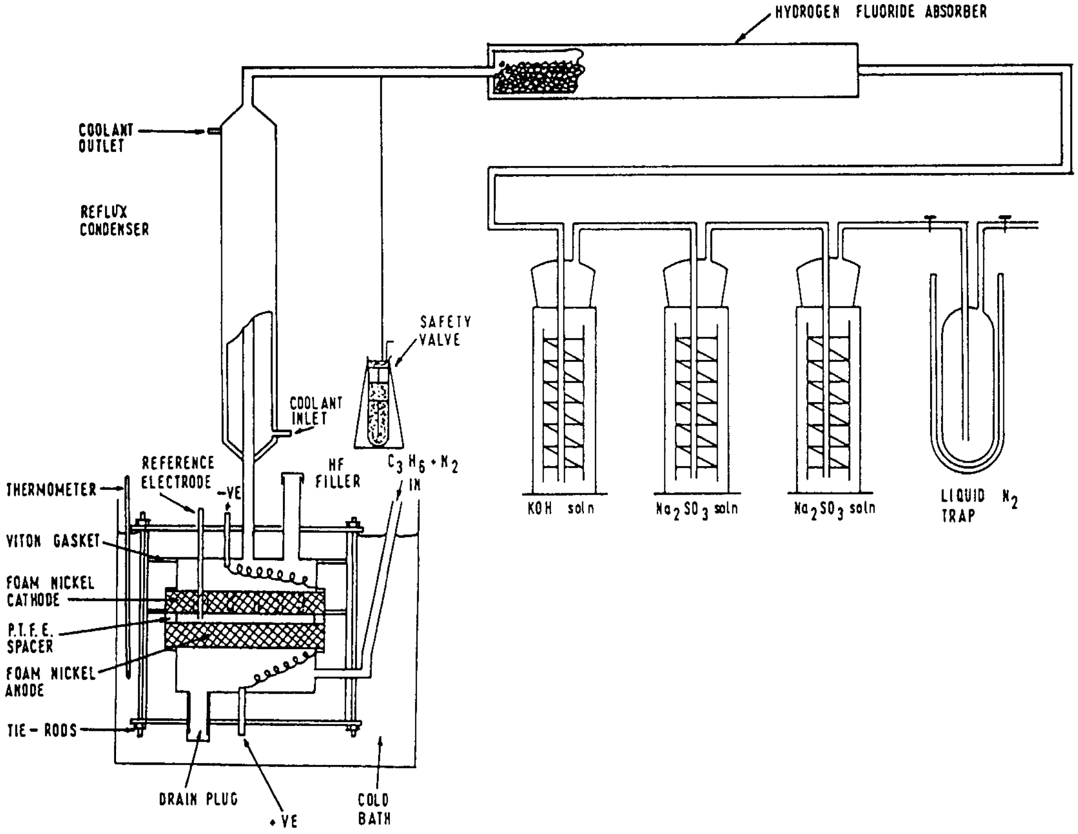


Fig. 3. Electrochemical fluorination apparatus.

1. THE E.C.F. OF PROPENE

EXPERIMENTAL

The apparatus illustrated in Fig. 3 is that designed for th fluorination of propene. The cell (capacity 170 ml) had an all P.T.F.E. cylindrical body in three sections, sealed with Viton gaskets. The base section was fitted with a gas inlet pipe and nickel electrical contact with the anode. The cell head section possessed an HF filler pipe, a reference electrode contact, a nickel cathode contact, and a gas outlet connected via a nickel reflux condenser (-20°C) to a scrubber system. The scrubber system consisted of a brass tube packed with solid potassium fluoride (to remove entrained HF as KHF_2) and aqueous potassium hydroxide solution (to remove any remaining HF), and two aqueous saturated sodium sulphite solutions(to remove any oxygen difluoride formed), and finally, a liquid nitrogen cooled trap for the collection of products.

The disc-shaped anode (diameter 5.5cm) was nickel foam (80 mesh, 1cm thick) situated between the bottom and middle sections of the cell. Electrical contact to the foam anode was made by compression against a sheet nickel annulus connected to nickel wire, then to a nickel bolt through the base of the cell.

The cathode was nickel foam through which was punched large holes (diameter 0.4cm) to facilitate the passage of gas through the cell. Electrical contact to the foam cathode was made by compression against a sheet nickel annulus connected to nickel wire, then to a nickel bolt through the head of the cell. The reference electrode was a nickel wire sheathed in P.T.F.E., except at the tip, which was in close proximity to the surface of the anode.

The anode potential was controlled by means of a Chemical Electronics Type 10/20A potentiostat.

Procedure

The experiments were designed to study the effect of variation of reaction conditions on the 'preparation' of the electrodes, and on the yield and product ratio of fluorinated compounds obtained. This was done by maintaining all parameters, except one, constant over a series of experiments and observing the effect of the variation in that particular reaction condition on the yield of products. A typical experimental procedure is described below:

The cell, cooled to -7°C by immersion in a thermostatically controlled bath, was filled with hydrogen fluoride. Nitrogen (8ml min^{-1}) was metered and passed through the cell. The anode was 'conditioned' by potentiostatically controlling its potential at +6.0V (versus reference electrode) for 40 min, during which time the current had risen to and was constant at 1.75 A with a total cell voltage of 7.7V. The anode potential was then lowered to +4.80V (versus reference electrode) and the cell allowed to reach equilibrium (I = 1.4A, T.P.D. = 6.12V). Propene (5.7 ml min^{-1}, $0.64gh^{-1}$) was passed through the cell for 18h with these electrical parameters, during which time the product was trapped (10.5g). The product was transferred to a vacuum system and allowed to expand to atmospheric pressure at room temperature. The gaseous products were analysed using the gas/liquid chromatographic, infrared, and mass-spectroscopic techniques and shown to consist of:

CF_4(2.0%), C_2F_6(2.7%), C_3F_8(37.7%),
C_3H_8(8.9%), C_3HF_7(10.1%), $C_3H_2F_6$(8.7%),
$C_3F_2H_6$(5.3%) and C_4H_{10}(24.5%).

These percentages are expressed as mol% total product, the chemical yield of fluorinated products being about 30%.

The total current passed during fluorination of the organic compound was 90,600C. This represents a current efficiency calculated for the introduction of fluorine to propene of 94%.

RESULTS AND DISCUSSION

General

Figure 4 illustrates the relationships between current and anode potential, and current and cathode potential, for virgin nickel electrodes in 6% wt% NaF in AHF at -3°C. The cathode current rises linearly from 0.0V (versus reference electrode) whereas the anode current is not significant until potentials of greater than above 3V (versus reference electrode), when the smooth curve becomes linear and steeply rising. The general form of this curve closely resembles that reported by Mantell[9].

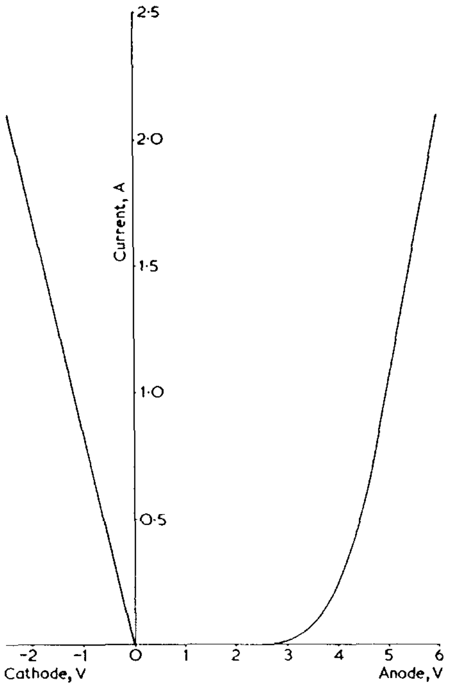


Fig. 4. Current versus potential for new electrodes. 6% by weight NaF in AHF at -3°C.

Figure 5 illustrates the relationships between current and anode potential for an electrode at various stages during its 'preparation' or 'conditioning' in 6% wt NaF in AHF at -5°C, with a nitrogen flow rate of 8ml min^{-1} through the cell. Curve a is that produced by new electrodes, and closely resembles that in Fig. 4. Curve b is that produced after the anode had been 'conditioned' at +6.0V (versus reference electrode) for 25 min. Curve c is that produced after the same anode had been 'conditioned' at +6.0V (versus reference electrode) for 2h. Curve d is that produced after propene had been added to the 'conditioned' electrode.

This series of curves demonstrates that, as the anode is 'conditioned', the surface of the electrode appears to develop a progressively lower fluorine overpotential, suggesting the formation of a growing film. Also, when excess organic compound was added, this film was apparently removed, returning the electrode to its higher overpotential, curve d.

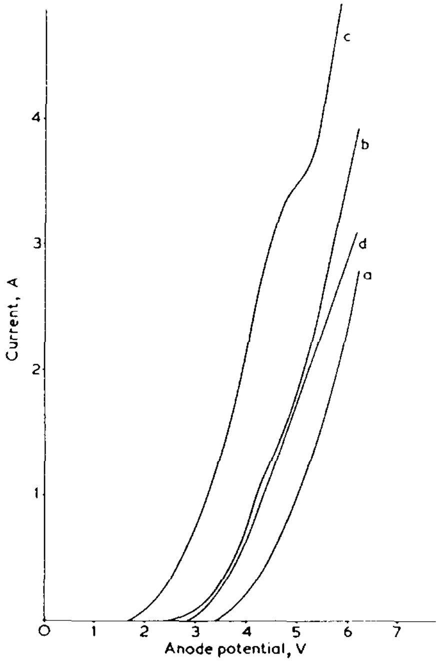


Fig. 5. Current versus potential during electrode preparation. 6% by weight NaF in AHF at -5°C. N_2 flow rate 8ml min^{-1}. (a) New electrodes; (b) anode 'matured' at +6.0V for 25 min; (c) anode 'matured' at +6.0V for 2h; (d) propene added (1.7ml min^{-1}).

The development of this film is also illustrated by Fig. 6, in which the current was recorded as a function of time for a potentiostatically controlled anode (A = +6.0V) in 1% wt NaF in AHF at 0°C. An initial high current was observed, probably due to electrolysis of water present. (The HF contained nominally 0.2% H_2O.) After about 10 min. the current had reached a minimum and then slowly increased during the course of 1h to a maximum, i.e. the current density increased with time at constant potential. The current then reached an equilibrium value with occasional breaks in the curve, presumably due to breakdown in film coverage followed by rebuilding. Some very preliminary E.S.C.A. studies on electrodes subject to different conditioning histories suggest that, initially, a nickel oxide is formed on the surface of the anode and this then is slowly converted through a complex series of nickel oxyfluorides until, at the equilibrium current plateau conditions, all the oxyfluoride had been converted to a nickel fluoride. The valence state of the nickel at this stage is not known. Watanabe[10] has extended this study of nickel anodes using E.S.C.A. techniques, with corroborating results.

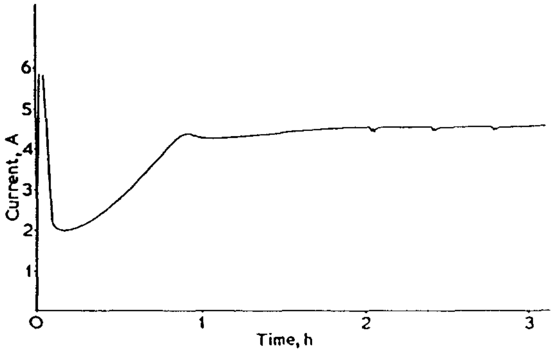


Fig. 6. Current vs time. 1% wt NaF in HF 0°C. Anode pot. +6.0V.

It was shown that the 'conditioning' phase of the anode surface was critical. Only when the surface was 'prepared' under controlled conditions, as described above, to give a reproducible film, did one obtain reproducible results in the fluorination products. Obviously, if the organic reaction is initiated at different points along the graph of Fig. 6, and not after the equilibrium current plateau ha been reached, then fluorination occurs in the presence of different fluorinating agents, i.e. different nickel oxyfluorides, and not the desired nickel fluoride. This could be one of the reasons why others[5] have observed such various results.

Fragmentation of organic compounds as a function of anode potential

Using this technique of 'conditioning' the anode to give a reproducible surface, a number of experiments were performed in which consistent results were obtained. Thus a series of experiments was performed in which only one reaction condition was varied, in this case the anode potential, and the effect on products studied. The results are given in Table 1.

The relationship between anode potential and degree of breakdown is shown graphically in Fig. 7, which illustrates clearly how breakdown increases drastically for anode potentials over about +5.0V.

TABLE 1.

Fragmentation versus anode potential

			Mol % of product							
A (+V)	I (A)	T.P.D. (V)	CF_4+C_2F_6	C_3F_8	C_3H_8	C_3HF_7	$C_3H_2F_6$	$C_3H_5F_3$	$C_3H_6F_2$	C_4H_{10}
+4.0	0.45	4.9	2.0	26.8	11.8	4.0	4.1	-	45.8	3.7
+5.0	1.6	7.2	2.5	38.0	8.1	2.1	3.5	-	12.0	25.8
+6.0	1.8	7.1	5.0	25.8	10.8	0.8	9.0	1.0	21.2	30.7
+7.0	5.0	8.9	11.0	6.1	11.1	1.0	1.0	1.0	13.0	50.0

Fragmentation expressed as 100 $(C_1+C_2)/(C_3)$

Anode potential is versus Nickel reference electrode.

Reaction parameters of temperature (0°C), F.R.H/C(8.9ml min^{-1}), F.R.N $_2$(15ml min^{-1}) etc., constant. Conductivity additive NaF(5g). Chemical yield 30-40%

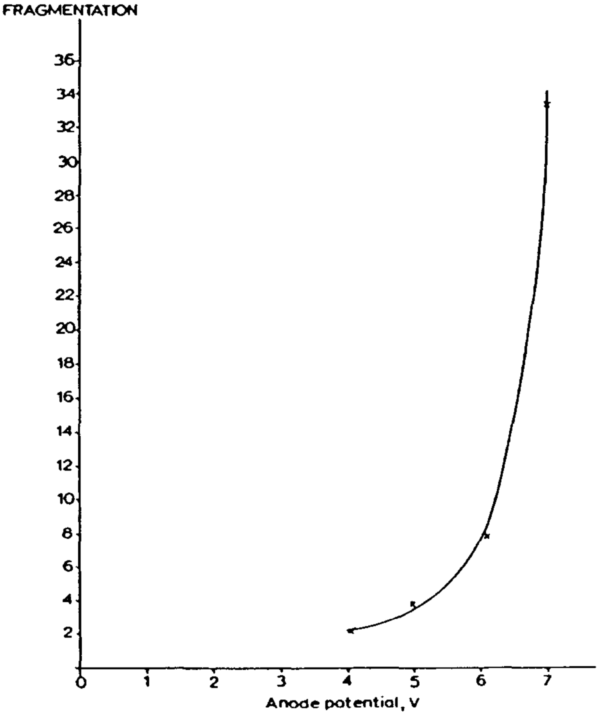


Fig. 7. Graph of fragmentation versus anode potential.

Fragmentation of organic compounds as a function of dilution

A series of experiments was conducted in which the dilution of propene (expressed as the ratio of the flow rates of hydrocarbon to nitrogen) was varied, with all other conditions held constant. The results are given in Table 2.

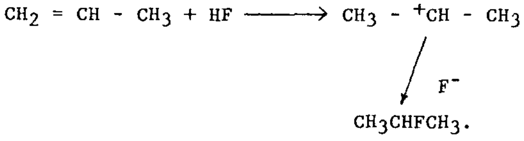
The results of Table 2 are expressed graphically in Fig. 8, which illustrates the linear inverse relationship between dilution and breakdown.

Degree of fluorination as a function of propene flow rate

A series of experiments was conducted in which only the flow rate of propene was varied and the degree of fluorination observed. The degree of fluorination vas expressed as a mol% of the fluoro-compound concerned in the total fluoro-organics produced. The results are given in Table 3. These are expressed graphically in Fig. 9, which illustrates clearly the so-called 'zipper' effect.

Reaction selectivity

In the series of experiments designed to look at the selectivity of the reaction (Tables 2 and 3) it was obvious that the degree of fluorination was an inverse function of the propene flow rate. The principal fluorinated products were octafluoropropane (C_3F_8), heptafluoropropane (C_3HF_7), hexafluoropropane ($C_3H_2F_6$), difluoropropane ($C_3H_6F_2$), and 2-fluoropropane (C_3H_7F). 2-Fluoropropane arose from the chemical addition of HF to propene:



$$CH_2 = CH - CH_3 + HF \longrightarrow CH_3 - {}^{+}CH - CH_3 \xrightarrow{F^-} CH_3CHFCH_3.$$

It is interesting to note that the sole difluorinated product of propene was 2,2-difluoropropane[11] demonstrating a very high degree of selectivity in substitution compared with the reported[12] selectivit in gas phase reactions, which are almost random.

TABLE 2.

Fragmentation versus dilution

			Mol % of product						
(F.R.H/C) (ml min^{-1})	(F.R.N_2) (ml min^{-1})	(D)	CF_4+C_2F_6	C_3F_8	C_3H_8	C_3HF_7	$C_3H_2F_6$	$C_3H_6F_2$	C_4H_{10}
15	5	5	3.5	6.4	13.5	-	-	21.4	38.1
15	10	10	5.0	3.3	6.2	-	4.3	52.8	19.2
15	20	20	2.5	4.8	10.3	1.8	-	40.0	27.3
8.9	15	25.2	2.5	38.0	8.1	2.1	3.5	12.0	25.8

Fragmentation expressed as ratio 100 $(C_1+C_2)/(C_3)$.

Dilution (D) expressed as ratio 15 (F.R.N_2)/(F.R.C_3H_6).

Reaction parameters of anode potential (+5.0V), temperature(0°C), etc., constant. Conductivity additive NaF(5g). Chemical yield 35-45%.

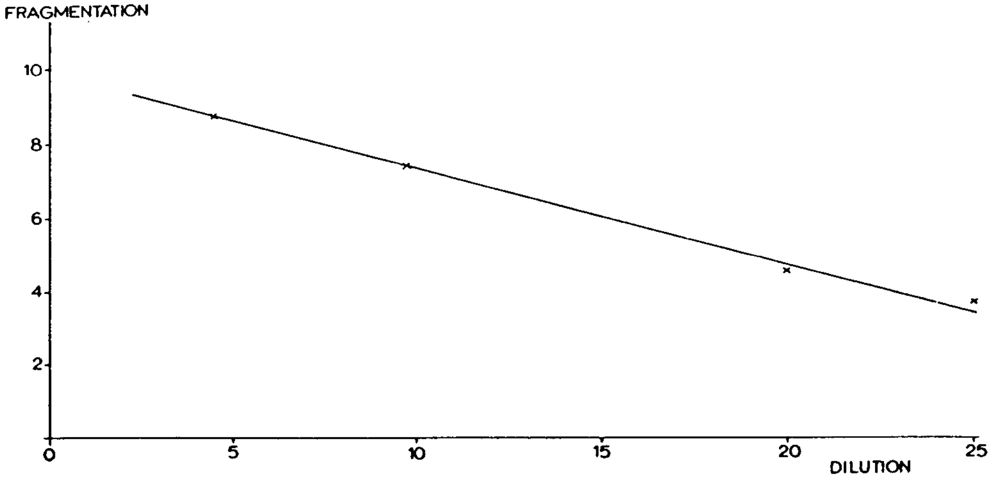


Fig. 8. Graph of fragmentation versus dilution.

TABLE 3

Degree of fluorination versus propene flow rate

F.R.C_3H_6 (ml min^{-1})	Mol % product									
	CF_4+C_2F_6	C_3F_8	C_3H_8	C_3HF_7	$C_3H_2F_6$	$C_3H_5F_3$	$C_3H_6F_2$	C_4H_{10}	D_8F	D_2F
1.7	2.6	71.1	5.2	5.1	-	-	2.6	10.4	87.3	3.2
1.8	5.2	67.5	0.9	5.0	13.1	-	2.7	-	72.2	2.9
5.7	4.0	37.7	8.8	10.1	8.7	-	5.3	24.5	57.2	8.1
17.0	3.5	6.4	13.5	-	-	-	21.4	38.1	20.4	68.4

Degree of fluorination expressed as $(D)_8 = 100(C_3F_8)/(\text{total F/C})$ and $(D)_2 = (C_3H_6F_2)/(\text{total F/C})$. Reaction parameters of anode potential, temperature, N_2 flow rate (8ml min^{-1}) etc. constant.

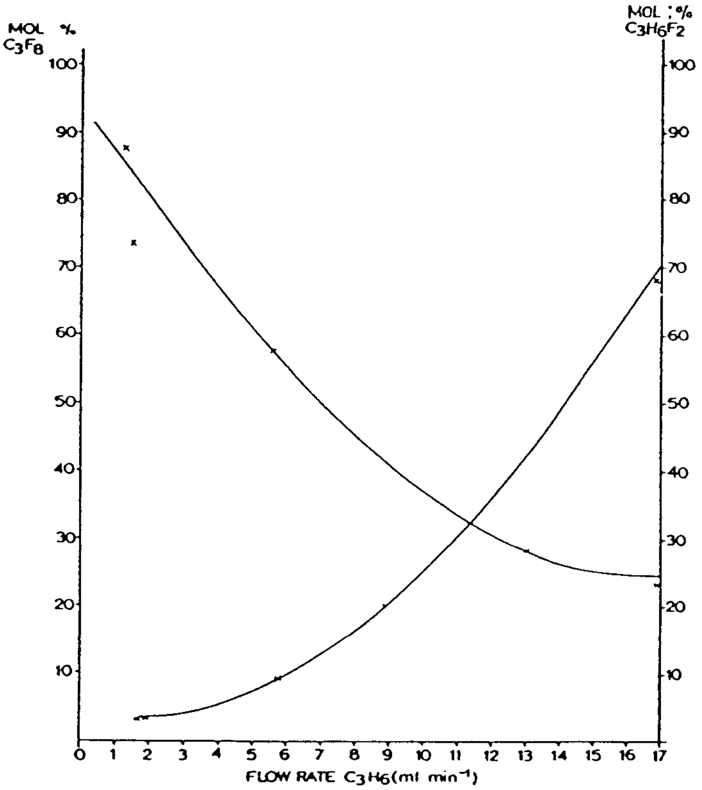
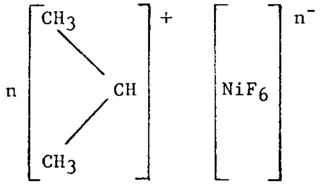


Fig. 9. Degree of fluorination versus propene flow rate.

This high specificity in E.C.F. substitution could well be the result of a close association of stereo-specific adsorption of the organic molecule to the fluorinating agent. If, as has been proposed, the agent is a complex nickel fluoride anion[15], or a 'loose' complex of nickel fluoride with fluorine on the anode surface[14], then the formation of species of the type



or

$(C_3H_6).(F_x).NiF_n$, (where n - depends on the oxidation state of nickel) would not be unreasonable.

The existence of this type of associated species would also account for the so called 'zipper' effect, by which reaction tends to produce only fully fluorinated products. The mechanism of this effect could be explained by the organic entity being retained in close proximity to the fluorinating agent until complete fluorination occurred, then the product being released and separated. Certainly from the results of Tables 2 and 3 it can be seen that over the full range of flow rates observed, difluoro- and octafluoro-propane together account for about 90% of the total fluorocarbon products, and even at the highest hydrocarbon flow rate (17ml min^{-1} C_3H_6) the degree of fluorination yielding octafluoropropane was 20.4%, much higher than would be expected from a simple, non-adsorptive, contact time consideration. All attempts to optimise the yields of intermediately fluorinated products, especially C_3HF_7, by regulation of propene and nitrogen flow rates produced the same disappointing result, indicating that whereas a low degree of fluorination and total fluorination could be achieved, partial fluorination was difficult.

CONCLUSIONS

Electrode materials

i) Nickel is apparently the only suitable anode material.

ii) Utilization of nickel foam as electrode material gives a much greater surface area per unit cell volume than other electrode configuration.

Preparation of anode surface

The power conditioning of the anode surface is critical. In order to achieve reproducibility it is necessary

i) to begin organic reactions with an electrode surface of constant constitution and

ii) to exclude electrode poisons.

Anode potential during fluorination

The potential of the anode must be controlled since

i) for anode potentials <3.5V (versus reference electrode), little fluorination is achieved and

ii) for anode potentials >5.0V (versus reference electrode), extensive breakdown results.

Contact of organic compound with anode

i) Increase in dilution of organic compound reduces amount of breakdown.

ii) Shorter contact times of organic compound with anode surface reduces breakdown.

Selectivity of fluorination

i) The degree of fluorination is difficult to control.

ii) A low degree of fluorination and total fluorination of propene can be achieved, but intermediate degrees are difficult due to the 'zipper' effect.

All the aforementioned conclusions are derived from the study with propene but could be expected to be applicable to the electrochemical fluorination of organic compounds in general.

2. THE E.C.F. OF OCTANOYL CHLORIDE

Using the conclusions and techniques derived from our previous work on the fluorination of propene, it was decided to investigate the preparation of perfluorooctanoic acid, a compound which already had an established market position.

EXPERIMENTAL

The project was executed in two stages. The first was the development of the system used in the fluorination of propene (capacity 170ml) to a cell of 1 litre capacity. The second stage involved the development of a pilot plant scale project in which the total capacity of the system was about 100 litres.

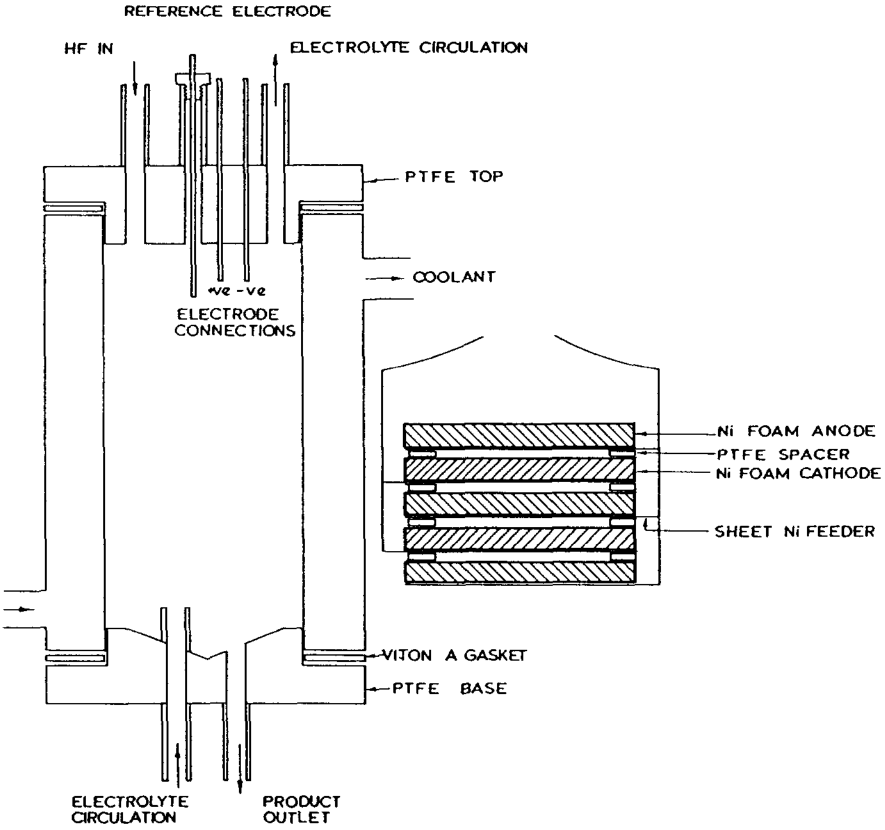


Fig. 10. Stage 1. Cell and electrode package.

Stage 1. The cell (Fig. 10) was a nickel cylinder (internal diameter 5.8cm, capacity 1 litre) surrounded by a cooling jacket. The PTFE base was fitted with two drain valves, and the PTFE head fitted with an HF filler pipe, a reference electrode contact, anode and cathode contacts, and an outlet pipe connected to the reflux condenser and a scrubbing system. The scrubbing system consisted of a brass tube packed with solid KF (to remove entrained HF as KHF_2), an aqueous KOH solution (to remove any remaining HF), a series of three aqueous saturated sodium sulphite solutions, and finally, a liquid nitrogen cooled trap for the collection of remaining condensable products.

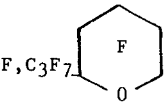
The electrode package consisted of alternate anodes and cathodes made of nickel foam (80 mesh, 1cm thick) separated by PTFE spacers (0.3 cm thick). Electrical contact with the foam was made by compression to a nickel strip. The reference electrode was a nickel wire sheathed in PTFE, except at the tip, and inserted down a hole drilled through the electrode package, which completely filled the cell, (Fig. 11.)

The anode potential was controlled by means of a Chemical Electronics Type 10/20A potentiostat. A typical experimental procedure is described below.

The cell, cooled to +5°C by circulation of thermostatically controlled coolant through the jacket, was filled with hydrogen fluoride and the anodes 'conditioned' by potentiostatically controlling their potential at 5.50V (versus the reference electrode) for 1 hour, during which time the current had risen to, and was constant at 15A, with a total cell voltage of 7.15V. The anode potential was then lowered to +4.3V and the current stabilized at 6A. Octanoyl chloride (300g), dissolved in hydrogen fluoride (200g) drained from the cell, was added to the cell and the mixture electrolysed with a constant anode potential of 4.3V until no more product was drained from the valves in the base of the cell. At the end of this period (8 days) the total product drained from the cell was 268.8g and the product in the liquid nitrogen trap was 59.5g.

Analysis of the products by the usual techniques of gas/liquid chromatography, infra-red, nuclear magnetic and mass-spectroscopy, as well as acidbase titration showed the products to be a mixture of:

$C_7F_{15}COF$,



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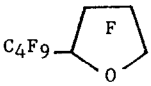


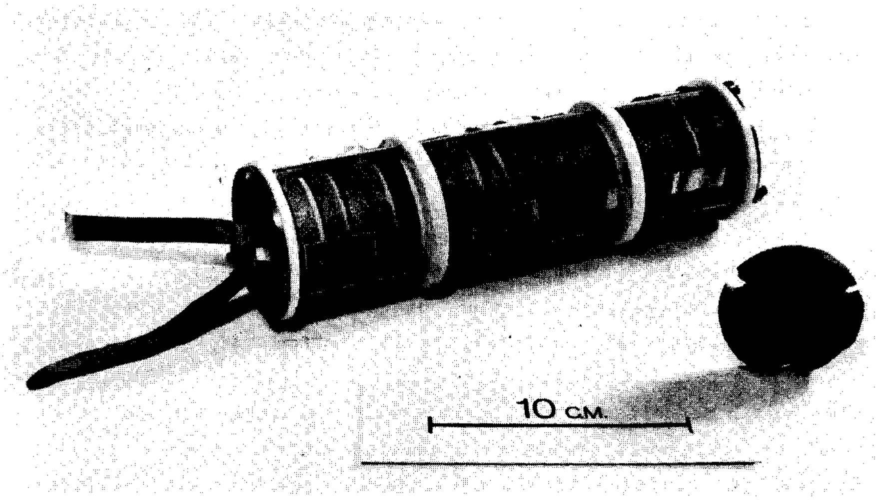


Fig. 11. Stage 1. Electrode Package.

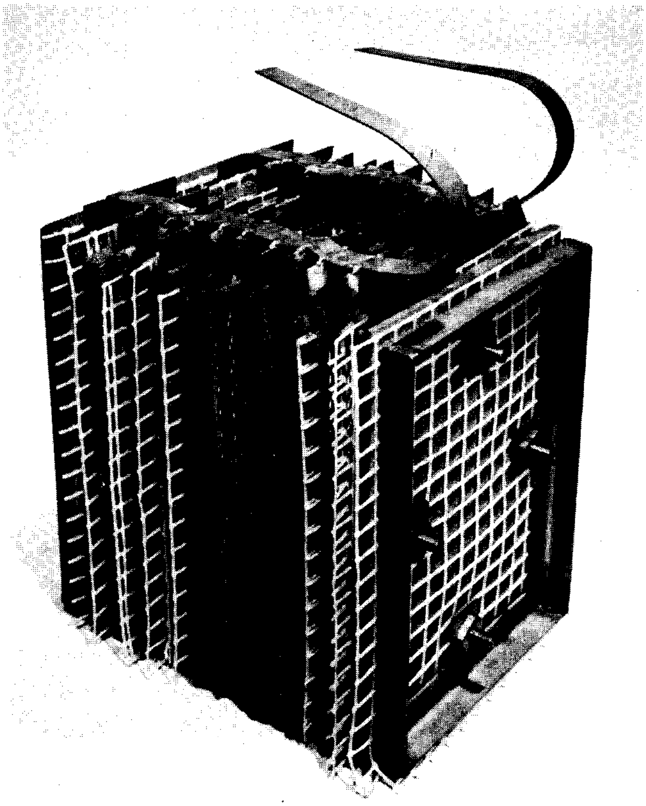


Fig. 12. Stage 2. Electrode Package.

with a small amount ofC_7F_{16}, and breakdown products. The proportion of perfluoroacyl fluoride to perfluorocyclic ethers varied during the course of the reaction, reaching a maximum of 40.3%.

Stage 2. The scaled-up plant is illustrated diagrammatically in Fig. 14. Figure 13 shows a partially cut-away view of the electrochemical cell.

The cell consisted of a rectangular nickel box (43cm x 30.5cm x 56cm) surrounded by a mild steel cooling jacket. The polythene base of the cell was fitted with a product drain port, an electrolyte level indicator loop which was connected to the cushion box, and a return port from the external circuit.

The polythene cell head was fitted with a starting material inlet port and an exit port, which was connected to the external pumping circuit and gas scrubbing system via a cushion box positioned between the cell and a nickel reflux condenser. The cushion box incorporated the hydrogen inlet port, and a Venturi extract system, driven by nitrogen, which allowed the removal and dilution of gases from the cell during the 'conditioning' stage of the anodes.

Nickel stubs through the cell head allowed sealed electrical connections to the electrode package, conductivity cell and auxiliary reference electrode circuit. The polythene head also incorporated sealed jackets to house internal thermocouple temperature probes.

The electrode package in the cell consisted of anode packs, each comprising two nickel foam sheets (45 mesh, 36.6cm x 25.4cm x 1cm) sandwiching a nickel mesh feeder plate (36cm x 25cm, 22 gauge expanded). These anodes packs alternated with cathodes of expanded nickel mesh, separated by polythene spacers, (Fig. 12).

The mixture of organic substrate and hydrogen fluoride was electrolysed in the cell. It was possible to pump the electrolyte in an external circuit via the cushion box and settling tank, in which product could be separated from electrolyte. Gaseous products from the reaction passed through the cushion box to the reflux condenser, where most of the hydrogen fluoride was stripped out and returned to the cell. Any remaining hydrogen fluoride entrained in the gas stream was removed by heated sodium fluoride scrubbers. A heated rubber packed scrubber and aqueous sodium sulphite scrubbers removed any traces of oxygen difluoride produced in the electrolysis.

Any condensable products remaining in the gas stream were collected in a liquid nitrogen cooled trap, and hydrogen was vented to atmosphere.

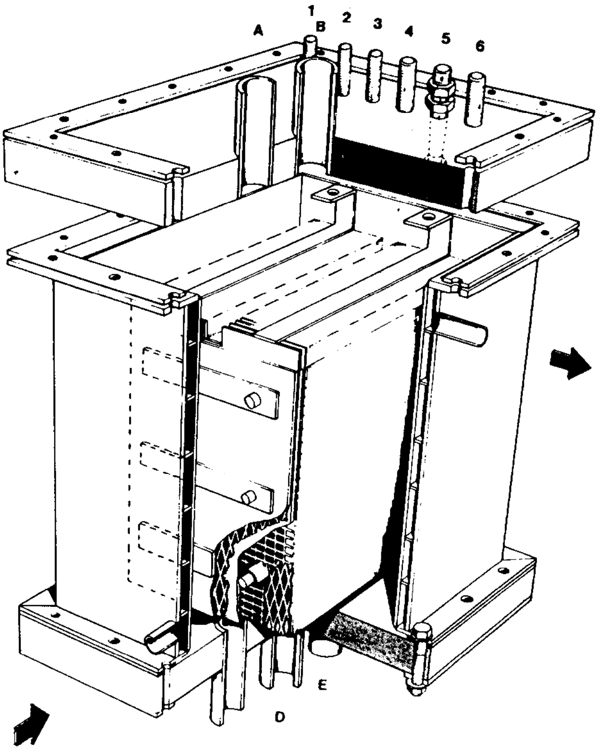


Fig. 13. Electrochemical cell for fluorination plant.

A typical experimental procedure using this scale of plant is described below.

The cell, cooled to 0°C by circulation of thermostatically controlled coolant through the jacket, was filled with hydrogen fluoride. The external circuit was not filled for a static experiment. The hydrogen fluoride was dried by passing a current of 1.8A for approximately 96 hours. Conditioning of the anodes was performed in the usual way, by holding the anode potential at 5.5V (versus the reference electrode) for about 6 hours. Octanoyl chloride dissolved in hydrogen fluoride was added to the cell and electrolysis continued until no further product was drained from the base of the cell, while the anode potential was maintained at 4.3 ± 0.2V(versus reference electrode).

A typical reaction would involve the electrolysis of 4kg of octanoyl chloride at approximately 25A and 6.0V total cell voltage for 60 days to give yields of perfluoro-octanoyl fluoride and perfluorocyclic ethers of around 70%.

Although a number of problems were encountered during these bench-scale studies, mainly associated with corrosion of contacts, pumping of electrolyte and similar engineering considerations, it was decided that the chemistry of the system was sufficiently favourable to pursue the project to the next stage of the development, that of a pilot plant scale of operation.

The pilot plant was built to an ultimate design specification of 100A current rating during the fluorination stage of reaction with a cell capacity of about 70 litres and a total plant capacity of 100 litres of electrolyte. The earlier experiments were conducted with a section of the cell blanked off by a nickel box, using a smaller electrode package. As the project progressed an electrode package which completely filled the cell was used. This arrangement (Fig. 10) successfully met the design specifications.

The experimental data were analysed at each stage of the project and although the relationships, for example between current and time, product ratio and organic concentration, product yield and time, etc., were complex, they were self consistent at each scale of operation.

Typical observations, measurements and derivations are illustrated below.

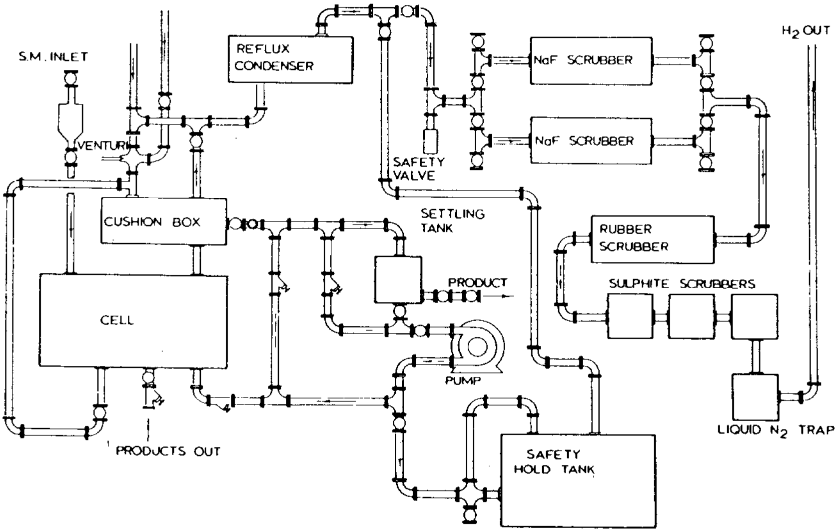


Fig. 14. Electrochemical fluorination plant.

RESULTS AND DISCUSSION

Conditioning of anodes

The anode 'conditioning' phase of the small-scale reactions were conducted in a very similar fashion to that employed in the propene studies producing analogous results. The applied constant anode potential induced an initial high current, due to electrolysis of water present, followed by a dramatic fall in current as the impedance increased. The current density, at constant potential, then increased as a function of time, until an equilibrium value was attained.

The conditioning of anodes in large-scale experiments was conducted in a slightly different way. Because the nominally anhydrous hydrogen fluoride may contain up to 0.2wt% water, i.e. approximately 200g of water in the completely filled pilot plant, it was necessary to dry the electrolyte thoroughly before fluorine evolution could begin. (The oxygen difluoride produced from this quantity of water represents a considerable explosion hazard.) Thus, the hydrogen fluoride was electrolysed at low voltage by passing a current of 1.8A for approximately 96 hours. At the end of this period it was estimated that the system was sufficiently anhydrous for the anode potential to be raised to 5.5V (versus reference electrode) with the subsequent evolution of fluorine, which was removed by venturi extraction, and formation of nickel fluoride on the surface of the anodes. After about 6 hours the current had increased to a constant maximum and electrodes were ready for the next stage of the reaction, fluorination of the organic substration.

Fluorination of organic substrate

Bench-scale exploratory experiments were carried out in the 1 litre capacity cell using various reaction parameters derived from earlier work on the fluorination of propene. The results of these experiments indicated that fluorination of the large octanoyl chloride molecule could be accomplished with minimum breakdown of the carbon skeleton.

Gas/liquid chromatography of esterified products drained from the fluorination cell showed that the principal products were the ethyl ester of perfluoro-octanoyl fluoride, an unresolved mixture of perfluoro cyclic ethers and a small quantity of perfluoroheptane (from the decarboxylation of the substrate), Fig. 15.

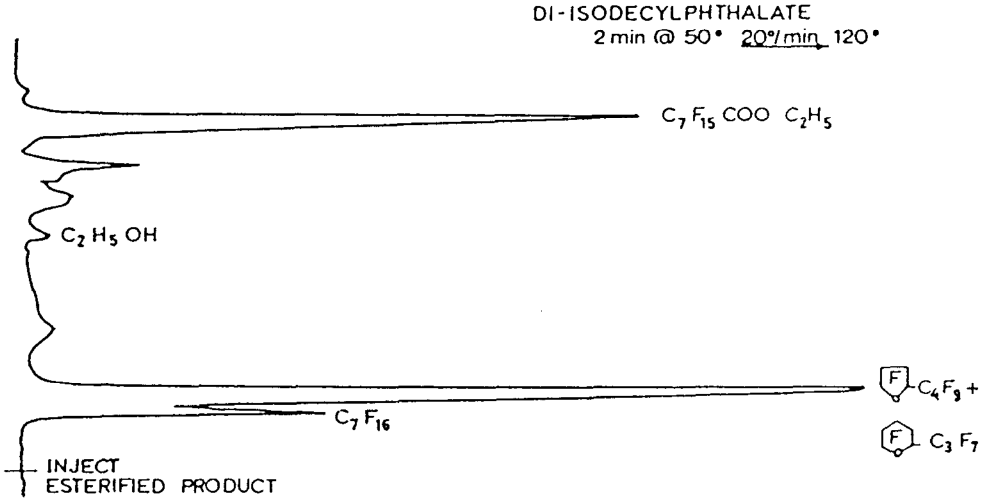


Fig. 15. Vapour phase chromatogram of esterfied product from fluorination cell (Bench Scale).

The ratio of perfluoroacyl fluoride to perfluorocyclic ethers was found to vary during the course of a reaction and as a function of organic starting material concentration. The proportion of perfluoroacyl fluoride was observed to range from a minimum of 8% to a maximum of 47% in the product mixture. A detailed study of this dependence was made in pilot plant experiments.

Current as a function of time

Figure 16 illustrates typical measurements of current during the course of a fluorination experiment. The electrode package filled approximately 25% of the cell volume. The initial current, after the electrode 'conditioning' phase, rose steeply from 12 A over a period of about 8 days to a plateau region of duration approximately 20 days with an average current of 25A. After 30 days the current decreased rapidly over the next 20 days and then reached an almost constant value of around 5A.

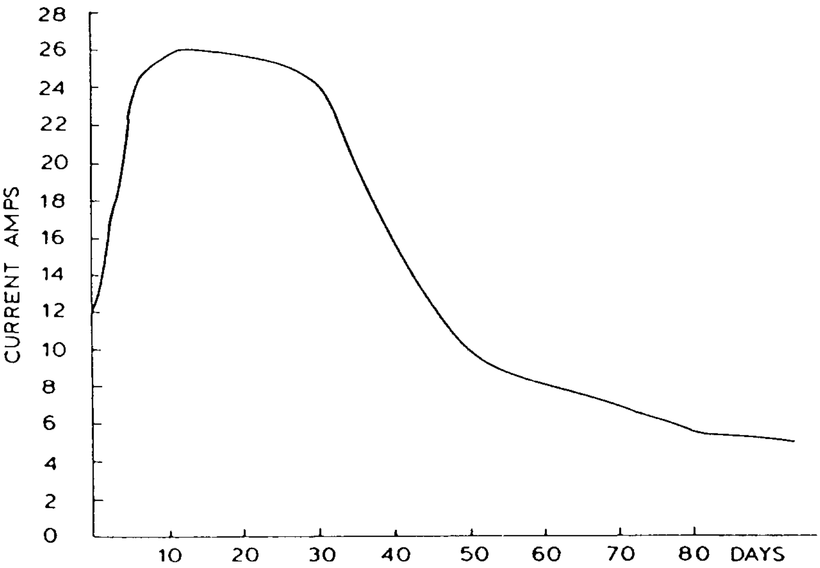


Fig. 16. Current versus time.

Rate of product separation as a function of time

Figure 17 illustrates the rate of separation product, expressed as g day^{-1} as a function of time. The vertical lines give an indication of the maximum possible experimental error involved in this procedure. As can be observed, the overall shape of the graph is similar to that of current versus time (Fig. 16). The most significant features

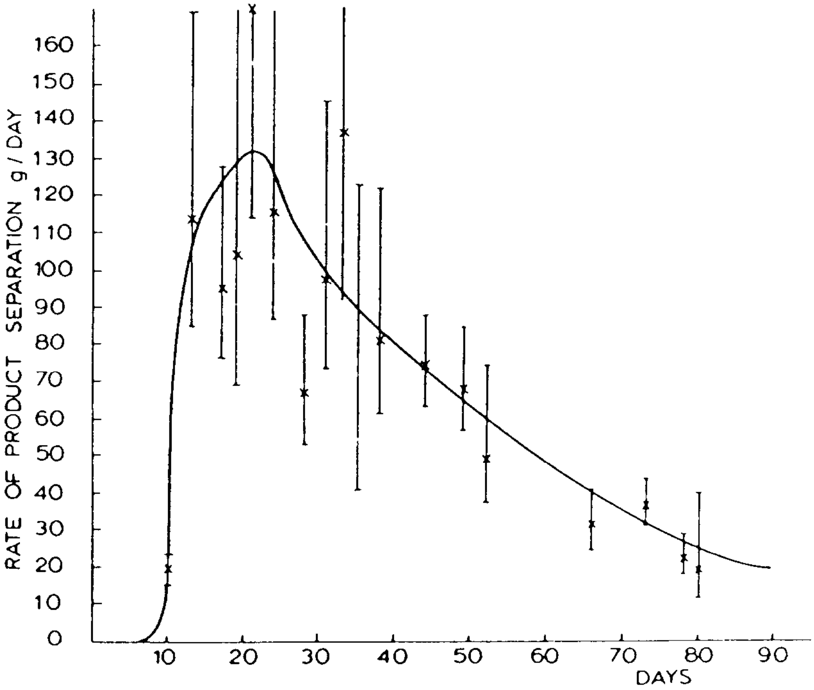


Fig. 17. Rate of product separation versus time.

of the observations are that during the first 10 days of cell operation no product is isolated. The rate of product separation then increases markedly to a maximum after about 20 days when the rate of production decreases to a minimum at 80 days.

This phenomenon of lack of product during the initial stages of the fluorination has been reported by other workers[15] and is probably due to the fact that although the perfluorinated products are reportedly insoluble in anhydrous hydrogen fluoride, they are significantly soluble in the complex mixture of organic starting material, partially fluorinated products and anhydrous hydrogen fluoride which make up the electrolyte. Thus, before separation of the product can occur a saturation level of perfluorinated products in the electrolyte must be reached.

Product ratio as a function of time

Figure 18 illustrates a typical graph of the ratio of perfluorooctanoyl fluoride to perfluorocyclic ethers as a function of time. The general shape of the graph is similar and to a remarkable extent mirrors the profile of product separation versus time (Fig. 17), in that the product ratio increases as the product rate increases, both reaching a concurrent maximum at 20 days, and decreasing a parallel to a minimum after about 50-60 days.

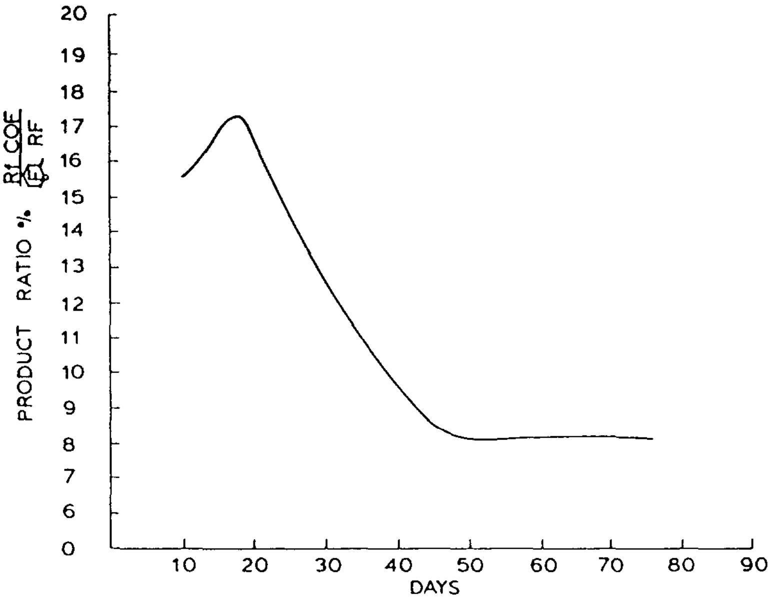


Fig. 14. Product ratio versus time.

Product ratio as a function of octanoyl fluoride concentration

In order to obtain a fuller understanding of the fluorination process and the mechanism which governed the ratio of products, it was necessary to have a complete picture of the effect of concentration of starting material on the yield and the ratio of products. Figure 19 shows a collection of data from a number of such experiments in which self consistency of results is observed. The yield of perfluoroacyl fluoride continues to rise with starting material concentration in a non-linear fashion to a maximum of about 34% at an octanoyl fluoride concentration of 20%. This value is on a still rising part of the curve but is short of the maximum value of 47% obtained in benchscale experiments.

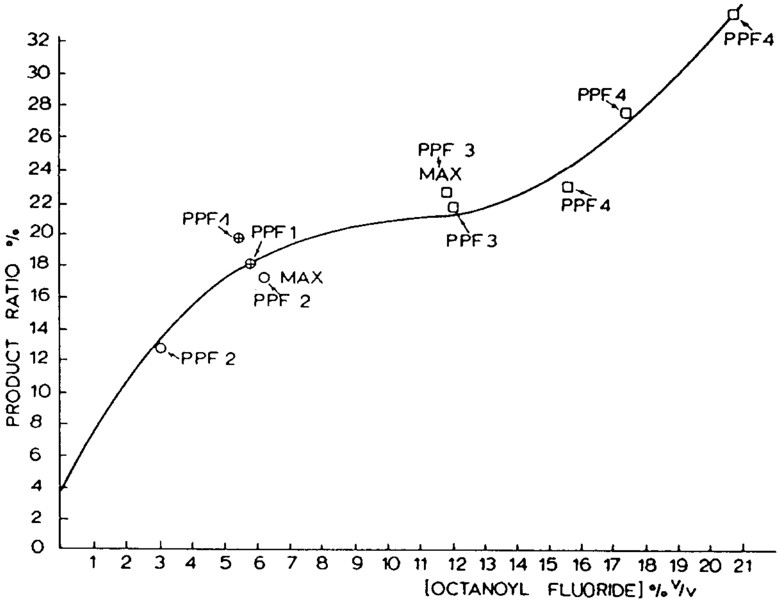
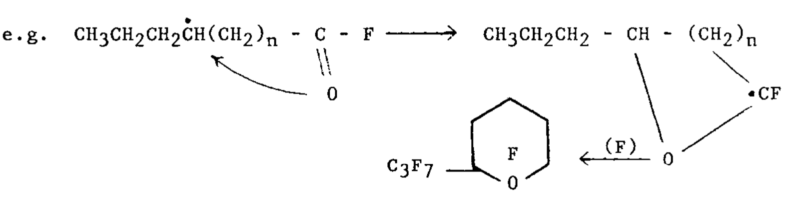


Fig. 19. Fluorinated product ratio versus octanoyl fluoride concentration.

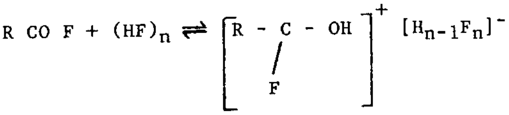
It is interesting to postulate why the ratio of perfluoro-octanoyl fluoride to perfluoro-cyclic ether should vary with octanoyl fluoride concentration. If the two types of product arose from a competition between fluorination of the simple isolated long chain acyl molecule (Reaction 1) and a reaction which also involved an intermediate radical species resulting in internal cyclisation (Reaction 2),[16] <u>i.e.</u>

$$C_7H_{15}COF \xrightarrow{(F)} C_7F_{15}COF \qquad (1)$$



(2)

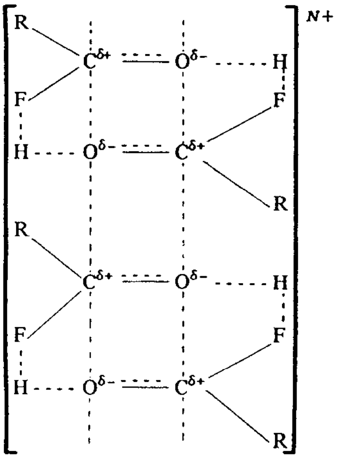
then one might expect the ratio of the two types of product to be the result of a random equilibrium and be independent of octanoyl fluoride concentration or alternatively, the production of perfluoroacyl fluoride to be favoured by a more selective fluorination reaction in dilute solutions. In practice, as described above, the production of perfluoroacyl fluoride is favoured by higher octanoyl fluoride concentrations. In order to rationalise this phenomenon it is necessary to understand the behaviour of octanoyl fluoride in hydrogen fluoride solution. In dilute solutions, octanoyl fluoride is protonated by the highly associated hydrogen fluoride solvent according to the equilibrium



$$R\ CO\ F + (HF)_n \rightleftharpoons \left[\begin{matrix} R - \underset{\displaystyle F}{\underset{/}{C}} - OH \end{matrix}\right]^+ [H_{n-1}F_n]^-$$

Further solvation of this organic cation would increase with increased dilution.

As the concentration of octanoyl fluoride increases it is possible that a considerable degree of association occurs, through hydrogen bonding, between protonated organic species, to give the loosely bonded polymeric structure illustrated overleaf.



$N[H_{n-1}F_n]^-$

The degree of association of acyl species will obviously be an equilibrium which varies as a function of octanoyl fluoride concentration, ranging from zero association in very dilute solution to a highly associated 'macro-molecular' type of structure in concentrated solutions. It is likely that the physical constraints of the more rigid arrangement prevents a radical species formed during fluorination from attacking its own carbon chain along its length and so inhibits cyclization, to the benefit of the perfluoroacyl fluoride formation.

A body of evidence exists in support of this proposed 'polymeric cation'. When hydrogen fluoride is added to octanoyl chloride before introduction to the fluorination cell, a dark colouration of the solution develops as would be expected in a highly conjugated system such as that described above. Further, during the course of fluorination the dark colouration gradually disappears as the organic material is depleted. Also, the viscosities of concentrated solutions are appreciably higher than either of their two components, a fact which would be consistent with the formation of a two or three dimensional polymer.

CONCLUSIONS

The following conclusions were reached:

(a) Proper 'conditioning' of anodes will lead to reproducible results in the electrochemical fluorination of octanoyl chloride, as in the fluorination of propene.

(b) Control over anode potential during fluorination prevents the breakdown of octanoyl fluroide such that the principal products are perfluoro-octanoyl fluoride and a mixture of perfluorocyclic ethers, with only a small amount of perfluoroheptane.

(c) The percentage of perfluoro-octanoyl fluoride in the organic product varied within the range 8-47%, dependent upon the reaction parameters.

(d) The process is controllable to give optimum yields of either perfluorooctanoyl fluoride or perfluoro-cyclic ethers.

(e) The techniques developed in these studies should be applicable to the electrochemical fluorination of related organic molecules and possibly, with come modifications, to a much larger range of compounds.

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