The electrochemical fluorination of octanoyl chloride

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A study of the electrochemical fluorination of octanoic acid halides has been made using techniques involving careful 'preparation' of the anodes prior to the introduction of organic substrate, followed by fluorination under controlled conditions. Studies were conducted on both bench scale and pilot plant scale operations. Reaction parameters are described in detail. The principal products were perfluoro-octanoyl fluoride and a mixture of perfluorocylic ethers. The experiments established that reproducibility of the results could be achieved and that, by proper attention to reaction conditions, breakdown of the carbon skeleton was minimized; the variation of product ratios could be regulated to optimize the yield of desired materials.

1. Introduction

It was apparent in the earliest days [1] that electrochemical fluorination (ECF) was a unique and valuable method of fluorination because it allowed the retention of certain functional groups within molecules to yield the perfluoro-analogues of the starting compounds, materials which were very difficult, if not impossible to prepare by other methods. The subject has been reviewed at regular intervals during the last two decades [2–4]. Here we report the second part of our programme [5] in which we investigated possible electrochemical routes to fluorinated organic compounds of commercial significance. The studies described, although applicable to a wide range of materials, concentrated on the electrochemical fluorination of a derivative of octanoic acid, to yield pentadecafluoro-octanoic acid, a compound with remarkable surfactant properties and a precursor for many textile, leather and paper treatments [6]. The work was concerned with the application of techniques developed in the electrochemical fluorination of the model compound propene [5] to the fluorination of octanoic acid, or its halides, in an attempt to improve the overall efficiency of the process, so reducing the production costs of the fluorinated products and hence encouraging the chemical industry to use these novel electrochemical methods.

In the original published work by Simons and co-workers [7–11] describing the fluorination of carboxylic acids and acid anhydrides, the yields of the perfluoro-acyl products were very low. A real advance [12] in the electrolytic production of perfluorocarboxylic acids occurred with the discovery that carboxylic acid fluorides were much better starting materials than carboxylic acids themselves or their anhydrides.

Alternatively, carboxylic acid chlorides may be used, since anhydrous hydrogen fluoride converts these by solvolysis to the acid fluoride with the evolution of hydrogen chloride.

$$RCOCl + HF \longrightarrow RCOF + HCl$$
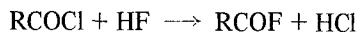
Murray [13] prepared a range of perfluoro acid fluorides, starting with the acid chlorides using a standard Simons Cell. His results were similar to those of Scholberg and Brice [14] in that the yield of perfluoroheptanoic acid was about 10%. More recent work involving a variety of techniques [15] such as high cell voltages [16] and porous carbon anodes [17, 18] has resulted in a further improvement of yields.

In the first part of our programme two distinct stages in the ECF process had been identified: the first, preparation of the anode surface and the second, fluorination of the organic substrate. The conclusions from this previous work are set out very briefly below.

1.1. Electrode materials

Nickel is apparently the only suitable anode material [19]. Utilization of nickel foam as an electrode material gives a much greater surface area per unit cell volume than other electrode configurations.

1.2. Preparation of anode surface

The proper conditioning of the anode surface is critical. In order to achieve reproducibility it is necessary to begin organic reactions with an electrode surface of the same constitution [20], and to exclude electrode poisons (see Section 2.1).

1.3. Anode potential during fluorination

The potential of the anode must be controlled since: for anode potentials < 3.5 V (versus H_2 reference electrode) (see Section 2.4) little fluorination is achieved, and for anode potentials > 5.0 V (versus H_2 reference electrode) extensive breakdown of the carbon skeleton results.

## 1.4. Contact of organic compound with anode

Dilution of the organic compound reduces the fragmentation of the organic compound. Shorter contact times of the organic compound with the anode surface reduces breakdown.
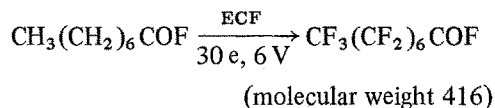
1.5. Selectivity of fluorination

The degree of fluorination is difficult to control. A low degree of fluorination and total fluorination can be achieved, but intermediate degrees are difficult due to the 'zipper' effect.

If these same principles were applicable to the controlled electrolysis of octanoyl chloride, then it should be possible to achieve results better than those previously reported, bearing in mind the theoretical energy considerations, as outlined below.

The first chemical step is

$$CH_3(CH_2)_6 COCl \xrightarrow{HF} CH_3(CH_2)_6 COF + HCl$$
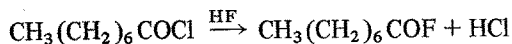
and the second electrochemical step can be represented by

$$CH_3(CH_2)_6 COF \xrightarrow[30 \text{ e}, 6 \text{ V}]{ECF} CF_3(CF_2)_6 COF$$

(molecular weight 416)

with the energy requirement for 1 kg of product being

$$30 \times 6 \times 26.8/416 = 11.6 \text{ kW h kg}^{-1}.$$

2. Experimental

2.1. Materials

The reactants used were commercial grade hydrogen fluoride (maximum 0.2% H_2O), technical grade octanoyl chloride, and nickel ($> 99.9\%$ pure). The only other materials in contact with the electrolyte were PTFE, Viton elastomer, polythene, polypropylene and high purity nitrogen The apparatus was fabricated with the least number of different materials in an attempt to obtain the simplest chemical system, thus avoiding complicated side-reactions or electrode poisons by other 'impurities'.*

2.2. Apparatus and procedure

The project was executed in two stages. The first was the development of the system used in the fluorination of propene (capacity 170 ml) 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.

2.2.1. Stage 1. The cell (Fig. 1) was a nickel cylinder (internal diameter 5.8 cm, 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

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* During one experiment a steel nut and bolt in the cell accidentally shorted with the anode circuit resulting in a film coating of Fe–Ni on the nickel anode. The effect of this was to greatly reduce the yields of fluoro-organic products in that experiment. The mechanism of this film formation is not clear but it probably involved corrosion of the steel to form a complex iron anion in solution which was then discharged at the anode.
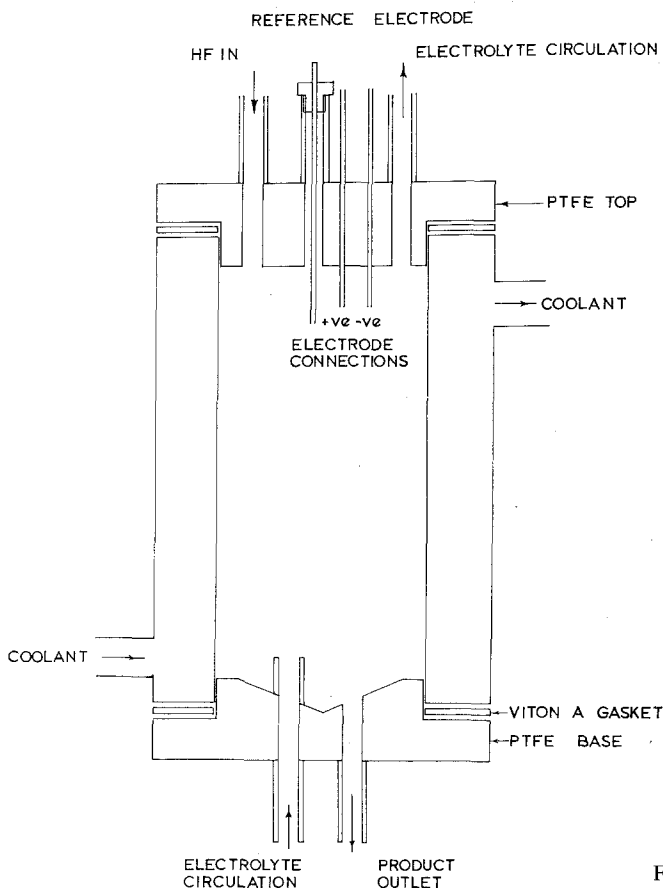
Fig. 1. Stage 1 cell.

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, 1 cm 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.

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 5·50 V (versus the reference electrode) for 1 hour, during which time the current had risen to, and was constant at 15 A, with a total cell voltage of 7·15 V. The anode potential was then lowered to + 4·3 V and the current stabilized at 6 A. Octanoyl chloride (300 g), dissolved in hydrogen fluoride (200 g) drained from the cell, was added to the cell and the mixture electrolysed with a constant anode potential of 4·3 V 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 268·8 g and the product in the liquid nitrogen trap was 59·5 g.

Analysis of the products by the usual techniques of vapour phase chromatography, infra-red, nuclear magnetic and mass-spectroscopy, as well as acid–base titration showed the products to be

a mixture of

$$C_7F_{15}COF, C_3F_7 \underset{O^F}{\bigcirc} , C_4F_9 \underset{O}{\bigcirc}^F$$
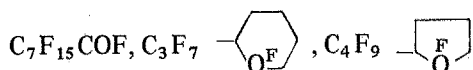
with a small amount of C_7F_{16}, and breakdown products. The proportion of perfluoroacyl fluoride to perfluorocyclic ethers varied during the course of the reaction, reaching a maximum of 40·3%.

2.2.2. Stage 2. The scaled-up plant is illustrated diagrammatically in Fig. 2 and a flow diagram of the system outlined in Fig. 3. Fig. 4 shows a partially cut away view of the electrochemical cell.

The cell consisted of a rectangular nickel box (43 cm × 30·5 cm × 56 cm) 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 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 auxilliary 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, 36·6 cm × 25·4 cm × 1 cm) sandwiching a nickel mesh feeder plate (36 cm × 25 cm, 22 gauge expanded). These anode packs alternated with cathodes of expanded nickel mesh, separated by polythene spacers.

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
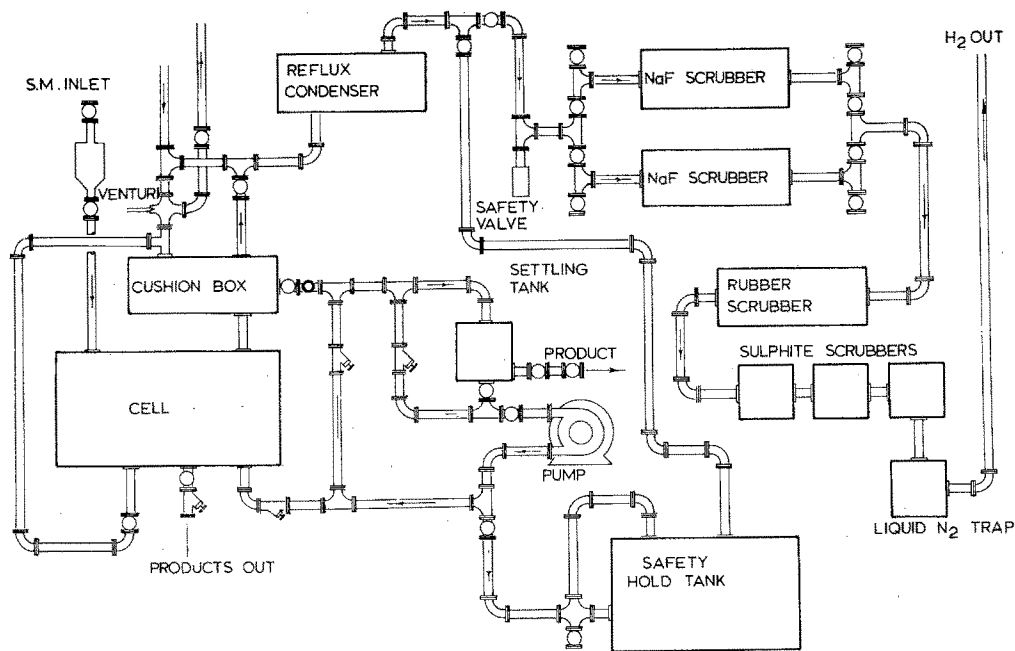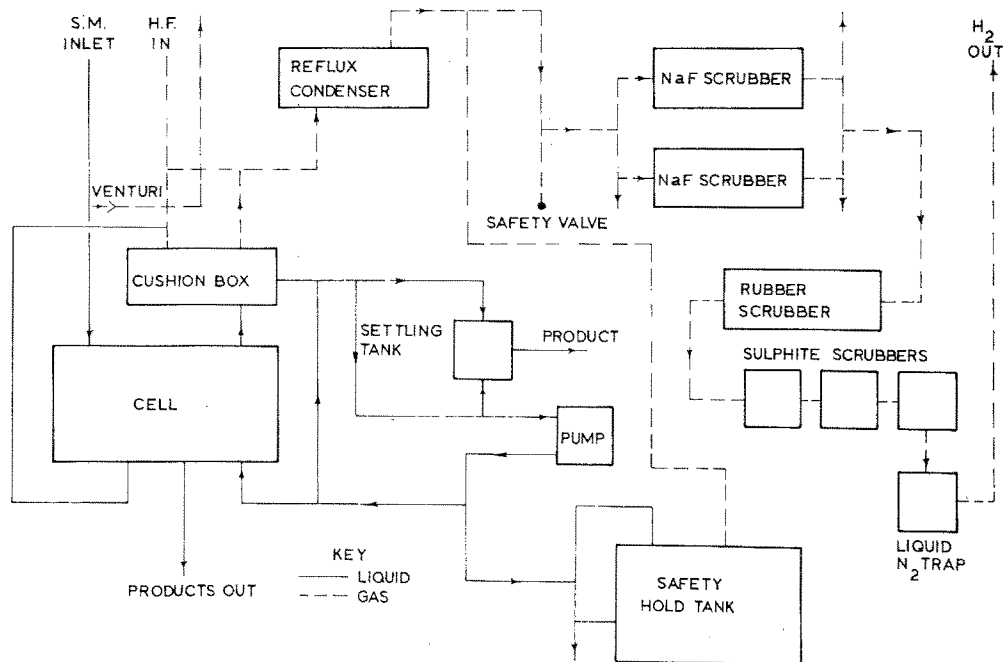

Fig. 2. Electrochemical fluorination plant.

Fig. 3. Block diagram of the electrochemical fluorination plant.

rubber packed scrubber and aqueous sodium sul-
phite scrubbers removed any traces of oxygen
difluoride produced in the electrolysis. Any con-
densable products remaining in the gas stream
were collected in a liquid nitrogen cooled trap, and
hydrogen was vented to atmosphere.

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 experi-
ment. The hydrogen fluoride was dried by passing
a current of 1·8 A for approximately 96 hours.
Conditioning of the anodes was performed in the
usual way, by holding the anode potential at 5·5 V
(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 main-
tained at 4·3 ± 0·2 V (versus reference electrode).

A typical reaction would involve the electro-
lysis of 4 kg of octanoyl chloride at approximately
25 A and 6·0 V total cell voltage for 60 days to
give yields of perfluoro-octanoyl fluoride and
perfluorocyclic ethers of around 70%.

2.3. Product analysis

2.3.1. Vapour phase chromatography (VPC). A
Perkin Elmer model F11 chromatograph fitted
with a hot wire detector system was used for
analytical scale VPC. Peak areas were determined
directly using a digital print-out integrator (Kent
Chromolog) coupled to the amplifier output. The
columns used were those in the Porapak series,
principally Porapak Q.

2.3.2. Infra-red spectroscopy. A Wilks Model 41
infra-red micro-cell VPC attachment was used to
trap the eluted compounds, whose spectra were
recorded on a Unicam SP200 spectrometer. The
spectra of products were compared and identified
with standard reference spectra in the literature.

2.3.3. Mass spectroscopy. The Wilks 41 micro-cell
attachment was modified so that trapped eluted
compounds could be transferred into an AEI MS
12 Spectrometer. Later, another coupled VPC–
mass spectrometer (PE 452/MS 12) was used to
record the spectra more conveniently. These
spectra were compared and identified with stan-
dard reference spectra in the literature.
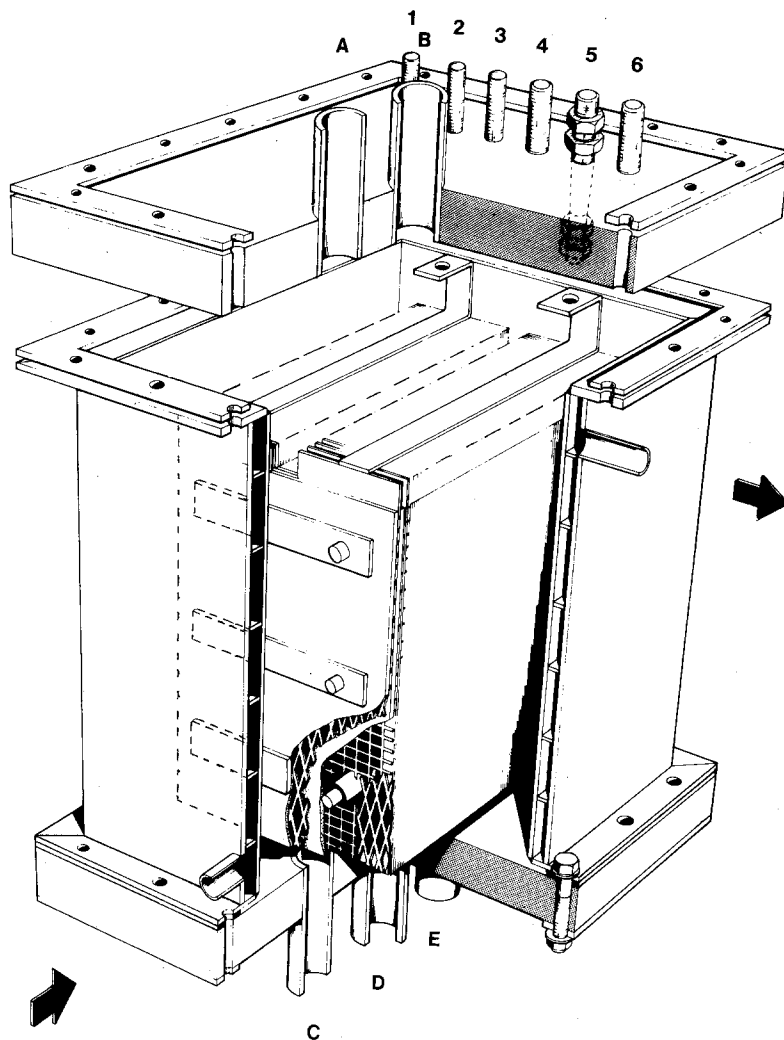
Fig. 4. Electrochemical cell for fluorination plant.

2.3.4. Volumetric analysis. As well as VPC of the esterified fluorocarboxylic acid, acidimetric titration of product directly from the electrolysis cell against standard alkali solution gave an estimate of the quantity of carboxylic acid produced according to the equation:

$$C_7F_{15}COF + 2NaOH$$

$$\longrightarrow C_7F_{15}COONa + NaF + H_2O.$$
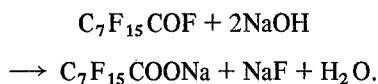
2.4. *Reference electrode*

In the small scale reactions, it was found that a simple sheathed nickel wire with its bare tip in close proximity to the anode surface, provided an adequate constant potential reference electrode for the purposes of the preparative experiments. For large-scale reactions, however, this system was not satisfactory and a new type of reference electrode was devised.

The polarization curves of nickel electrodes in hydrogen fluoride have well-defined shapes [21]. The anode polarization curve is characterized by a high fluorine overpotential, such that no current flows until the potential is significantly in excess of + 3·0 V (versus hydrogen electrode), whereupon the current rise is practically linear with potential. The cathode polarization curve, on the other hand, demonstrates a very low hydrogen overpotential and the current rises linearly with potential.

These facts were utilized in the fabrication of a new type of reference electrode. An auxilliary electrode system was set up within the cell in such a way that the earthed auxiliary cathode, which was also the reference electrode in the main electrode system, had a fixed potential difference (usually 3·0 V) from the auxiliary anode applied by a power supply with a current limiting device of 10 mA. Thus, for the requirements of these experiments the reference electrode was constant at within a few millivolts of 0·0 V (versus hydrogen electrode).

3. Results and discussion

3.1. 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 (see Section 2.2).

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 0·2 wt% water, i.e. approximately 200 g 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 1·8 A 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 5·5 V (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 the electrodes were ready for the next stage of the reaction, fluorination of the organic substrate.

3.2. 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.

Vapour phase 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).

The ratio of perfluoroacyl fluoride to perfluoro cyclic ethers was found to vary during the course of a reaction and as a function of organic starting material concentration. The proportion of perfluoro-acyl 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.

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 development, that of a pilot plant scale of operation.

The pilot plant was built to an ultimate design specification of 100 A 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. 4) 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.

3.2.1. Current as a function of time.

Fig. 5 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 25 A. After 30 days the current decreased rapidly over the next 20 days and then reached an almost constant value of around 5 A.

3.2.2. Rate of product separation as a function of time.

Fig. 6 illustrates the rate of separation of product, expressed as g/day 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. 5). The most significant features 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 [22] 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 an-
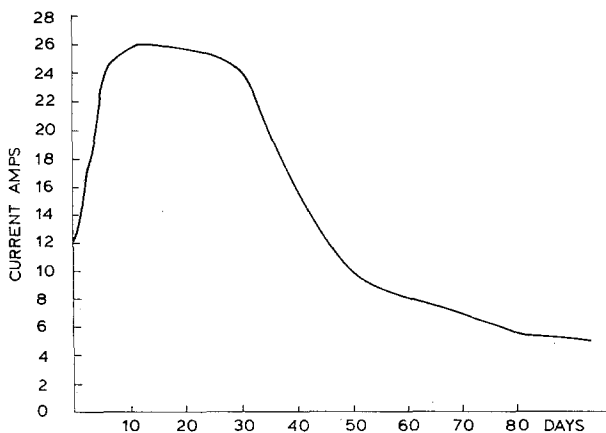

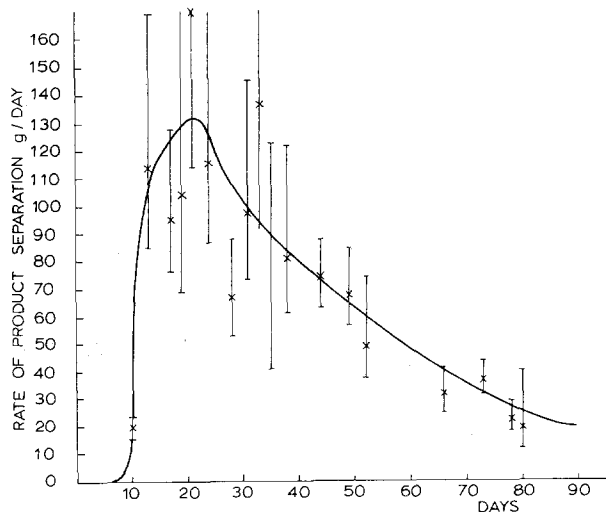Fig. 5. Current versus time plot.

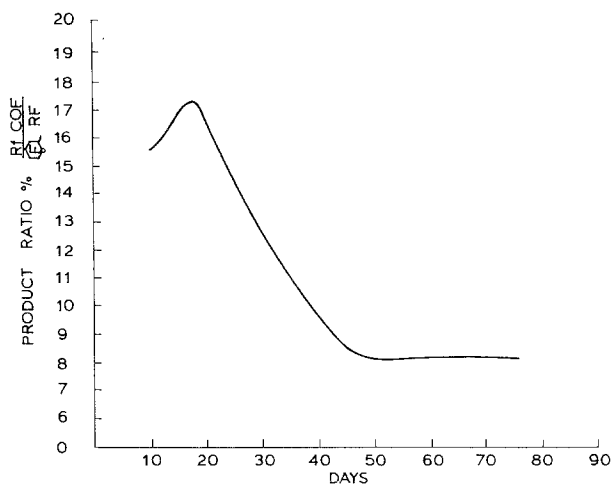Fig. 6. Rate of product separation versus time.

Fig. 7. Product ratio versus time.

hydrous hydrogen fluoride which make up the electrolyte. Thus, before separation of product can occur a saturation level of perfluorinated products in the electrolyte must be reached.

Because of the vapour pressure of the products and the inefficiency of the condenser system it was observed that significant amounts of fluorinated material were lost from the cell. A series of trapping experiments of the gas effluent from the condenser quantified this loss which will be described in a later section.

3.2.3. Product ratio as a function of time. Fig. 7 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. 6), in that the product ratio increases as the product rate increases, both reaching a concurrent maximum at 20 days, and decreasing in parallel to a minimum after about 50–60 days.

3.2.4. 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. However, this gave rise to a serious technical problem. It was impossible because of the time lag in product appearance previously described, together with the difficulty of chemical analysis for octanoyl

fluoride in the electrolyte in all but the first few days of a fluorination run, to measure directly the product ratio for an analysed starting material concentration at any given point in time.

This being the case, it was necessary to devise a method by which the variation of octanoyl fluoride with time could be calculated indirectly and subsequently related to the varying product ratio.

The technique involved using measured values of current passed (Fig. 5) to calculate the theoretical quantity of octanoyl fluoride consumed.

From this it was possible to derive the theoretical octanoyl fluoride concentration as a function of time, and by assuming a current efficiency for the organic reaction of 80%, a realistic estimate of the actual octanoyl fluoride concentration at any point in time was made. These derivations are illustrated in Fig. 8.

By combining the data from this graph (Fig. 8) with the data from the graph of product ratio versus time (Fig. 7), it was possible to establish the relationship between octanoyl fluoride concentration and fluorinated product ratio, for a given experiment, as shown in Fig. 9.

The ratio of perfluoro-octanoyl fluoride to perfluorocyclic ethers increases with increased octanoyl fluoride concentration. At the highest and lowest concentrations the errors of this estimation technique, resulting from the product appearance time lag and reaction rate assumption, respectively, would be expected to be greatest. Taking this into account the ends of the curve
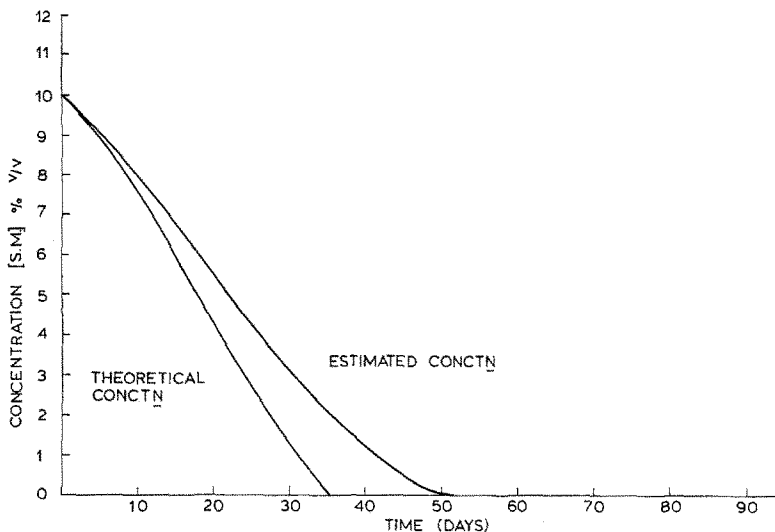
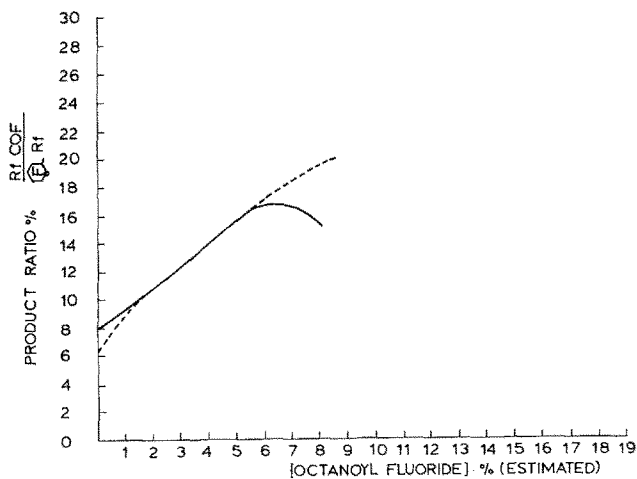Fig. 8. Octanoyl fluoride concentration versus time.

Fig. 9. Fluorinated product ratio versus octanoyl fluoride concentration.

may be modified to give a more realistic represen- tation of the relationship, illustrated by the broken lines in Fig. 9.

The range of octanoyl fluoride concentrations covered by this particular experiment was limited and it was therefore necessary to apply similar estimation techniques to other experiments in which different starting material concentrations were studied.

Fig. 10 shows a collection of data from a num- ber of such experiments in which self consistency of results is observed. It can also be seen that the modified curve of Fig. 9 constitutes the lower portion of the larger concentration range covered by Fig. 10. The yield of perfluoro-acyl fluoride

continues to rise with starting material concen- tration in a non-linear fashion to a maximum of about 34% at an octanoyl fluoride concen- tration of 20%. This value is on a still rising part of the curve but is short of the maximum value of 47% obtained in bench scale experiments.

It is interesting to postulate why the ratio of perfluoro-octanoyl fluoride to perfluoro-cyclic ethers should vary with octanoyl fluoride concen- tration. 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 attacking a carbon atom along its own skeleton (Reaction 2), i.e.
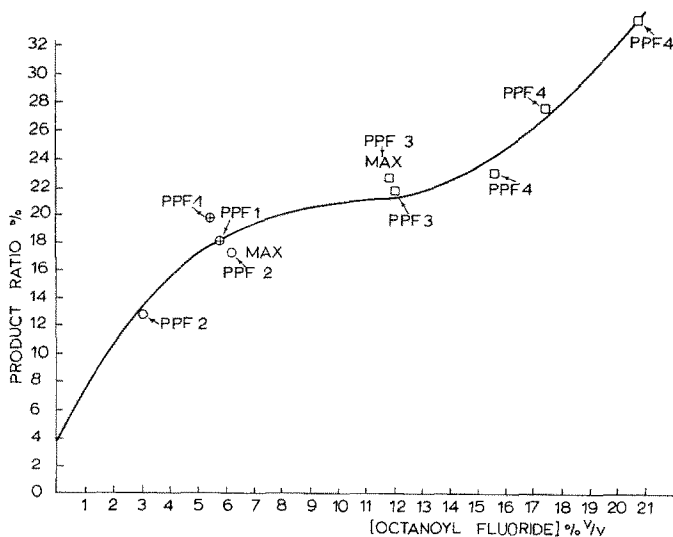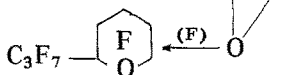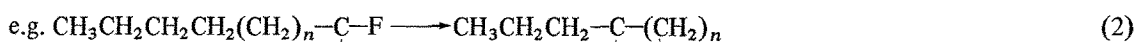
Fig. 10. Fluorinated product ratio versus octanoyl fluoride concentration.

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

e.g.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_n\!-\!\text{C}\!-\!\text{F} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\!-\!\text{C}\!-\!(\text{CH}_2)_n \qquad (2)$$

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 rationalize 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

$$\text{R CO F} + (\text{HF})_n \rightleftharpoons \left[\text{R}\!-\!\text{C}\!-\!\text{OH} \right]^+ [\text{H}_{n-1}\text{F}_n]^-. \quad (3)$$
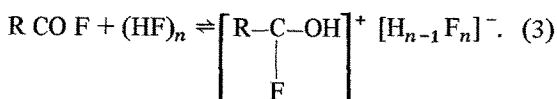
Further solvation of this organic cation would increase with increased dilution.

As the concentration of octanoyl fluoride increases it is possible that a considerable degree

of association, through hydrogen organic bonding, between protonated organic species occurs to give the loosely bonded polymeric structure illustrated below

$$N[\text{H}_{n-1}\text{F}_n]^-$$
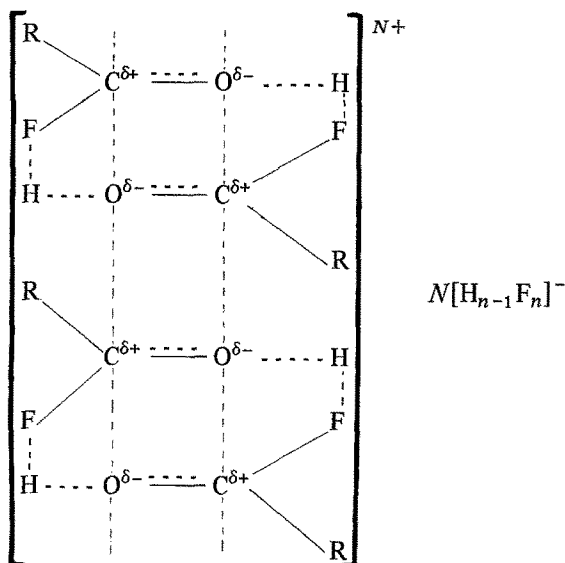
The degree of association of acyl species will

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.

3.2.5. Mass balance, chemical yield and current efficiency. In a typical fluorination at 100 A a series of gas effluent trapping experiments indicated that average rate of loss of material through the condenser was: (a) Fluorocarbon 8 g h^{-1}, (b) hydrogen fluoride $30 \cdot 6 \text{ g h}^{-1}$. Thus, over 28 days period, starting with 5000 g octanoyl chloride

mass of fluorocarbon drained
  from cell $= 4609 \text{ g}$
mass of fluorocarbon through
  condenser $= \underline{5376 \text{ g}}$
total fluorocarbon product $= \underline{9985 \text{ g}}$
theoretical yield of fluorocarbon
  product $= 5000 \times 416/146$
                                            $= \underline{14250 \text{ g}}$
therefore estimated chemical
  yield $= \underline{70 \cdot 0\%}$

The current efficiency was calculated according to the equation:

$$C_7H_{15}COF \xrightarrow[30\,e]{ECF} C_7F_{15}COF$$
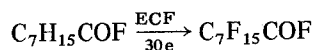
and found to be 28·7% for the production of fluorocarbon.

4. Conclusions

The following conclusions were reached:

(a) Proper 'conditioning' [5] of the 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 fluoride 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 perfluoro-octanoyl 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 some modifications, to a much larger range of compounds.

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