JOURNAL OF APPLIED ELECTROCHEMISTRY 6 (1976) 23–32

The electrochemical fluorination of propene

F. G. DRAKESMITH, D. A. HUGHES

The Electricity Council Research Centre, Capenhurst, Chester, U.K.

Received 2 December 1974

A study of the electrochemical fluorination of propene under rigidly controlled conditions has led to the development of a number of techniques which improve the reproducibility and chemical yields of the process. It has been shown that controlled 'conditioning' of the anode was critical to the reproducibility of the reactions. Control of the anode potential within specific limits during fluorination was essential to minimize breakdown of the organic compounds. The experimental data are discussed within the context of the possible reaction mechanisms.

---

1. 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 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 two 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 heptafluoropropene, 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.

$$\therefore \text{Energy for 1 Kg product} = \frac{12 \times 26{\cdot}8 \times 6}{170}$$

$$= 11{\cdot}35\,\text{kWh}$$

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 repored 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. Also, at the time of commencement of this project, 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, 7] 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. The apparatus and the experiments described in this paper were designed to study the electrochemical fluorination of gases 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.

2. Experimental

2.1. *Materials*

The reactants used were commercial grade hydrogen fluoride (maximum 0·2% H_2O), propene of C.P. grade, and AnalaR reagent grade sodium fluoride. The only other materials in contact with the system were P.T.F.E., Viton elastomer, nickel ($>$ 99·9% pure) and high purity nitrogen. The reason for fabricating the apparatus with the least number of different materials was in an attempt to obtain the simplest chemical system, thus avoiding complicated side-reactions by other 'impurities', e.g. it was observed very early in this project that 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 product 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.

2.2. *Apparatus*

The apparatus is illustrated in Fig. 1. 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 5·5 cm) was nickel foam (80 mesh, 1 cm 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 0·4 cm) 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.

2.3. *Product analysis*

2.3.1. *Vapour phase chromatography*. A Perkin Elmer model F11 chromatograph fitted with a hot

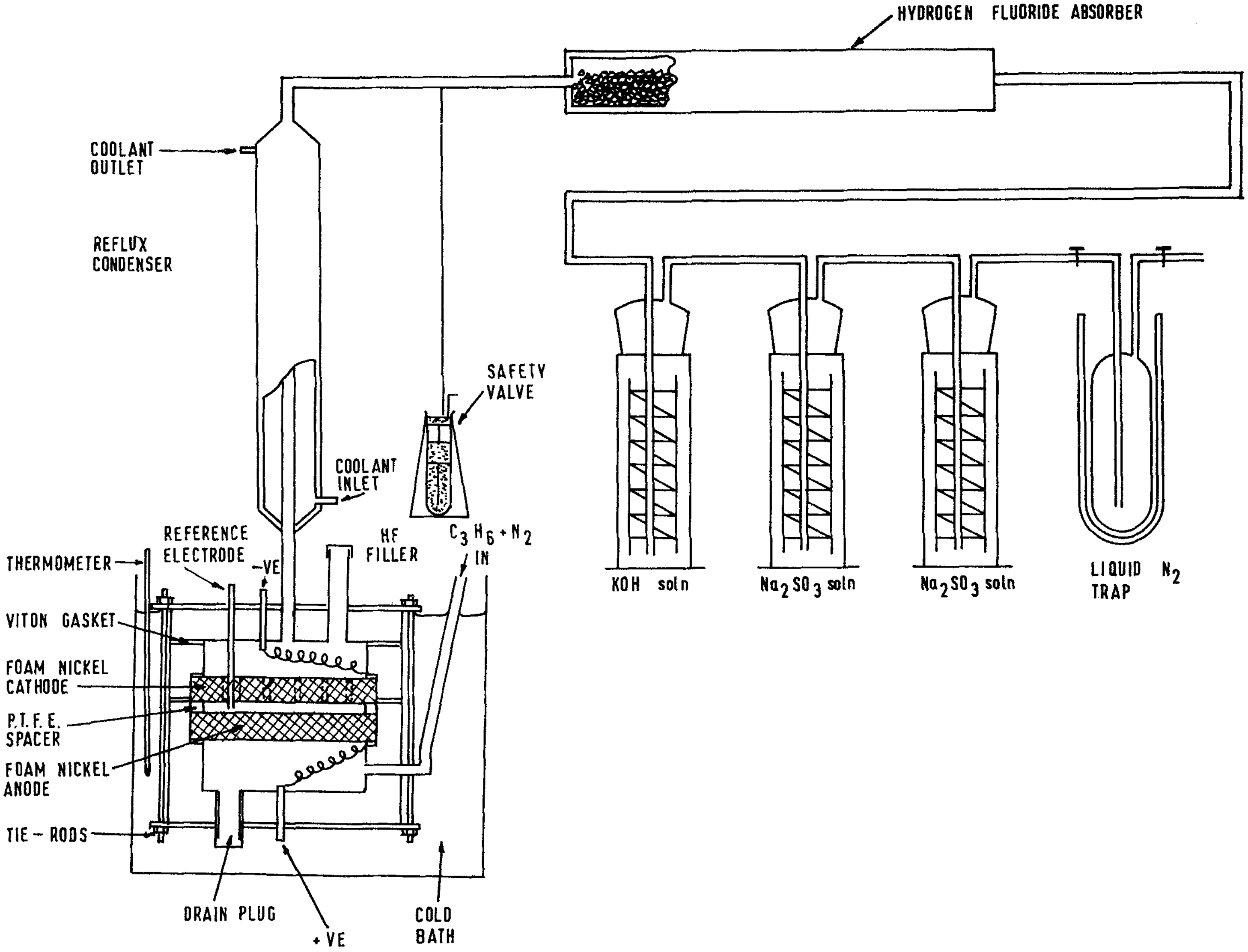


Fig. 1. Electrochemical fluorination apparatus.

wire detector system was used for analytical scale v.p.c. 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 microcell v.p.c. 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 [8, 9, 10].

2.3.3. *Mass spectroscopy*. The Wilks 41 micro-cell attachment was modified so that trapped eluted compounds could be transferred into an A.E.I. MS 12 spectrometer. Later, another coupled v.p.c. – mass spectrometer (P.E. 452/MS 12) was used to record the spectra more conveniently. These spectra were compared, and identified with standard reference spectra in the literature [8, 11].

2.4. *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 (8 ml min^{-1}) was metered and passed through the cell. The anode was 'conditioned' by potentiostatically controlling its potential at + 6·0 V (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 7·7 V. The anode potential was then lowered to + 4·80 V (versus reference electrode) and the cell allowed to reach equilibrium (I = 1·4 A, T.P.D. = 6·12 V). Propene (5·7 ml min^{-1}, 0·64 g h^{-1}) was metered and mixed with nitrogen (8 ml min^{-1}) and passed through the cell for 18 h with these electrical parameters, during which time the product was trapped (10·5 g).

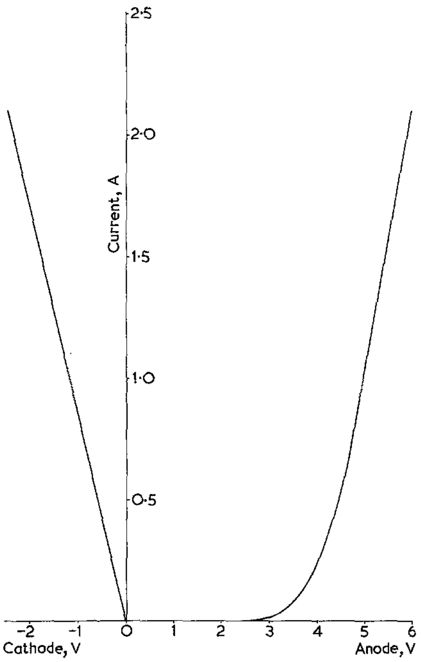


Fig. 2. Current versus potential for new electrodes. 6% by weight NaF in AHF at −3°C.

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 vapour phase chromatographic, infra-red, and mass-spectroscopic techniques described above and shown to consist of:

$$CF_4(2{\cdot}0\%),\ C_2F_6(2{\cdot}7\%),\ C_3F_8(37{\cdot}7\%),$$

$$C_3H_8(8{\cdot}9\%),\ C_3HF_7(10{\cdot}1\%),\ C_3H_2F_6(8{\cdot}7\%),$$

$$C_3F_2H_6(5{\cdot}3\%)\text{ and }C_4H_{10}(24{\cdot}5\%).$$

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 90 600 C. This represents a current efficiency calculated for the introduction of fluorine into propene of 94%.

3. Results and discussion

3.1. *General*

Fig. 2 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

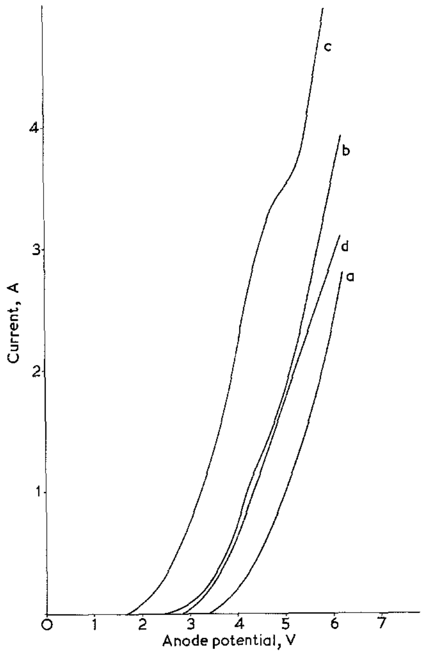


Fig. 3. Current versus potential during electrode preparation. 6% by weight NaF in AHF at −5°C. N_2 flow rate 8 ml min^{-1}. (a) New electrodes; (b) anode 'matured' at + 6·0 V for 25 min; (c) anode 'matured' at + 6·0 V for 2 h; (d) propene added (1·7 ml min^{-1}).

from 0·0 V (versus reference electrode) whereas the anode current is not significant until potentials of greater than about 3 V (versus reference electrode), when the smooth curve becomes linear and steeply rising. The general form of this curve closely resembles that reported by Mantell [12]. Fig. 3 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 8 ml min^{-1} through the cell. Curve a is that produced by new electrodes, and closely resembles that in Fig. 2. Curve b is that produced after the anode had been 'conditioned' at + 6·0 V (versus reference electrode) for 25 min. Curve c is that produced after the same anode had been 'conditioned' at + 6·0 V (versus reference electrode) for 2 h. 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.

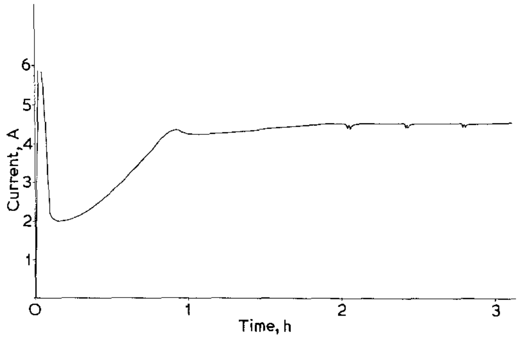


Fig. 4. Current versus time. 1% by weight NaF in HF at 0°C. Anode potential + 6·0 V.

The development of this film is also illustrated by Fig. 4, in which the current was recorded as a function of time for a potentiostatically controlled anode (A = + 6·0 V) 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, but possibly absorbed more water during transfer from the cylinder to the cell). After about 10 min the current had reached a minimum and then slowly increased during the course of 1 h 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 condition, all the oxyfluoride had been converted to a nickel fluoride. The valence state of the nickel at this stage is not known, but it is hoped that further work will reveal this. 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. 4, and not after the equilibrium current plateau has 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

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(8·9 ml min^{-1}), F.R.N_2(15 ml min^{-1}) etc., constant.
Conductivity additive NaF(5g).
Chemical yield 30–40%.

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 (+5·0 V), temperature (0°C), etc., constant.
Conductivity additive NaF(5g). Chemical yield 35–45%.

the reasons why others [5] have observed such spurious results.

3.2. *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. 5, which illustrates clearly how breakdown increases drastically for anode potentials over about +5·0 V.

3.3. *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. 6, which illustrates the linear inverse relationship between dilution and breakdown.

3.4. *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

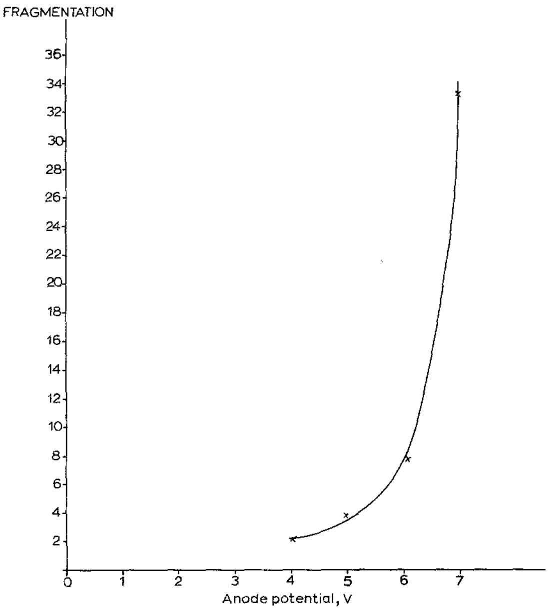


Fig. 5. Graph of fragmentation versus anode potential.

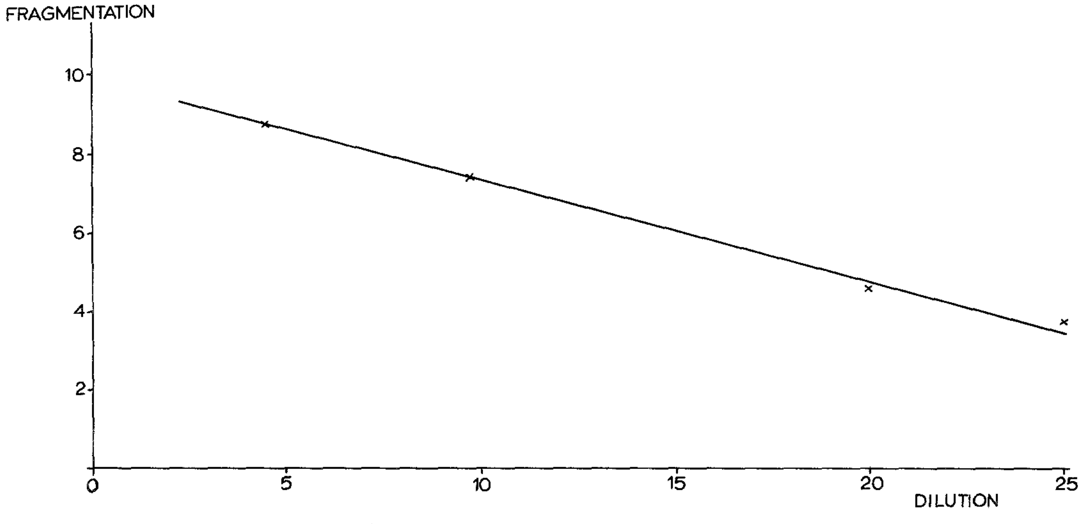


Fig. 6. Graph of fragmentation versus dilution.

fluorination was 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. 7, which illustrates clearly the so-called ‘zipper’ effect.

3.5. *Reaction mechanisms*

A number of possible mechanisms have been postulated for the process of electrochemical fluorination. Perhaps the most obvious is one in which elementary fluorine is generated at the anode and subsequently reacts with the organic substrate. This mechanism, however, is probably much too simple, as it fails to account for the observed induction period and also the fact that fluorine is evolved during induction but not afterwards.

Another hypothesis is that the products are formed in a reaction with simple high valence nickel fluorides, generated at the anode, such as NiF_3 or NiF_4. This scheme is a possibility since it is known that NiF_2 is formed on the electrode. But it has been argued that the process $Ni^{2+} \rightarrow Ni^{3+} + e$ occurs at more anodic potentials than the liberation of F_2 from F^-. Also, reactions of organics with high valence fluorides of other metals bear little resemblance to those occurring in the electrochemical method.

A further suggestion is that the fluorination agent is a loose complex of NiF_2 and F_2 formed at the anode; fluorination would take place between this complex and the substrate, possibly also absorbed on the nickel fluoride layer. This ‘loose’ complex of F radicals on NiF_2 was proposed by Rogers, Evans and Johnson [13] as the fluorinating agent for NH_4HF_2 and ClF_3. But chlorine trifluoride is also fluorinated to ClF_5 at a glassy carbon anode, so complex nickel fluorides are not necessary for the fluorination of these inorganic compounds. Also a recent patent from Philips

Table 3. Degree of fluorination versus propene flow rate

	Mol % product									
$F.R.C_3H_6$ (ml min^{-1})	$CF_4 + C_2F_6$	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 $(D)_8 = 100\ (C_3F_8)/(\text{total F/C})$ and $(D)_2 = (C_3H_6F_2)/(\text{total F/C})$.
Reaction parameters of anode potential, temperature, N_2 flow rate (8 ml min^{-1}) etc. constant.

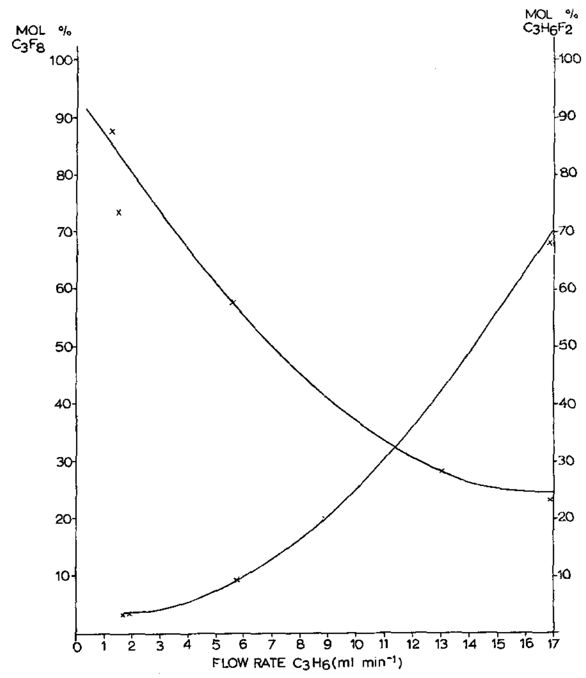


Fig. 7. Degree of fluorination versus propene flow rate.

Corporation, U.S.A. [14] claims high chemical and current yields from organic compounds within a porous carbon anode, where reaction of the organic is said to occur at the three phase interface of organic gas, liquid HF, and solid carbon.

Yet another theory states that the observed products are formed in a reaction with complex high valence nickel fluorides generated at the anode such as $(R)_2NiF_6$ and $(R)_3NiF_6$ (where R is the organic substrate). This mechanism probably has more than most to commend it as its development appears to satisfy many of the observed requirements. It is known that complex high valence nickel fluorides, e.g. K_3NiF_6 and K_2NiF_6 can be formed by the action of fluorine on mixtures of KCl and $NiCl_2$, suggesting that the oxidation potential for the formation of these compounds is less than that required to generate F_2. Further, Engelbrecht *et al.* [15] showed that K_2NiF_6 is formed in KF–HF melts and suggested the following mechanism:

Primary step	$Ni + 2F^- \longrightarrow NiF_2 + 2e$
Induction period	$NiF_2 + (2)F^- \longrightarrow NiF_{3(4)} + (2)e$ (formation of black deposit on anode)

Corrosion $NiF_{3(4)} + 3(2)F^- \longrightarrow NiF_6^{3(2)-}$ (nickel dissolves as a complex in solution)

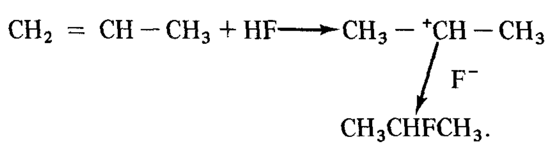
Nickel fluoride deposition $NiF_6^{3(2)-}$ + substrate $\longrightarrow$ NiF_2 + fluorinated substrate.

It is interesting to compare this with the work of Plevey *et al.* at Birmingham University, who demonstrated that $KCoF_4$ (formed by the reaction of KF and CoF_3) is a considerably milder fluorinating agent than CoF_3 alone, e.g. thiopene gives fewer breakdown products. Also, Stein, Neil, and Alms [16] have shown that, at a nickel anode in liquid HF, Ni (III) and (IV) species are produced with high enough oxidation potentials to liberate oxygen from water. During the course of our work coloured compounds have been isolated from the cell which react in a similar fashion.

It is obvious that a number of possible mechanisms exist and it is quite conceivable that more than one of these may take place either simultaneously or during different stages of the reaction.

3.6. *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 [17] demonstrating a very high degree of selectivity in substitition compared with the reported [18] selectivity in gas phase reactions, which are almost random, e.g.

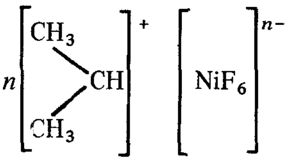
for $X^{\bullet} + RH \longrightarrow R^{\bullet} + HX$ at 300 K

the relative selectivities in fluorination (i.e. when $X = F$) for $-CH_3$, $> CH_2$ and $\gg CH$ are 1, 1.2 and 1.4 respectively.

The relative selectivities are:

Halogen	*Temperature*	*Relative selectivities at each position*			
	°C	$CH_2F -$	$CH_2 -$	$CH_2 -$	CH_3
$F^{\bullet}$	20	0·3	0·8	1·0	1·0

This high specificity in E.C.F. substitution could well be the result of a close association or stereospecific adsorption of the organic molecule to the fluorinating agent. If, as has been proposed, the agent is a complex nickel fluoride anion, or a 'loose' complex of nickel fluoride with fluorine on the anode surface, 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 (17 ml min^{-1} C_3H_6) the degree of fluorination of 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.

4. Conclusion

4.1. *Electrode materials*

(1) Nickel is apparently the only suitable anode material.
(2) Utilization of nickel foam as electrode material gives a much greater surface area per unit cell volume than other electrode configurations.

4.2. *Preparation of anode surface*

The proper conditioning of the anode surface is critical. In order to achieve reproducibility it is necessary (1) to begin organic reactions with an electrode surface of constant constitution and (2) to exclude electrode poisons.

4.3. *Anode potential during fluorination*

The potential of the anode must be controlled since (1) for anode potentials $<3{\cdot}5$ V (versus reference electrode), little fluorination is achieved and (2) for anode potentials $>5{\cdot}0$ V (versus reference electrode), extensive breakdown results.

4.4. *Contact of organic compound with anode*

(1) Increase in dilution of organic compound reduces amount of breakdown.
(2) Shorter contact times of organic compound with anode surface reduces breakdown.

4.5. *Selectivity of fluorination*

(1) The degree of fluorination is difficult to control.
(2) 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.

References

[1] J. H. Simons, *J. Electrochem. Soc.* 95 (1949) 47.
[2] A. J. Rudge in *Industrial Electrochemical Processes* (A. T. Kuhn, ed.), Elsevier, London, 1971, p. 74.
[3] J. H. Simons, *Fluorine Chemistry*, Vol. I, Academic Press, New York, 1950, p. 225; J. Burdon and J. C. Tatlow, *Advances in Fluorine Chemistry*, Vol. I. Butterworth's Scientific Publications, London, 1960, p. 129; S. Nagase in *Fluorine Chemistry Reviews* (P. Tarrant, ed.) Vol. I, Marcel Dekker Inc, New York, 1967, p. 77; A. J. Rudge in *Industrial Electrochemical Processes* (A. Kuhn, ed.) Elsevier, London, 1971, p. 70.
[4] R. D. Dresdner and J. A. Young, *J. Amer. Chem. Soc.* 81 (1959) 574.
[5] V. Ya. Kazakov, L. A. Savelev, R. A. Dzerzhinstaya, E. A. Shuskkin and I. L. Gudimov, *Zhur. Prikladnoi Khimi* 41 (1968) 2212.
[6] P. Sartori and M. Schmeisser, *Chem.-Ingr.-Tech.* 36 (1964) 9.
[7] P. Sartori, *Angew. Chem.* 75 (1963) 417.
[8] A.P.I. Research Project 44, Texas A & M University, Texas.
[9] J. R. Latcher, A. Kianpour and J. D. Park, *J. Phys. Chem.* 60 (1956) 1454.
[10] J. K. Brown and K. J. Morgan, The Vibrational Spectra of Organic Fluorine Compounds in *Advances in Fluorine Chemistry*, Vol. 4, Butterworth's, London, 1965, p. 253.
[11] U. R. Majer, Mass Spectrometry of Fluorine Compounds in *ibid*, Vol. 2, Butterworth's, London, 1961, p. 55.
[12] C. L. Mantell, *Electrochemical Engineering*, McGraw-Hill Inc, New York, 1960, p. 299.
[13] H. H. Rogers, S. Evans and J. H. Johnson, *J. Electrochem. Soc.* **116** (1969) 601.
[14] Phillips Petroleum Corporation, Brit. Patent 1,257,185 of Dec. 15th 1971.
[15] A. Engelbreckt, E. Mayer and Ch. Pupp, *Monash* 95 (1964) 663.
[16] L. Stein, J. M. Neil and G. R. Alms, *Inorg. Chem.* 8 (1969) 2472.
[17] N. M. R. Spectrum by Dr. R. Abraham, University of Liverpool.
[18] P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.* (1960) 144.