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Electrochemical perfluorination of organic acids. Contribution to the knowledge of the mechanism

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Electrochemical perfluorination of octane-sulphofluoride (OSF) and octanoic-fluoride (OF) to the perfluoro compounds (POSF and POF) has been studied over a wide range of experimental conditions. Significant improvement of the reported yield of perfluoro-product has been achieved with electrolysis at high potential. The results are explained in terms of a model involving simultaneous adsorption of the reactant and of fluorine on a NiF_2 surface.

1. Introduction

Perfluoro derivatives have found a broad range of applications for the formation of low-energy surfaces, as soil-repellents in the textile industry, and generally as surfactants.

Since the pioneering work of J.-H. Simons [1], electrochemical perfluorination has been the object of many investigations. This method allows the complete fluorination of a large number of organic compounds, with retention of functional groups [2, 3, 9]. However, in many cases the reported yields are poor due to the cleavage of the molecule during electrolysis, which leads to a variety of lighter by-products, as well as to polymeric materials [4]. For some products, studies of the numerous parameters involved in the process have been reported, but most of the published reports are concerned with the elucidation of the reaction mechanism which is considered to be very complex. One of the proposed mechanisms [5] seems to fit the experimental evidence best. A loose complex of nickel fluoride with elemental fluorine is formed on the anode, and acts, after an induction period, as the fluorinating compound.

We studied the conditions of fluorination of some compounds [9]. This paper concerns some aspects of our results with octane-sulphofluoride and octanoic acid which support the model proposed by Hackerman [5], but allow a better definition and an extension of this model.

2. Experimental

2.1. *Cell*

The electrolyses were performed in 40 ml cylindrical nickel cells filled with distilled anhydrous HF. Commercial purity HF (H_2O content $<0{\cdot}02\%$) was used after careful distillation from a cylinder directly into the refrigerated electrolysis cell. With the low water content thus obtained, we verified that a pre-electrolysis did not significantly change the results. A cylindrical Ni-anode ($0{\cdot}35$ dm^2) was placed at the centre of the cell and connected through the polypropylene cover to a variable power supply. At the bottom of the cell, a drain allows the removal of the insoluble perfluorinated heavy products. An external cooling coil allows the removal of heat and the regulation of temperature. The cover was fitted with a reflux condenser (stainless), a temperature sensor dipping into the electrolyte, and a viton-membrane for adding the starting product. This cell allows the process to be conducted under pressures up to 2 atm. Some experiments were repeated with a scaled-up 2 litre cell which allowed the agitation of the electrolyte. The results obtained with this larger cell were essentially the same as those obtained with the above described equipment.

2.2. *Starting products*

The fluorides of the carboxylic and sulphonic acids have been used as starting material [10]. As the fluorides of the carboxylic acids are quite unstable, they were prepared directly in the cell, starting with carboxylic acid.

$$RCOOH + HF \rightleftarrows RCOF + H_2O$$

The water formed in this reaction was eliminated by low-voltage electrolysis and this produced a shift of the equilibrium in favour of the fluoride.

2.3. *Analysis*

The insoluble heavy products were drained from the bottom of the cell, washed with 5% $NaHCO_3$, dried and analysed by gas chromatography. For the main products, a confirmation of the structure was obtained through IR spectra and preparation of derivatives, which was sometimes coupled with NMR and mass-spectra determinations.

3. Results

The octane-sulphofluoride $C_8H_{17}SO_2F$ (OSF) and the octanoic-fluoride (OF) have been perfluorinated in anhydrous HF with the process variables chosen in the following ranges:

Concentration: 5–60 wt %
Temperature: $-20 - +35$°C
Cell voltage: 6–13 V

The reactions taking place at the electrodes for the octane-sulphofluoride are:

$$\begin{array}{lll}
\text{anode:} & & \\
C_8H_{17}SO_2F + 34F^- & \rightarrow & C_8F_{17}SO_2F + 17HF + 34e^- \\
\text{cathode:} & & \\
34HF + 34e^- & \rightarrow & 34F^- + 17H_2 \\
\hline
\text{overall:} & & \\
C_8H_{17}SO_2F + 17HF & \rightarrow & C_8F_{17}SO_2F + 17H_2 \\
196{\cdot}3 + 17\ [20] & \rightarrow & 502 + 34{\cdot}3 \\
\text{OSF} & & \text{POSF}
\end{array}$$

The yield of perfluorinated product decreases with increasing concentration, and the best conditions are found with low concentrations. The temperature dependence shows a flat maximum at the temperature of 30°C.

The influence of the cell voltage on the yield is very significant, although this point is not emphasized in the available literature.

We have reported our results concerning the OF fluorination to POF in Table 1, where our results are compared with those of Scholberg and Brice [6].

The most remarkable feature of these results lies in the absence in our crude products of the perfluorinated cyclic ethers which were present in large amounts in the experiments of Scholberg and Brice.

The results of the perfluorination of OSF, obtained with three different cell-voltages, are reported in Table 2, together with the values of Gramstad and Haszeldine [7] and of Brice and Trott [8]. Our results agree very satisfactorily with those published for low and intermediate cell voltages, but a sharp improvement in yield, coupled with a reduced corrosion rate, appears at higher potentials.

The influence of the potential on this perfluorination is further evidenced in considering the current efficiency. This relationship is is expressed in Fig. 1.

4. Discussion

The results obtained allow a distinction between two potential ranges, where the perfluorination reaction takes place differently.

The main characteristics of these two regions are summarized below.

(a) At low cell voltage (4–8 V) the current efficiency and yield in desired product are both low while the corrosion rate of the

Table 1. Perfluorination of OF to POF. Comparison of results. Brice et al. report the presence of large amounts of perfluorinated cyclic ethers in their crude product.

Reference	*Cell voltage* *V*	*Concentration* *(OF) wt %*	*Crude product (g)* / *OF introduced (g)*	*Concentration* *POF in crude* *product wt %*	*Yield* *POF obtained (mol)* / *OF introduced* *(mol)* *%*
[6]	5–6	9	1·5	20	11
our results	10	15	0·87	87	20

Table 2. Perfluorination of octane sulphofluoride. Comparison of our results with published results

Reference	*Cell voltage (V)*	*Temperature (°C)*	*Concentration (wt %)*	*Current density* *($A\ cm^{-2}$)*	*Molar yield* *POSF obtained* / *OSF introduced* *%*	*Current efficiency* *%*	*Current efficiency of nickel dissolution** *%*
[7]	5	—	5	0·003	25	50	—
[8]	5–6	18–20	10–20	0·018	25	20	—
our results	6·5–7	20	10	0·01	30	27	0·15
	9·0	20	10	0·02	38	48	0·13
	12	30	10	0·055	60	86	0·026

* This current efficiency was computed from the weight decrease of the anode, according to the reaction Ni → $Ni^{2+} + 2e^-$

nickel anode is high. Furthermore, the rate of formation of product appears to be delayed; no perfluorinated products are obtained during the flow of the first 30% of the theoretical charge. This induction period has been evaluated by collecting the crude product formed at the bottom of the cell at different times during the electrolysis. The results are reported in Fig. 2a. The analysis of this crude product revealed the presence of partially fluorinated products and a rather high level of by-products resulting from C—S bond breakage. The results are poorly reproducible.

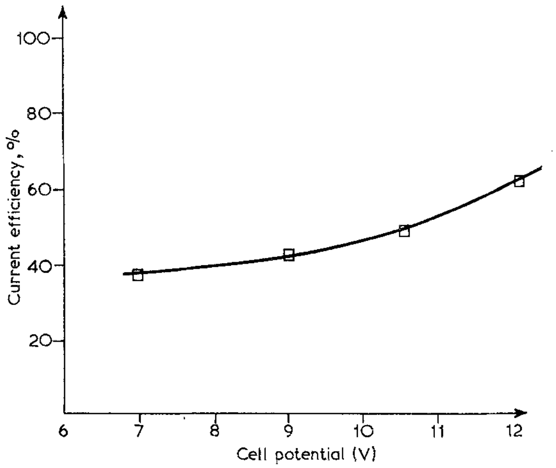

Fig. 1. Perfluorination of OSF to POSF: current efficiency as a function of cell potential for the following conditions: Temperature, 30–35°C; Concentration, 10%.

(b) At higher cell voltages (8–13 V) the current efficiency reaches 90%. At these high cell potentials no significant fluorine evolution has been observed.* In the crude product the impurities only amount to 10%, whereas no partially fluorinated products are observed. The corrosion rate of the anode is markedly diminished, and the rate of formation of the product is proportional to the charge passed, as shown in Fig. 2b.

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* For quantitive evaluation this polarization of the fluorine evolution process should be studied with a reference electrode. This would allow the anode potential to be determined.

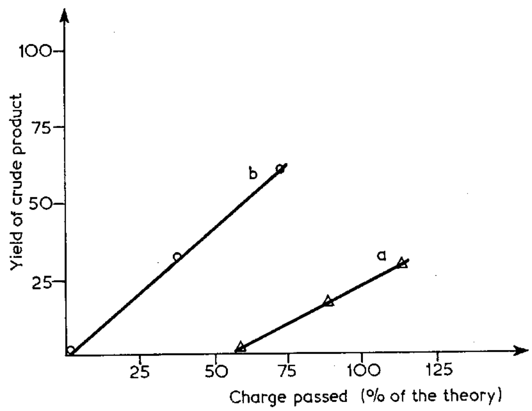

Fig. 2. Yield of POSF as a function of electrical charge passed through the cell
(a) at low cell potential (4–8 V)
(b) at high cell potential (8–12 V).

These observations can be correlated using a refinement of the model proposed by Hackerman [5], according to which a compact layer of NiF_2 is formed on a Ni-anode in anhydrous HF. At high anodic potentials, near the evolution potential of elemental fluorine, this layer contains a high concentration of adsorbed fluorine. The surface concentration has been measured by Chang *et al.* [3], who found $\sim 10^{-8}$ mol cm^{-2}.

Our observations allow an extension of this model, according to which, at high potentials, an adsorption of the organic reactant on the NiF_2-layer occurs, causing the reaction to proceed differently from that at low potential, where the coverage of the surface is not complete.

In the range of the low potentials, this adsorption is very weak, and the reaction mechanisms proceed mainly via radical-formation. These radicals subsequently react with HF to give fluorinated derivatives.

These radicals are probably unstable and can be degraded either to shorter chains (C—C bond rupture) or, in a parallel reaction, form polymeric material. Both products have been observed in our experiments and are reported in the literature. With this radical formation, the reaction proceeds almost statistically, and the rate of the product formation shows an induction period, as indicated in Fig. 2a.

At higher potentials the organic substrate becomes adsorbed on the nickel–nickel surface. This adsorption is strong enough to maintain the organic substrate in contact with the surface, as long as the complete substitution is not achieved. The rate of product formation observed is proportional to the charge passed as indicated in Fig. 2b. No partially fluorinated substrates are found in the crude product, though some polymeric material is still present.

The proposed model covers most of the published experimental evidence, and allows a reasonable explanation of our results. However, further supporting experiments will have to be carried out before the complete perfluorination mechanism can be considered as fully understood.

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