Journal of Fluorine Chemistry, 51 (1991) 357–379

Received: September 13, 1990; accepted: January 21, 1990

SYNTHESIS OF PERFLUOROALKYL CARBOXYLIC ACIDS BY REACTION OF PERFLUOROALKYL IODIDES WITH ELECTROGENERATED SUPEROXIDE ION

C. DAPREMONT-AVIGNON, P. CALAS, A. COMMEYRAS

USTL, Place E. Bataillon, 34095 Montpellier Cedex 5 (France)

C. AMATORE*

ENS, Laboratoire de Chimie, URA CNRS 1110, 24 rue Lhomond, 75231 Paris Cedex 05 (France)

SUMMARY

The electrogenerated superoxide ion $O_2^{\circ-}$ is shown to react with perfluoroalkyliodides to afford F-alkyl carboxylic acids. A mechanism is proposed on the basis of the results obtained in preparative experiments and by cyclic voltammetry.

INTRODUCTION

Reactivity of the superoxide ion has been the object of a large interest for chemists and biochemists. Potassium dioxide is a chemical source of superoxide ion $O_2^{\circ-}$, but its use is limited by its low solubility in organic solvents (except in the presence of crown ethers) [1].

---

* Author to whom correspondence should be addressed.

0022-1139/91/$3.50

Twenty years ago, the possibility to produce $O_2^{\circ -}$ through electrochemical reduction of O_2 has been evidenced, and a large number of papers presented in this field [2]. Particularly, the reactivity of the electrogenerated species $O_2^{\circ -}$ as a nucleophile has been studied toward alkyl and aryl halides yielding generally alcohols and phenols [1- d,e,f][2,f,g][3].

We have investigated the behaviour of the electrogenerated anion $O_2^{\circ -}$ in the presence of F-butyl iodide and of F-octyl iodide. Preparative experiments establish the formation of F-butyric acid (n-$C_3F_7CO_2H$) and of F-octanoïc acid (n-$C_7F_{15}CO_2H$). A study by cyclic voltammetry (CV), affords some elements on the mechanism involved.

RESULTS

Preparative scale electrolysis

Electrolysis of O_2 has been conducted at a preparative scale in the presence of n-C_4F_9I or n-$C_8F_{17}I$. The cell used, described in the experimental part, is equipped with a vitreous carbon cathode (40 mm in diameter). C_4F_9I or $C_8F_{17}I$ was added at ca. 20% in volume in the solvent Dimethylformamide (DMF). Experiments have been conducted under a flow of pure oxygen or under nitrogen. Two supporting electrolytes, LiCl and TBAF (Tetrabutylammonium tetrafluoroborate) , have been used. Experiments are realized under galvanostatic conditions (constant applied current).

Electrolysis under nitrogen

The nature of the compounds formed is dependent upon the value of the applied current.

Results are summarized in Table1.

TABLE 1

Galvanostatic electrolysis of C_4F_9I under nitrogen (without O_2)
catholyte : C_4F_9I : 0.5 ml (1g), DMF : 4.5ml, LiCl : 0.1M
anolyte : DMF : 2ml, LiCl : 0.1M

Imposed current (mA)	Products[a]	Faradays/mole of C_4F_9I consumed
50	C_8F_{18}: 80% C_4F_9H: 20%	0.98
80	C_8F_{18}: 17% C_4F_9H: 80%	1.92

[a] The electrolysis have been stopped after the consumption of 0.8 F/mole of C_4F_9I introduced; product yields are given with respect to C_4F_9I consumed.

At low current density , the main product is the dimer C_8F_{18} (liquid at room temperature), which separates spontaneously from the catholyte owing to its poor solubility.

At higher current density, electrolysis affords C_4F_9H. Accordingly, the faradic consumption which is around 1 F/mole at low current density , reaches a value of 2 F/mole at higher current.

Electrolysis under oxygen

The experiments are performed under small bubbling of pure O_2 in the catholyte. The electrolysis have been followed by ^{19}F n.m.r , composition of the samples being quantitatively determined by addition of known amounts of ϕ-CF_3. Under these conditions, electrolysis leads to propionic acid and C_4F_9H. The oxygen flow results in a continuous evaporation of the starting iodide, C_4F_9H and C_8F_{18} which are quite volatile, leading to some difficulties in the interpretation of the results. Consequently we have conducted similar experiments with $C_8F_{17}I$, this compound and the corresponding $C_8F_{17}H$ being less volatile than the C_4 analogues. The results are presented in Table 2.

Discussion of the preparative experiments

Formation of acids in the above electrolysis corresponds to the overall reaction :

$$R_F'\text{-}CF_2\text{-}I + O_2 + 4e^- \longrightarrow R_F'\text{-}CO_2^- + I^- + 2F^-$$

from which it appears that the consumption of four Faradays by mole of converted R_FI must be observed ($R_F = C_nF_{2n+1}$, $R_F' = C_{n-1}F_{2n-1}$).
From Table 2, we can note that the faradaic consumption starts from 2 F/mole and increases toward 4 F/mole.
When the electrolysis is pursued, i.e. for higher values of F/mole of R_FI, diffusion between the two compartments occurs which results in serious experimental difficulties.

TABLE 2

Galvanostatic electrolysis under a stream of O_2 of $C_8F_{17}I$ (0.8 ml; 1.64g) in DMF (4.2 ml) 0.1M in TBAF. imposed current : 45 mA

Faradays by mole of starting R_FI	% of starting R_FI electrolysed	Faradays by mole of R_FI electrolysed	Products distribution		
			$C_7F_{15}CO_2H$ (a)	$C_7F_{15}CO_2H$ (b)	$C_8F_{17}H$ (c)
0.5	26	1.92	11	44	-
1	44	2.27	19	43	-
2	50	4	22	44	-
3	56	5.35	32	58	19
4(d)	74	5.40	34	46	14

a) Total yield in product relative to initial R_FI
b) Yield in product relative to R_FI consumed
c) significant amounts of $C_{16}F_{34}$ are found in the cell at the end of the electrolysis
d) The electrolysis has been interrupted when the concentration of $C_8F_{17}I$ in catholyte dropped to 10% of its starting value.

Conclusion of the preparative experiments

We conclude that under a static atmosphere of nitrogen, the electrolysis of C_4F_9I yields C_8F_{18} and C_4F_9H as previously described elsewhere [4]. The dimer is largely favoured at low current densities. It is not possible to perform similar experiments on the $C_8F_{17}I$, because the dimer $C_{16}F_{34}$, now a solid insoluble in DMF, quickly inhibits the electrode.

However, in the presence of oxygen, acids n-$C_3F_7CO_2H$ and n-$C_7F_{15}CO_2H$ are obtained respectively from C_4F_9I and $C_8F_{17}I$. A cyclic voltammetric investigation of this reaction was then undertaken to clarify its mechanism.

Cyclic voltammetric investigation of the mechanism:

Electrochemical reduction of O_2 in Dimethylformamide

Molecular oxygen dissolved in DMF from air at the atmospheric pressure, is reducible at a glassy carbon electrode, exhibiting a reversible pattern [3,c], E ≈ -1V/SCE :

$$O_2 + e^- \rightleftharpoons O_2^{\circ-}$$

However to the best of our knowledge, solubility of O_2 in DMF, 0.05M NBu_4BF_4, is unknown. In order to obtain a determination of the solubility of oxygen in this medium under our electrochemical conditions, we have used a comparison of the reduction pattern of oxygen with the reversible oxidation of ferrocene (known as monoelectronic) . No direct comparison of the observed currents (reduction of O_2 and oxidation of ferrocene) can be made, because the diffusion coefficients of the two species can be different. Yet this limitation can be easily overcame by comparison of the peak currents in CV and limiting currents at rotating disk or at ultramicrocylinders [5]. Using this recent method, the following values were obtained for solutions in DMF, 0.05M in TBAF.

$D_{O2} = 4{,}1.\ 10^{-5}\ cm^2.s^{-1}$

$D_{Fe} = 11.\ 10^{-5}\ cm^2.s^{-1}$

$C_{O2} = 0{,}94.10^{-3}$ mol/l at partial pressure of oxygen: 0,2
atm (air)

Although different, this value is within the same range as the one quoted in the litterature [3,a] for DMSO ($0{,}48.10^{-3}$ mol/l).

Electrochemical study of the reduction of O2 in the presence of n-C4F9I

F-butyl iodide n-C_4F_9I is reducible at a potential more cathodic tha the one observed for O_2, at a glassy carbon disk. We have previously shown [5] that the reduction leads to F-alkyl radicals:

$$C_4F_9I + e^- \longrightarrow C_4F_9^\circ + I^-$$

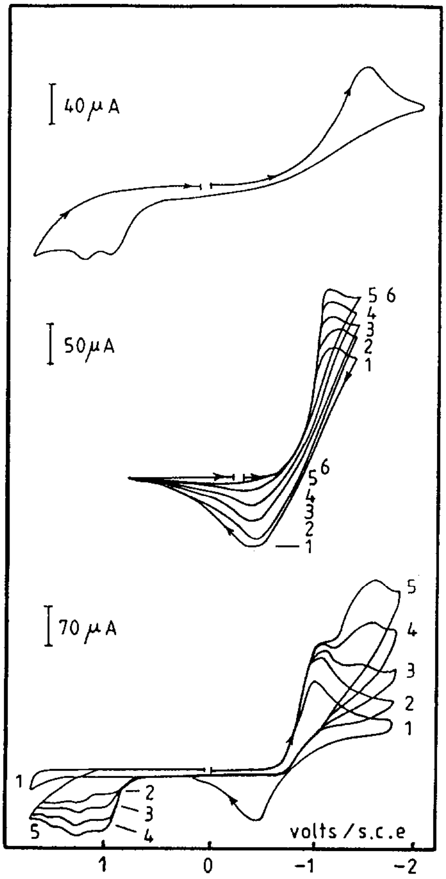


FIG. 1.

(a) Cyclic voltammogram of C_4F_9I at a steady glassy carbon disk, in DMF, TBAF 0,05M
Scan rate: 1V/s
$C_{RfI} = 5.78\ 10^{-3}$ mol/l

(b) Cyclic voltammogram of oxygen at a steady glassy carbon disk; in DMF, TBAF, 0,05M in presence of increasing amounts of C_4F_9I (1: 0μl; 2: 2μl; 3: 4μl; 4: 6μl;; 5: 8μl; 6: 10μl) added in 13 ml of solvent.
Scan rate: 1 V/s
$C_{O2} = 0.94\ 10^{-3}$ mol/l

(c) Cyclic voltammogram of oxygen at a steady glassy carbon disk; in DMF, TBAF 0,1M in presence of increasing amounts of C_4F_9I(1: 0μl; 2: 3μl; 3: 6μl; 4: 9μl; 5: 12μl) added in 13 ml of solvent.
Scan rate: 1 V/s
$C_{O2} = 0.94\ 10^{-3}$ mol/l

In Fig. 1 are displayed from the top to the bottom, the voltammograms obtained at a stationary vitreous carbon disk, for R_FI alone (a), and for O_2 in the presence of increasing amounts of C_4F_9I for two cathodic limits of the scan: -1.3 (b) and -1.9 (c) Volts.

From Fig. 1 it is seen that addition of C_4F_9I to the medium results in the following effects:

a) the reduction wave of O_2 becomes progressively irreversible.

b) irreversibility is obtained more quickly when the cathodic limit is -1.9 Volts; in this case, the height of the peak of reoxidation of $O_2^{\circ -}$ is largely decreased because of the larger reaction time imposed by the large cathodic limit used.

c) the reduction peak of O_2 largely increases in height, however a trend to saturation is observed for large quantities of C_4F_9I.

d) the reduction peak of C_4F_9I is not visible until an amount of this compound corresponding to the above saturating effect has been added. For larger amounts, the reduction peak of C_4F_9I appears at its normal position and increases linearly with added C_4F_9I. At the same time, the height of the reduction peak of O_2 remains unchanged.

Figure 2 reports the evolution of the reduction peak of O_2 together with that corresponding to oxidation of $O_2^{\circ -}$, at different initial concentrations of C_4F_9I .

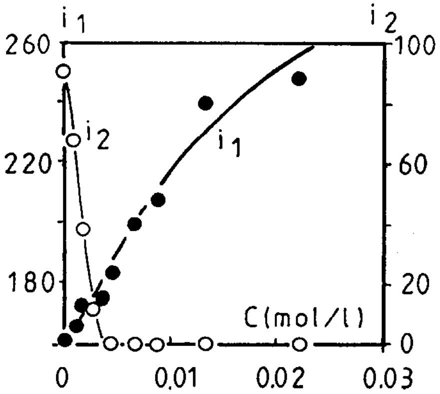


FIG. 2. Evolution of the reduction peak current (i_1, µA) of oxygen and of the oxidation peak current (i_2, µA) of $O_2^{\circ -}$ in presence of different concentrations of C_4F_9I (C,mol/l); $C_{O2} = 4.7.10^{-3}$ mol/l cathodic limit : -1.3 V vs s.c.e.

The electrochemical irreversibility of the reduction of O_2 is quickly obtained, indicating that the electrochemically produced species $O_2^{\circ -}$ undergoes a fast follow-up reaction. As well known in electrochemistry, the reduction peak current of O_2, becoming irreversible, must be enhanced [6] in height by a factor 1.1 if the reductive process remains monoelectronic, or by 1.1.n if the irreversible process involves globally n electrons. As shown on Figure 2, the observed peak is here enhanced by a factor ca. 1.65 , for the largest concentration of C_4F_9I used (0.022 M). This evidences that $O_2^{\circ-}$ reacts with C_4F_9I, and that the total process consumes additional electrons.

A determination of the stoichiometry $C_4F_9I/O_2^{\circ-}$ of the overall process within the time scale of CV can be obtained from the data in Figure 1c, viz from the current peak of C_4F_9I observed for large amounts of added C_4F_9I. This current peak is plotted on Figure 3, as a function of the initial C_4F_9I concentration (C, mol/l).

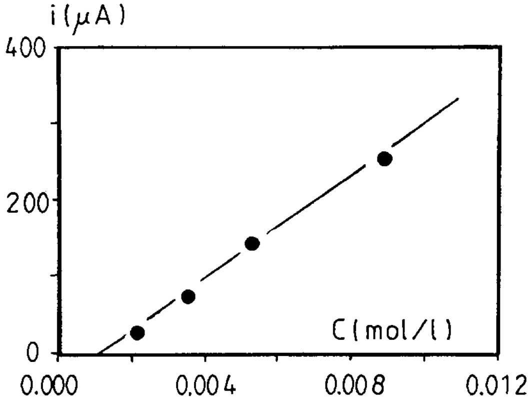


FIG. 3. Values for the reduction current of C_4F_9I (i, μA) measured at a steady glassy carbon disk in presence of oxygen (air) at the atmospheric pressure, whei adding increasing amounts of C_4F_9I (C, mol/l).

C_{O2} = 0.94 10^{-3} mol/l

Scan rate: 0.5 V/s

The slope of the linear variation observed in Figure 3 is identical to that measured in the absence of O_2. Therefore the intercept (horizontal axis) gives the concentration of C_4F_9I consumed in the overall reaction with electrogenerated $O_2^{\circ-}$. This value ($0.96.10^{-3}$ mol/l) is very close to the concentration of O_2 in the medium as determined above. We thus conclude that in cyclic voltammetry , the overall reaction involves one C_4F_9I by O_2, and results in the overall exchange of additional electron (s).

From the above observations, one can propose the following mechanistic Scheme A :

$$O_2 + e^- \longrightarrow O_2^{\bullet -}$$

$$R_FI + O_2^{\bullet -} \xrightarrow{k} R_FO_2^{\bullet} + I^-$$

$$R_FO_2^{\bullet} \xrightarrow{[e]} \ldots\ldots$$

Scheme A

The kinetic behavior of mechanism in Scheme A, is controlled by its rate limiting step, i.e. the overall nucleophilic displacement of an iodide ion from R_FI by a superoxide ion, with a rate constant k. From these considerations it follows that the apparent number of electrons exchanged during the reduction of O_2 in the presence of R_FI, i.e. $j = i^p / i_o^p$ where i^p is the O_2 current peak in the presence of R_FI at a scan rate v and i_o^p that in the absence of R_FI at the same scan rate, depends [6] on a single dimensionless parameter kRTC/Fv where C is the R_FI initial concentration. The experimental results reported on Figure 4 show that this prediction is satisfactorily followed within the accuracy of measurements of i^p and i_o^p. Comparison of the experimental results to the theoretical prediction (solid line) then allows to estimate $k = (1.0 \pm 0.3).10^4$ $mol^{-1}.l.s^{-1}$ for the rate constant of the overall nucleophilic attack in Scheme A.

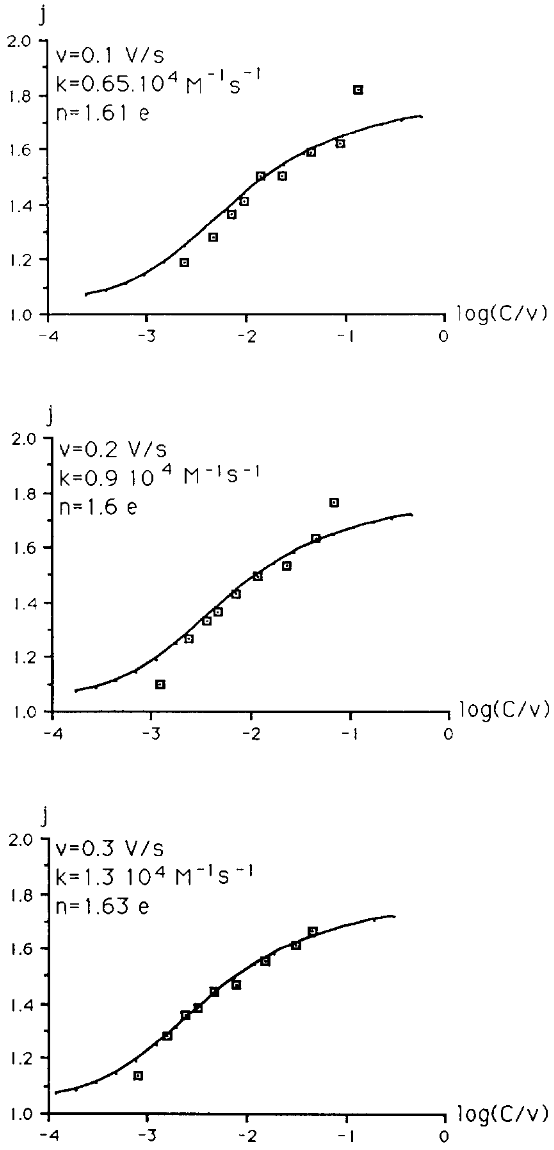


Fig. 4. Comparison between the relative experimental variation of the O_2 reduction peak current $j = i^p / i_o^p$, as a function of C_4F_9I concentration and scan rate, v, and the theoretical variation (solid line) predicted for Scheme A (see text) for k and n as indicated for each curve. (C in mole.l^{-1}, v in V.s^{-1})

However it is seen that the fitting between the experimental data and the theorical curves in Fig. 4 requires that a non integer value ($n \approx 1.6\ e^-$) of the overall number of electron is assumed. This shows that ca. 0.6 e^- are consumed during the further evolution of $R_FO_2°$ in Scheme A. This implies that $R_FO_2°$ follows at least two different routes , each one consuming a different number of electron within the time scale of cyclic voltammetry (see discussion).

It is also noticed that for the largest concentrations of R_FI, and smaller scan rates (i.e. the largest time scales) deviation from the theoretical curves are observed (see curves in Fig. 4). This may be tentitatively ascribed to further electron consumption taking place at longer time (see discussion), in agreement with the result of preparative scale electrolysis , since acid formation requires 4 e^- per mole of R_FI and O_2.

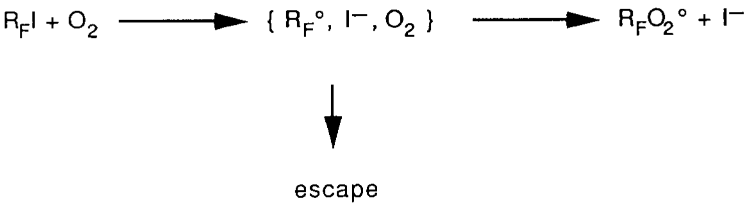
DISCUSSION

The formation of propionic acid corresponds to the following reaction:

$$CF_3\text{-}(CF_2)_2\text{-}CF_2\text{-}I + 4\ e^- + O_2 \longrightarrow CF_3\text{-}(CF_2)_2COO^- + I^- + 2F^-$$

which implies the overall consumption of 4 electrons per R_FI and O_2. In cyclic voltammetry, a lower faradic balance (ca. 1.6 e^-/O_2) is observed, however with a trend to be increased at larger reaction times (see curves in Fig. 4).

Since on the other hand a stoichiometry of one R_FI per $O_2^{\circ-}$ is observed for the same time scale , this indicates that the reaction between $O_2^{\circ-}$ and R_FI is quantitative. This reaction may be considered as a direct nucleophilic attack yielding quantitatively $R_FO_2^{\circ}$ as indicated in Scheme A , or as proceeding via the intermediate in-cage formation of F-alkyl radicals [7] :



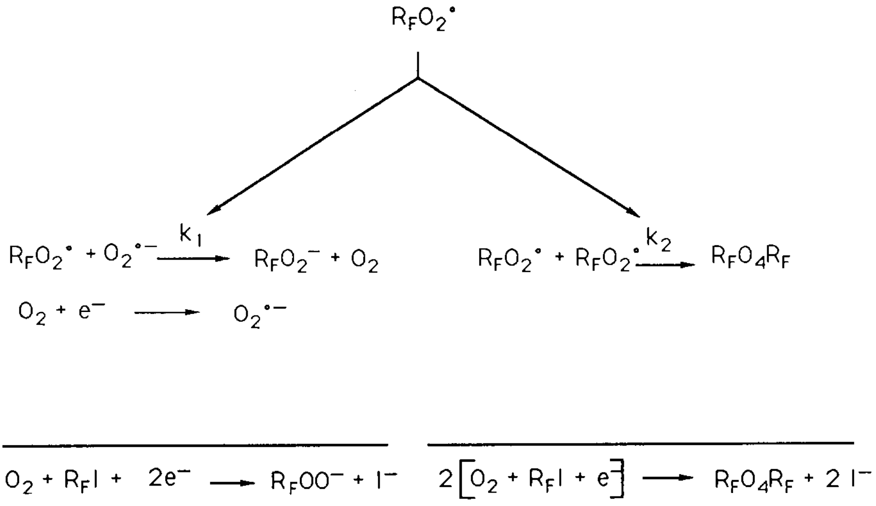
$$R_FI + O_2 \longrightarrow \underset{\substack{\big\downarrow \\ \text{escape}}}{\{ R_F^{\circ}, I^-, O_2 \}} \longrightarrow R_FO_2^{\circ} + I^-$$

Under cyclic voltammetric conditions , cage escape of the radicals should lead to dimer by-products [4,5] as observed in preparative electrolysis :

$$2\ R_F^{\circ} \longrightarrow R_F\text{-}R_F$$

with the result of a one-electron consumption. However if $R_FO_2^{\circ}$ formed by cage-collapse were to evolve during the cyclic voltammetry time scale to afford the acid (4 e^- process), one would expect an overall electron consumption larger than <u>ca.</u> 1.6 e^- as observed. Therefore one is led to the conclusion that $R_FO_2^{\circ}$ can not give rise to acid formation during the time scale of cyclic voltammetry, but only intermediate products on the route to the acid.

Based on the known reactivity of analogous perhydroderivatives [8] or on the reactivity of perfluoroalkylsulfinates [9], one can reasonably propose the two routes in Scheme B :



Scheme B

In Scheme B, the route on the right-hand-side [8] corresponds to an overall consumption of one electron per oxygen and involves a 1/1 stoichiometry between $O_2^{\circ -}$ and R_FI, to afford eventually $R_FO_4R_F$. Further evolution of this species, via elimination of O_2, to yield R_FO° and then R_FOH is expected [8] but may be too slow to be observed within the time duration of the cyclic voltammograms, except perhaps at the slower scan rates (see curves in Fig. 4):

$$R_FO_4R_f \longrightarrow 2\ R_FO^\bullet + O_2$$

$$\text{or}\begin{cases} R_FO^\bullet \xrightarrow{O_2^{\bullet -}} R_FO^- \xrightarrow{SH} R_FOH \\ R_FO^\bullet + SH \longrightarrow R_FOH + S^\bullet \xrightarrow{O_2^{\bullet -}} S^- \end{cases}$$

Since it is well known that primary perfluoroalkylalcohols [10], $R_F'CF_2OH$ spontaneously decompose to the acid, $R_F'CO_2H$, such a mechanism should yield eventually the perfluoroacid within the larger time scale of electrolysis.

The route on the left-hand side corresponds to an overall stoichiometry of two-electron and one R_FI per oxygen within the time scale of cyclic voltammetry to afford $R_FO_2^-$. Under preparative scale conditions, this latter species should evolve slowly to yield the acid via hydrolysis of its fluoride derivative [9] :

$$R_F'\text{-}CF_2O_2^- \longrightarrow R_F'\text{-}CF{=}\overset{+}{O}\text{-}O^- + F^-$$

$$R_F'\text{-}CF{=}\overset{+}{O}\text{-}O^- \longrightarrow R_F'\text{-}CF{=}O + 1/2\ O_2$$

Therefore although both routes in Scheme B are expected to lead to acid formation under preparative scale electrolysis conditions, each corresponds to a 1/1 stoichiometry between O_2 and R_FI, but involves a different electron consumption in cyclic voltammetry : two-electron for the left-hand-side route, and one-electron for the right-hand-side route. Thus, competition between these two routes, together with the possible occurence of R_F-R_F dimer formation* (see above) which also corresponds to a one-electron consumption, may reasonably explain the observation of a non integer electron consumption under cyclic voltammetric conditions. Further work is in progress to clarify these aspects.

---

*Note that dimer formation during preparative scale electrolysis must arise from direct electrolysis of R_FI [4,5] at the electrode owing to the close proximity of the O_2 and R_FI reduction waves (see Figure 1c). Indeed because of partial blocking of the electrode surface area during electrolysis, the effective current density may be higher than expected from its value at the begining of electrolysis.

Finally, in view of the above results it appears necessary to question a previous interpretation proposed by some of us [12] to account for the formation of carboxylic acids during the electrolysis of perfluoroalkyl iodides. Indeed, in a previous work [12], concerning the electrochemical synthesis of perfluorohexyl sulfinic acid and perfluoropentyl carboxylic acid starting from perfluoro n-hexyl iodide, and of α, ω disulfinic or carboxylic-sulfinic diacids from α, ω diiodoperfluorobutane, we suggested that the carboxylic derivatives could be formed by a reaction of O-alkylation of the solvent dimethylformamide by the produced radicals R_F° .

It would follow from this present study that the mechanism of carboxylic acid formation proposed in our previous work should now be amended and attributed to the electrochemical reduction of oxygen present in the solvent; ingress of air into the cell by diffusion would have been possible during those long duration experiments (20h).

EXPERIMENTAL

Voltammetric experiments

Electrodes and electrochemical apparatus

Electrochemical experiments were performed in a three-electrode cell. The working electrode was a 3mm diameter carbon disk (Tacussel). The reference electrode was a SCE separated from the solution by a bridge compartment filled with the same solvent/supporting electrolyte solution as the one used in the cell. The counter electrode was a platinum wire.

The potentiostat and the program potential generator were home made [5].

Procedure

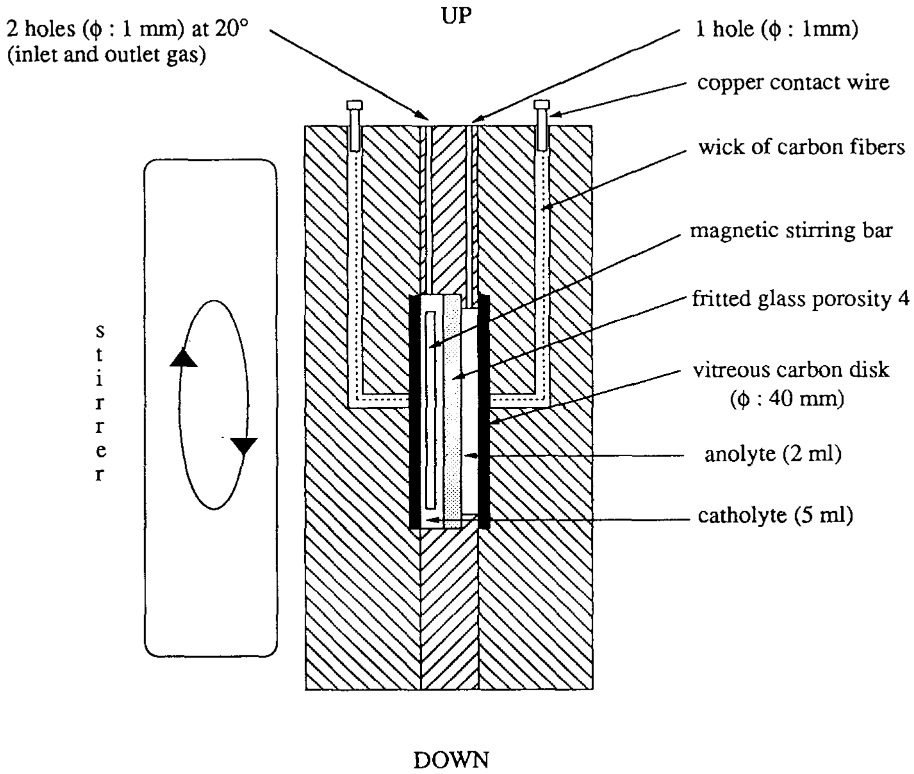
NBu_4BF_4 (0.26g, 0.05M) was added in DMF (16 ml). 3ml of this solution are introduced in the bridge compartment and 13ml in the cell. The solution was stirred 20mn under nitrogen or air or pure O_2, to achieve saturation or degassing according to the experimental conditions.

Preparative electrolysis

Electrodes and electrochemical apparatus

The cell used for preparative experiments was in PTFE. Compartments were of cylindrical geometry equipped with glassy carbon electrodes, 40 mm in diameter, separated with a fritted glass of porosity n°4. Cylindrical cathodic and anodic compartments contained respectively 5 and 2 ml.

Cathodic compartment was stirred by a magnetic stirring bar. Two holes in the upper part of the cathodic compartment allowed the circulation of oxygen or nitrogen. The electrical connection from the copper wire to the vitreous carbon disk is achieved by a bundle of carbon fibers. A potentiostat-Galvanostat (PJT 35V, 2A, Tacussel), coupled with an electronic integrator IG5-N (Tacussel), was used to control the electrolysis current.



Scheme of the cell used.

Procedure for the electrolysis of $C_8F_{17}I$

Supporting salt NBu_4BF_4 (0.33g,0.1M) was introduced in DMF(10ml). Anodic compartment was filled with 4ml of this solution (2ml for fritted glass) and cathodic compartment with 4.2ml of this solution and 0.8ml of $C_8F_{17}I$ (1.64g; 0.6M). When a constant current of 0.045 A was applied to the cell, the voltage between anode and cathode was *ca.* 10 Volts. A coarse frit (n°4) was used, but could not prevent a progressive equilibration of catholyte and anolyte compartments during the electrolysis. No attempt has been made to avoid this phenomenon, and therefore to optimize the conversion yields. By example, the total duration of the experiment reported in Table 2 was 7h10 min.

At the end of the electrolysis, 1ml is taken from the catholyte. Concentration of the remaining $C_8F_{17}I$ and of the produced compounds (R_FH, R_FR_F, $R_F'CO_2^-$) is determined with respect to an added reference adduct $C_6H_5CF_3$, using ^{19}F n.m.r. Similar analysis performed on the anolyte demonstrate that diffusion of starting compounds and products occurs through the fritted glass. Particularly, we have observed that the concentration of the produced acid, under its anionic form, becomes very high in the anolyte, as compared to its value in the catholyte.

Extraction of the electrolysis product

Catholyte is poured in 30ml water. The residual R_FI separates spontaneously. The aqueous solution is then acidified with HCl 15% in order to convert the salt in $R_F'CO_2H$, and extracted with ether. The extract is dried on $MgSO_4$, filtered and concentrated under reduced pressure. The oil obtained is composed by a mixture of DMF and acid $R_F'CO_2H$ according to the litterature [11].

Compounds used

Perfluorobutyliodide was a generous gift from ATOCHEM Cie. DMF stored on CaH_2 is filtered and residual dimethylamine eliminated by a stream of nitrogen. Supporting electrolyte NBu_4BF_4 was prepared as previously reported [5].

Identification

^{19}F NMR spectra were measured on a Varian EM 360 spectrometer at 56.4 MHz. Chemical shifts are reported in ppm (δ) relative to $CFCl_3$.

* CF_3-CF_2-CF_2-CF_2-I δ$(CF_2)_a$ -72 ; b -115 ; c -125 ; d -81
d c b a

* CF_3-CF_2-CF_2-CO_2H δ$(CF_2)_a$ -127 ; b -119 ; c -79
c b a

* CF_3-CF_2-CF_2-CF_2-H δ$(CF_2)_a$ -139 ; b -130 ; c -127 ; d -81.5
d c b a

* $(CF_3$-CF_2-CF_2-CF_2-$)_2$ δ$(CF_2)_a$ -119 ; b -123.4 ; c -80
c b a a

* CF_3-$(CF_2)_6$-CF_2-I δ$(CF_2)_a$ -63.3 ; b -113 , -121 , -126 ; c -81
c b a

* CF_3-$(CF_2)_6$ -CF_2-H δ$(CF_2)_a$ -139 ; b -129 , -123 , -127 ; c -81
c b a

* CF_3-$(CF_2)_5$-CF_2-CO_2H δ$(CF_2)_a$ -117 ; b -121 , -126 ; c -81
c b a

ACKNOWLEDGEMENTS

Partial support from CNRS (URA 1110 and URA 1097) as well as from Ecole Normale Supérieure and USTL is acknowledged.

REFERENCES

1 a. A.A. Frimer, 'The chemistry of Peroxides', S. Pataï, Ed. Wiley, New York, (1983), ch. 14, p 429;

b. E. J. Corey, KC. Nicolaou, M. Shibasaki, Y. Machida and C. Shirer, Tetrahedron Lett., (1975) 3183;

c. E. Oldfield and A. Allerhand, J. Am. Chem. Soc., 97 (1975) 8;

d. A G. Giumanini, S. Roveri, Dario Del Mazza, J. Org. Chem., 40 (1975) 1678 ;

e. D T. Sawyer and M J. Gibian, Tetrahedron, 35 (1979) 1471;

f. M J. Gibian and T. Ungermann, J. Org. Chem., 41 (1976) 2500.

2 a. D T. Sawyer and J L. Roberts, JR, J. Electroanal. Chem., 12 (1976) 90;

b. E L. Jonhson, K H. Pool, and R E. Hamm, Anal. Chem., 38 (1966) 183;

c. D. L. Maricle and W. G. Hodgson, Anal. Chem., 37 (1965) 1563;

d. A D. Goolsby and D T. Sawyer, Anal. Chem., 40 (1968) 83;

e. C P. Andrieux, P. Hapiot and J M. Savéant, J. Am. Chem. Soc., 109 (1987) 3768;

f. M V. Merritt and D T. Sawyer, J. Org. Chem., 35 (1970) 2157;

g. F. Magno, G. Bontempelli and Andreuzzi Sedea, J. Electroanal Chem., 97 (1979) 85.

3 a. M. Gareil, J. Pinson, and J M. Savéant, Nouveau Journal de Chimie, 5 (1981) 311;

b. F. Ojima, T. Matsue, and T. Osa, Chem. Letters, 2235, (1987);

c. R. Dietz, A. E. J. Forno, B. E. Larcombe, and M.E. Peover, J. Chem. Soc., 816 (1970).

4 P. Calas and C. Amatore, L. Gomez and A. Commeyras, J. Fluorine Chem., 49 (1990) 247.

5 C. Amatore, M. Azzabi, P. Calas, A. Jutand, C. Lefrou and Y. Rollin, J. Electroanal. Chem., in press.

6 C.P. Andrieux and J.M. Savéant, in C.F. Bernasconi (ed.) 'Electrochemical Reaction', Investigation of rates and mechanism, Wiley, New York, (1986), Vol 6, 4/E, Part 2, Chapt. 7, 305.

7 D. Lexa, J.M. Savéant, K.B. Su and D.L. Wang, J. Am. Chem. Soc., 110 (1988) 7617.

8 T G. Traylor and J P. Ciccone, J. Am. Chem. Soc., 111 (1989) 8413.

9 Chang-Ming Hu, Ze-Qi Xu and Feng-Ling Qing, Tetrahedron Lett., 30 (1989) 6717.

10 M. Haupstschein, C. S. Stokes and A. V. Grosse, J. Amer. Chem. Soc., 74 (1952) 1974.

11 K. von Werner, A. Gisser, H. Blank, Germ. Pat. DE 2 848 197 (1980).

12 S. Benefice-Malouet, H. Blancou, P. Calas and A. Commeyras, J. Fluorine Chem. 39 (1988) 125.