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Reactivity of the electrogenerated superoxide $O_2^{\bullet -}$ anion with α,ω-diiodoperfluorobutane. Synthesis of 4-iodoperfluorobutanoic acid

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Abstract

The electrolysis of O_2 dissolved in dimethylformamide was performed in the presence of α,ω-diiodoperfluorobutane. Selective formation of 4-iodoperfluorobutanoic acid was observed.

Keywords: Electrolysis; Oxygen; Superoxide; α,ω-Diiodoperfluorobutane; 4-Iodoperfluorobutanoic acid

1. Introduction

The synthesis of perfluoroalkanoic acids has been widely studied [1–9] on the basis of their particular properties as tensioactive agents [10]. In particular, some of us reported an electrochemical synthesis based on the reduction of *F*-alkyl iodides under a CO_2 atmosphere [8]. More recently, we reported that such acids can be prepared through the reaction of the electrogenerated anion $O_2^{\bullet -}$ with *F*-alkyl iodides [9]. In this reaction the *F*-alkyl chain is decreased by one carbon atom. In this work we report that electrolysis of oxygen in dimethylformamide (DMF) and in the presence of α,ω-diiodoperfluorobutane results in the selective formation of 4-iodoperfluorobutanoic acid.

2. Experimental details

2.1. Preparative electrolyses

2.1.1. Apparatus

The electrolysis of O_2 in DMF was conducted under pressure ($P_{O_2} = 5$ or 8 bar), the cell being placed in a steel reactor (SOTELEM, 500 ml). The cell consisted of a glassy carbon beaker (diameter 30 mm, height 30 mm, Carbone Lorraine) used as the cathode. The anode was a graphite rod (diameter 7 mm, Carbone Lorraine). The anodic and cathodic compartments were separated by an alundum cartridge (diameter 15 mm, height 50 mm, Prolabo). The catholyte was stirred via a magnetic barrel. The current applied to the cell was generated by a galvanostat (PJT 35V, 2A Taceussel).

2.1.2. General procedure

A 10 ml aliquot of DMF, 0.1 M in tetrabutylammonium tetrafluoroborate (TBAF), was introduced into the cathodic compartment together with 250 μl of I–C_4F_8–I (1.4 mmol, 0.14 M). The anolyte consisted of 3 ml of DMF/0.1 M TBAF. The reactor containing the electrolysis cell was purged with O_2 and a selected pressure of this gas was then established (5 or 8 bar). A constant current was applied (5 or 15 mA). When the desired number of coulombs had been consumed, the reactor was opened and the catholyte was analysed by ^{19}F NMR spectroscopy after the addition of a known amount of benzotrifluoride for calibration. The anolyte was analysed quantitatively in the same way. The total yield of 4-iodoperfluorobutanoic acid was evaluated by this method. In addition, the acid produced was extracted as follows. The catholyte and anolyte were treated with 20 ml of HCl (20%) in order to convert the carboxylate into I–C_3F_6–COOH. This acid was then extracted with Et_2O (30 ml). The extract was dried over sodium sulphate, filtered and concentrated in vacuo. The oil obtained contained the expected acid, unreacted starting diiodide and residual DMF. It was possible to obtain the monoacid I–C_3F_6–COOH alone, free of the starting diiodide yet with residual DMF present, after extraction with Et_2O/H_2O under basic conditions, separation of the

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aqueous phase and its re-extraction with Et_2O under acid conditions.

^{19}F NMR spectra were recorded with a Varian EM 360 spectrometer working at 56.4 MHz when the following data were obtained. Chemical shifts are referred to $CFCl_3$ in $CDCl_3$ and are given in ppm.

$\overset{a}{I}-\overset{a}{CF_2}-(\overset{b}{CF_2})_2-\overset{a}{CF_2}-I$: $\delta(CF_2)$: a: −58; b: −111 ppm.

$\overset{a}{I}-\overset{a}{CF_2}-\overset{b}{CF_2}-\overset{c}{CF_2}-CO_2^-$: $\delta(CF_2)$:

a: −58; b: −117; c: −113.6 ppm.

$\overset{a}{H}-\overset{a}{CF_2}-\overset{b}{CF_2}-\overset{c}{CF_2}-CO_2^-$: $\delta(CF_2)$:

a: −137; b: −131.6; c: −120 ppm.

2.2. Experiments using cyclic voltammetry (CV)

The analytical cell was a classical three-electrode one. Working electrode: glassy carbon disk 2 mm in diameter; auxiliary electrode: platinum wire; reference electrode: calomel electrode saturated in KCl and separated by a salt bridge. The solvent of analytical grade (10 ml) contained the supporting salt, 0.05 M TBAF (0.246 g). The cell was purged for 15 min with nitrogen or air when the presence of oxygen was required. Measurements were performed with a SIRIUS computerised unit (from E.S.I.I.).

2.3. Chemical synthesis and electrochemical behaviour of the monoacid I–$(CF_2)_3$–COOH

Potassium superoxide (KO_2; 0.750 g, 0.01 mol) was placed in an Erlenmeyer flask (50 ml) and anhydrous benzene (15 ml) added immediately. Dicyclohexano-18-crown-6 ether (3.72 g, 0.01 mol) and 1,4-diiodoperfluorobutane (2.27 g, 0.005 mol) were added to this suspension and stirred vigorously. The reaction was followed by ^{19}F NMR spectroscopy. Addition of complementary KO_2 appeared necessary in order to convert all the starting diiodide. The solution was washed with 15 ml of 20% HCl and extracted with diethyl ether (25 ml). The organic phase was dried over sodium sulphate and concentrated under vacuo. ^{19}F NMR analysis of the oil recovered revealed the presence of the monoacid I–$(CF_2)_3$–COOH and also of the starting diiodide (40%). During the course of the reaction, this later compound was probably adsorbed on to the solid KO_2 and thus was not detectable in the medium.

A cyclic voltammetric study in DMF/TBAF of the oil obtained revealed two peaks. The first corresponded to the reduction of the starting diiodide (−1.44 V/SCE, see below). The second one at −1.62 V/SCE was thus ascribed to the reduction of the carbon–halogen bond in the monoacid I–$(CF_2)_3$–COOH. It must be emphasised that in the monoacid the C–I bond is slightly more difficult to reduce (by 0.180 V) relative to the C–I bond in the starting diiodide.

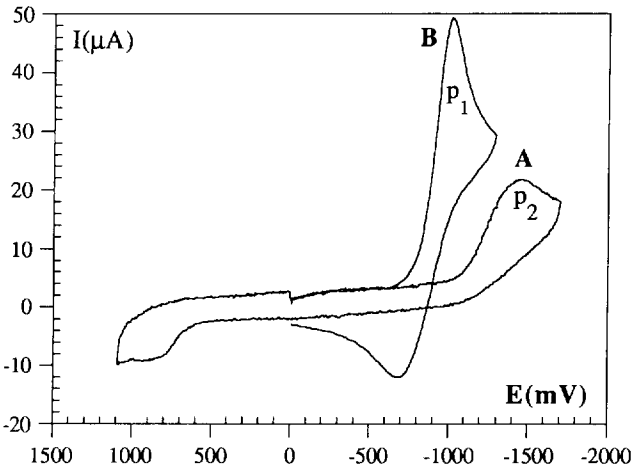


Fig. 1. Curve A: cyclic voltammogram of I–$(CF_2)_4$–I at a steady glassy carbon disk (2 mm diameter) in DMF/0.05 M TBAF; scan rate = 200 mV s^{-1}, concentration $\approx 3.6\times10^{-4}$ M. Program of potential: 0; −1.7; +1.1; 0 V vs. SCE. Cathodic peak p_2 at ca. −1.45 V vs. SCE. Anodic oxidation of iodide ions formed during the cathodic scan may be observed at ca. +0.9 V. Curve B: cyclic voltammogram of oxygen at a steady glassy carbon disk in DMF/0.05 M TBAF. $C_{O_2}\approx 0.94\times10^{-3}$ M (partial pressure of oxygen 0.2 bar [9]). Program of potential: 0; −1.3; 0 V vs. SCE. Cathodic peak p_1 at ca. −1 V vs. SCE (reversible system).

2.4. Solubility of oxygen in DMF

To the best of our knowledge, the solubility of O_2 in DMF/0.05 M TBAF was unknown. In a preceding paper [9], we reported a determination of this value. The method used [11] was based on a comparison of the oxidation current for ferrocene and that for the reduction of oxygen observed when using two kinds of electrodes, i.e. a stationary disk and an ultramicrocylinder or a rotating disk, are employed. We obtained $C_{O_2}=0.94\times10^{-3}$ mol l^{-1}. This value corresponds to a partial pressure of 0.2 bar (air). For higher oxygen partial pressures, we resorted to the relationship $C_{O_2}(P)=(P/0.2)0.94\times10^{-3}$ mol l^{-1}, where P is the partial pressure of oxygen again expressed in bar. Such values correspond to the temperature used for all the experiments, i.e. 20 °C.

3. Results and discussion

3.1. Electrochemical reduction of I–$(CF_2)_4$–I

The CV experiment revealed a single reduction peak at −1.44 V/SCE (Fig. 1, peak p_2). The position of the peak is equivalent to that observed for the reduction of the monohalide $CF_3(CF_2)_3$ [9] but its shape is considerably broadened, thus suggesting that the reduction of the two carbon iodine bonds in one molecule may occur at slightly different potentials.

The reduction of O_2 is also depicted in Fig. 1. This appears (peak p_1) to be significantly less cathodic than that of the

Table 1
Product distribution during preparative electrolysis relative to initial diiodide [a]

Run No.	i (mA)	Charge consumed [F (mol initial diiodide)$^{-1}$]	Oxygen pressure (bar)	Products (mol%)				
				IC_4H_8I	$IC_3F_6CO_2^-$	$^-O_2CC_2F_4CO_2^-$	$HC_3F_6CO_2^-$	unrecovered
1	5	2	5	36	43	<1	0	21
2	5	4	5	31	53	–	0	16
3	5	4	8	40	50	–	0	10
4	5	8	8	30	52	–	0	18
5	15	4	5	50	30	–	10	10

[a] Experiments conducted under oxygen pressure with a constant current applied. Cathodic surface area (vitreous carbon), 21 cm^2. Anolyte: 3 ml DMF/0.1 M TBAF. Catholyte: 10 ml DMF/0.1 M TBAF; 250 μl IC_4F_8I (1.4 mmol).

diiodide. It is reversible and known to afford the superoxide anion $O_2^{\bullet -}$ [9]. Consequently, it appears to be possible to produce the superoxide anion $O_2^{\bullet -}$ in the medium without any reduction of the diiodide.

3.2. Preparative electrolyses

Electrolysis of the system O_2/I–$(CF_2)_4$–I in DMF was conducted under an oxygen pressure (see Experimental details) and the results obtained are reported in Table 1.

Formation of the monoacid was mainly observed, corresponding to the overall equation:

$$I\text{–}(CF_2)_4\text{–}I + 4e^- + O_2 \longrightarrow I\text{–}(CF_2)_3\text{–}COO^- + 2F^- + I^-$$

When the current value used was 15 mA instead of 5 mA, significant formation of H–$(CF_2)_3$–COO^- was observed (Table 1, column 8), possibly corresponding to the cathodic reduction of I–$(CF_2)_3$–COO^-. When a current of 5 mA was used, this latter compound was formed exclusively. Run 1 in Table 1 employed only 2 F per mole of initial diiodide. In this partial electrolysis, the number of Faradays consumed per mole of I–$(CF_2)_3$–COO^- effectively formed was near the expected value (4 F). In contrast, when the electrolysis was continued and ultimately attained 4 F per mole of initial diiodide, the yield of monoacid was not significantly enhanced (Run 2). The percentage of unreacted initial diiodide remained at ca. 30%, suggesting that the electrolysis is limited by the occurrence of a reduction/oxidation cycle, presumably I_2/I^-, between the anode and the cathode. This phenomenon becomes more and more important as the iodine concentration increases in the anodic compartment. In order to circumvent this technical limitation it would be necessary to use more efficient separators (e.g. Nafion membranes) than those available for this work. The same value (5 mA) for the applied current, but with a higher oxygen pressure (8 bar in the place of 5 bar), and with the consumption of 4 F or 8 F (Runs 3 and 4) gave similar results. This indicates that the limiting diffusion current for the reduction of O_2 was not reached.

It can be concluded that the electrogenerated superoxide $O_2^{\bullet -}$ reacts with the diiodide to form the monocarboxylate ion I–$(CF_2)_3$–COO^-. Further electrolysis of this compound does not occur during the reported experiments, except when a higher current density was used; partial formation of H–$(CF_2)_3$–COO^- was then observed. What appears remarkable is that the diacid $^-OCC\text{–}CF_2CF_2\text{–}COO^-$ is not formed in significant quantities. In all the experiments, a very small signal (<1%) was observed (^{19}F NMR δ: −111.6 ppm); this can be ascribed to this diacid, but definite attribution was impossible due to the small yield of material. This suggests that any attack of the anion $O_2^{\bullet -}$ on the monocarboxylate ion I–$(CF_2)_3$–COO^- is not favoured.

3.3. Reactivity of $O_2^{\bullet -}$ with I–$(CF_2)_4$–I: cyclic voltammetric investigation

The electrochemical behaviour of the system O_2/I–$(CF_2)_4$–I at a carbon cathode in DMF was also studied using cyclic voltammetry (CV). The concentrations used for this kind of experiment were generally limited to the range 10^{-3} to 10^{-4} M. Such values (0.94 mM; cf. Experimental details) were obtained in aerated DMF (1 atm). During the preparative experiments, we used pure oxygen under pressure (5 or 8 bar), corresponding to estimated oxygen concentrations of ca. 25 and 40 mM, respectively. It was thus possible to undertake significant preparative electrolyses without exceeding the limiting diffusion current for O_2 reduction. Despite the difference between the two conditions, mechanistic information obtained from CV studies is of interest and its relevance to preparative electrolyses will become apparent below.

The oxygen voltammogram in DMF exhibited reversible behaviour (Fig. 1, peak p_1, and Fig. 2, curve 1). Addition of increasing amounts of I–$(CF_2)_4$–I results in an enhancement of the cathodic peak (p_1), with a concommitant decrease in the anodic one (Fig. 2). In these experiments the cathodic scan was limited to −1.3 V/SCE in order to only study the evolution of the oxygen reduction peak and the corresponding anodic peak on the reverse scan. The results demonstrate that the $O_2^{\bullet -}$ produced at p_1 reacts with the diiodide I–$(CF_2)_4$–I to yield iodide ions whose oxidation current is observed on the return scan at ca. +0.9 V. This behaviour appears similar to that observed previously [9] relating to the monohalide n-C_4F_9I. Moreover, it is seen that the increase in p_1 is quantitatively much more limited in the case of the diiodide (Fig. 3), the upper limit being here in the range of 1.3 rather than

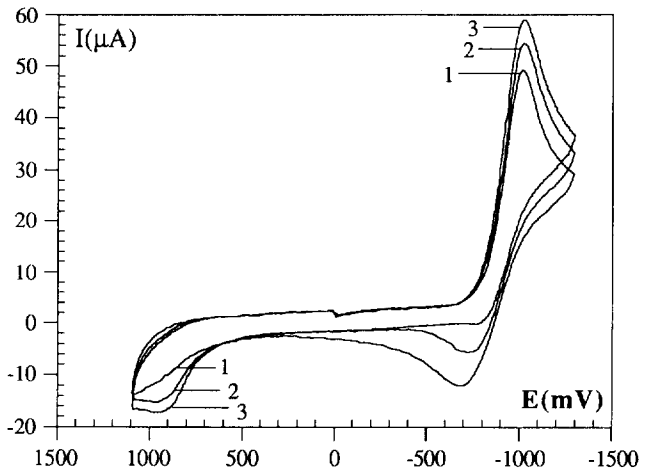


Fig. 2. Cyclic voltammogram of oxygen at a steady glassy carbon disk (2 mm diameter) in DMF/0.05 M TBAF in the presence of increasing amounts of diiodide (curve 1, 0 μl; curve 2, 5 μl; curve 3, 15 μl of a solution of 0.181 M I–$(CF_2)_4$–I in DMF) added in the solvent (10 ml); scan rate = 200 mV s^{-1}, $C_{O_2} \approx 0.94 \times 10^{-3}$ M (partial pressure of oxygen 0.2 bar [9]). Program of potential: 0; −1.3; +1.1; 0 V vs. SCE. Anodic oxidation of iodide ions formed on the cathodic scan is observed at ca. +0.9 V.

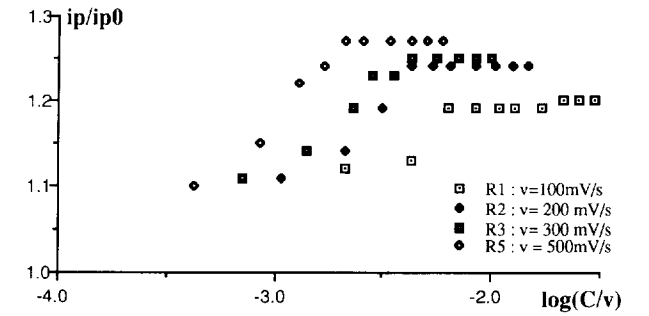
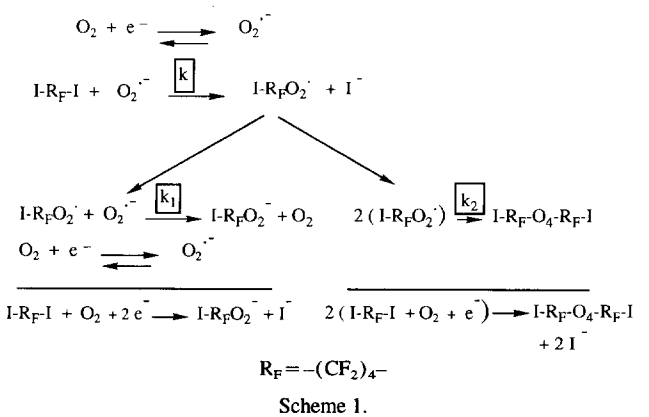


Fig. 3. Values observed for the ratio i_p/i_{p0} (i_p = peak current for the reduction of O_2 in the presence of I–$(CF_2)_4$–I at different concentrations (C); i_{p0} = same parameter in the absence of diiodide) v = scan rate; $C_{O_2} \approx 0.94 \times 10^{-3}$ M ($P_{O_2} = 0.2$ bar).



Scheme 1.

1.7 as for the monohalide. This increase appears to depend on the scan rate (Fig. 3) in contrast to what was observed with the monohalide. This pre-empted the use of the method presented in Ref. [9] for the determination of the rate constant of the nucleophilic substitution of I–$(CF_2)_4$–I by the superoxide ion. In spite of this, the half-lifes for the two reactions can be still compared, yielding an approximate decrease in reactivity by a factor 2–4 in passing from the monohalide to the dihalide. Similarly, the mechanism appears to be more complicated than in the case of the monohalide (Scheme 1). Indeed such a mechanism predicts a dependence of i_p/i_{p0} on C/v although independent variations with C and v were observed experimentally. Such unpredicted dependence may result from the fact that the degree of involvement of the two competitives routes [indicated by k_1 ($2e^-$ route) or k_2 ($1e^-$ route) in Scheme 1] may depend strongly on the timescale. Although this could not be established quantitatively, this is in agreement with the fact that the limit of i_p/i_{p0} (viz. the maximum electron consumption) when C increases depends strongly on the scan rate, i.e. on the timescale of the experiment. If so, this may suggest that the rate constants k_1 and k_2 may be considerably smaller for the I–R_F–$O_2^\bullet$ radical than for the $R_FO_2^\bullet$ species [9].

As in previous work with the monohalide n-C_4F_9I, it is necessary to consider that the radical species formed initially, i.e. I–$(CF_2)_4$–$OO^\bullet$, is involved in two different routes as shown in Scheme 1, i.e. attack by $O_2^{\bullet -}$ (k_1) corresponding to an overall consumption of 2 F per mol of initial diiodide or dimerization (k_2) involving only 1 F per mol. Further evolution of I–$(CF_2)_4OO^-$ and of I–$(CF_2)_4$–OOOO–$(CF_2)_4$–I towards the iodomonocarboxylate ion finally yields I–$(CF_2)_3COO^-$ as discussed previously [9].

On the basis of the increase observed for the reduction peak of oxygen on adding the diiodide (Figs. 2 and 3), we conclude that k_1/k_2 is ca. 0.2. In the case of the monohalide $CF_3(CF_2)_3I$, the same parameter was ca. 0.55 (the normal enhancement for the reversible reduction peak of O_2 is 1.1 (1e) and 2.2 if the overall mechanism becomes bielectronic.

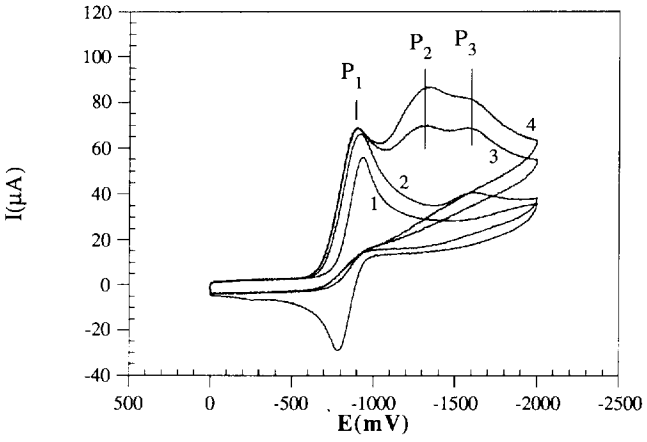


Fig. 4. Cyclic voltammogram of oxygen at a steady glassy carbon disk (2 mm diameter) in DMF/0.05 M TBAF in the presence of increasing amounts of diiodide (curve 1, 0 μl; curve 2, 15 μl; curve 3, 40 μl; curve 4, 50 μl of a solution of 0.424 M I–$(CF_2)_4$–I in DMF) added in the solvent (10 ml); scan rate = 200 mV s^{-1}, C_{O_2} as in Fig. 2. Program of potential: 0; −2; 0 V vs. SCE.

The observed enhancement was 1.7 for the monohalide and 1.3 for the dihalide).

Additional information on the mechanism can however be obtained by examining the variations of the voltammogram at more negative potentials (Fig. 4). When increasing amounts of I–$(CF_2)_4$–I were added, it was observed initially that, as described above, the oxygen reduction peak was increased and became irreversible (peak p_1). When this peak reached a maximum value, a new peak (p_3) was observed at ca. −1.6 V/SCE (Fig. 4, curve 2). This peak may be attributed to the reduction of the monohalide I–$(CF_2)_3$–COO^- (see Experimental details for the chemical synthesis and voltammetric study of this compound). Addition of larger amounts of the diiodide (curves 3 and 4 in Fig. 4) result in the emergence of a new peak at ca. −1.4 V/SCE. This peak (p_2) corresponds to the reduction of the unreacted diiodide I–$(CF_2)_4$–I (cf. Fig. 1, curve A).

Fig. 5 depicts the variations of the peak current value for p_2 and p_3 as a function of the concentration of I–$(CF_2)_4$–I and the same parameter for the reduction of I–$(CF_2)_4$–I and of n-C_4F_9I at the same concentration, studied alone in the same medium under nitrogen. To facilitate comparison, these peaks are normalised to that of n-C_4F_9I under nitrogen.

Since the monoelectronic character of the reduction of n-C_4F_9I has been previously established [9,11], the reduction of I–$(CF_2)_4$–I appears to be bielectronic [Fig. 5, curves for I–$(CF_2)_4$–I (+) and n-C_4F_9I (▲)] indicating that the two C–I bonds in the diiodide are capable of being reduced at the peak potential. The stoichiometry for the reaction of O_2 with I–$(CF_2)_4$–I is unity (intersection of curve for points □ with the horizontal axis in Fig. 5). The evolution of peak p_3 is more complex (Fig. 5, curve for points ●). This peak represents the amount of monohalide I–$(CF_2)_3$–COO^- formed in the diffusion layer by the reaction of $O_2^{\bullet -}$ electrogenerated at p_1 with I–$(CF_2)_4$–I. For sufficiently low concentrations of added diiodide ($C_{diiodide}/C_{O_2} < 1$) the slope of the curve is unity, as expected for the quantitative production of I–$(CF_2)_3$–COO^- since reduction of the C–I bond in this compound is monoelectronic as for that in n-C_4F_9I (but occurring at a potential which is more cathodic by 200 mV).

Moreover it should be noted that extrapolation of this line to low values of the $C_{diiodide}/C_{O_2}$ ratio intersects the horizontal axis not at the origin but at ca. 0.25. This indicates that when the $O_2^{\bullet -}$ concentration is high as compared to that of the diiodide, a different mechanism occurs. Since I–$(CF_2)_4$–I is consumed quantitatively over this concentration range, this suggests that the two C–I bonds of this compound are attacked leading to the formation of diacid with no monoacid being detected ($p_3 = 0$). This hypothesis is in agreement with the detection of a material ascribed as the diacid in the preparative experiments, as reported above. This behaviour may also be the origin of the unexpected variations of i_p/i_{p0} with the scan rate as shown in Fig. 3. Indeed, such a competitive route will necessarily influence the overall electron consumption and hence the i_p/i_{p0} values. When the diiodide is in excess ($C_{diiodide}/C_{O_2} > 1$), the intensity of peak p_3 is decreased

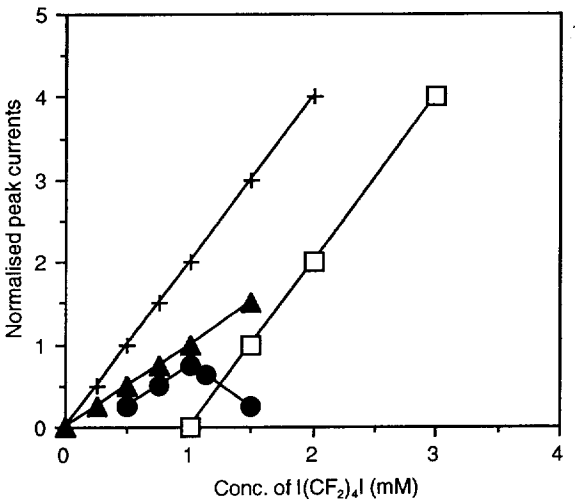


Fig. 5. Peak current intensities for peaks p_3 [●, reduction of I–$(CF_2)_3$–CO_2H] and p_2 [□, reduction of I–$(CF_2)_4$–I] as a function of the initial concentration (C in mM) of I–$(CF_2)_4$–I in air (1 atm) saturated DMF/0.05 M TBAF ($C_{O_2} = 0.94$ mM) Peak currents were measured in experiments similar to those presented in Fig. 4 and are displayed as the ratio to that determined for $CF_3(CF_2)_3I$ (1 mM) alone in nitrogen-degassed DMF/0.05 M TBAF. The same current parameters are also shown for $CF_3(CF_2)_3I$ (▲, C in mM; slope = 1) or I–$(CF_2)_4$–I (+, C in mM; slope = 2) alone in nitrogen-degassed DMF/0.05 M TBAF for comparison.

although a plateau is more likely to be formed. This particular behaviour can be attributed to the reaction of the iodomonoacid, or its precursors, with species resulting from the direct reduction of the diiodide at p_2. Indeed this occurs as soon as the diiodide wave appears and the stoichiometry deduced from the relative slopes of I–$(CF_2)_3$–COO^- (●) (1e wave) and I–$(CF_2)_4$–I (□) (2e wave) is 1:1 since the ratio of the slopes is 2. The products derived from such a reaction do not appear in the preparative experiments despite the large excess of diiodide employed because the limiting reduction current for O_2 was not reached, and hence the diiodide was not directly reduced. This allows the exclusive formation of the highly interesting iodocarboxylate anion I–$(CF_2)_3$–COO^-.

4. Conclusions

On the basis of preparative electrolyses, it is concluded that reaction of the electrogenerated superoxide anion with the α,ω-diiodoperfluorobutane yields the 4-iodoperfluorobutanoic acid almost exclusively. Formation of a diacid ^-OOC–$(CF_2)_2$–COO^- also probably occurred but only in very low yield. Studies using cyclic voltammetry also indicated that the monocarboxylate ion I–$(CF_2)_3$–COO^- is formed when the concentration of the diiodide is at least comparable to that for oxygen and the applied current density is sufficiently low to prevent a direct reduction of the initial diiodide.

Despite the fact that the electrolyses were conducted under oxygen pressures up to 8 bar, the oxygen concentration is a

limiting parameter because its low solubility in DMF makes the applied current small. In order to produce the diacid it will be necessary to work with low concentrations of the starting diiodide, for example through continuous addition. The electrolysis of oxygen in the presence of the α,ω-diiodoperfluorobutane, $I-(CF_2)_4-I$, appears to be a practical route for producing the monocarboxylate ion $I-(CF_2)_3-COO^-$, a powerful intermediate for further syntheses. It has been possible to define precisely the necessary electrochemical operating conditions for its efficient formation under oxygen pressure.

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