Reduction of Polyfluorinated Compounds

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Reduction of perfluoroalkylphenylcyanides and perfluorodecalin was investigated by cyclic voltammetry and interpreted by intramolecular dissociative electron-transfer models, taking into account the dependence of the diffusion coefficient on the molecular volume of the substrate. In both cases, reduction is governed by the first electron transfer and the following chemical reaction corresponding to F⁻ expulsion. In the case of perfluoroalkylphenylcyanides, at the first reduction stage, one electron is exchanged for each fluorinated carbon atom. For perfluorodecalin, the first stage involves a transfer of four electrons, leading to the formation of a diene, in agreement with literature data on the electrochemical behavior of fluorinated olefins. Comparison of the different parameters obtained (standard reduction potentials and cleavage rate constants) with existing thermodynamic values allows us to observe the effect of lowering the C–F bond dissociation energy on the cleavage rate constant when going from primary to tertiary fluorinated carbon atoms. Moreover, deviations from the existing model become more important when the number of electron-withdrawing groups increases, indicating interactions between the radical and fluoride ion fragments. In the special case of perfluorodecalin, the slowness of the electron transfer could be attributed to the nature of the σ^* orbital that receives the extra electron.

Introduction

Beside their large technological applications, fluorocarbons have the disadvantage of being global-warming gases with atmospheric lifetimes that can exceed 2000 years.[1] For this reason electrochemical activation of carbon–fluorine bonds in fluoro-organic compounds still attracts interest.[2] The understanding of the electrochemical cleavage of the C–F bond is also interesting with respect to the possible derivatization of fluorinated polymers.[3,4]

To our knowledge, the reduction of perfluoroalkanes in organic solvents has been described in the literature qualitatively only. A major difficulty for a quantitative study of their electrochemical reduction is their poor solubility in aprotic nonfluorophilic solvents. Pud et al. have circumvented this problem by using a perfluoroalkane impregnated cotton thread attached to a glassy carbon electrode; they could identify its reduction potential and its possible reduction intermediates formed upon F⁻ ion loss.[5] However, since the intermediates are reduced more easily than the starting material, they could not be isolated and the reduction products could not be identified, as already observed for other acyclic perfluoroalkanes.[6,7] For cyclic perfluoroalkanes possessing a tertiary carbon atom, reduction by the benzophenone radical anion in THF leads to the total aromatization of the substrate.[7] The authors pointed out the importance of the presence of a tertiary carbon–fluorine bond and postulated a mechanism involving a succession of monoelectronic electron transfers and F⁻ expulsions. This mechanism has also been postulated to explain the reactivity of perfluorodecalin toward arenethiolates[8] and also photosensitized amines.[9] In the latter work, the intermediate perfluoroalkene obtained after two successive electron transfers and fluoride expulsions could be observed by ¹⁹F NMR, confirming the analogy with the reduction mechanism of *vic*-dihalogenated compounds.[10,11]

CHART 1. Compounds
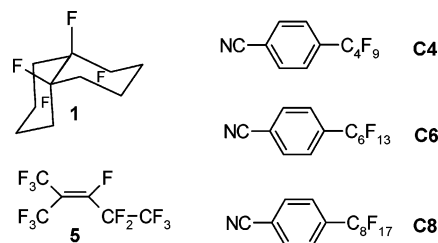
More generally, an electron-transfer pathway has been suggested to rationalize defluorination of perfluoroalkanes in the gas phase or the liquid phase by reduction at a metal (Ni or Fe),[12] by an organic reducer,[7,13,14] by an early transition metallocene catalyst,[15] or by photochemical assistance.[16]
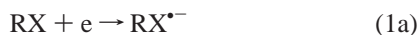
In a previous study we had investigated the reductive cleavage of C–F bonds in fluoromethylarenes.[17] In this paper, we have first studied the reductive behavior of perfluoroalkylphenylcyanides (**C4**, **C6**, **C8**, Chart 1) of longer perfluoroalkyl chains and compared it to that of fluoromethylarenes.

Such a study was useful to determine a procedure for investigating perfluoroalkane reduction, since perfluoroalkylphenylcyanides possess a smaller number of different leaving groups than the intermediate compounds that appear during the reduction of a perfluoroalkane and they exhibit a better solubility in DMF than perfluoroalkanes. Then we have investigated the reduction of *cis*-perfluorodecalin (**1**, Chart 1) as a model compound for perfluoroalkanes. The study of the reductive behavior of compound **5** (Chart 1) was also undertaken to mimic a perfluoroalkene intermediate in the reduction of perfluorodecalin.

In all cases, our main goal was to determine the electrochemical characteristics of the first steps of reduction of these

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polyfluorinated compounds. Since such substrates possess more than one leaving group, the estimation of the number of electrons involved in the first reductive steps was the first difficulty encountered. This question is of importance because reduction of perfluoroalkenes was shown in the literature to occur at rather positive potentials.[18,19]

In this aspect, an interesting issue was to determine whether the first electron transfer and the first fluoride expulsion proceed in a stepwise (path 1a + 1b) or a concerted (path 2) mechanism

$$RX + e \rightarrow RX^{\bullet -} \qquad (1a)$$

$$RX^{\bullet -} \rightarrow R^{\bullet} + X^{-} \qquad (1b)$$

$$RX + e \rightarrow R^{\bullet} + X^{-} \qquad (2)$$

as postulated for other carbon–halogen bonds, whether, in a rough approximation, the halogen atom is borne by an aromatic or an aliphatic moiety.[20] The behavior of cyclic perfluoroalkanes could be different, since, due to the high C–F bond energy, stable radical anions can be formed in the gas phase, by electron attachment[21-24] and γ-ray irradiation,[25] or in apolar solutions[26] or in weakly polar solid glasses at low temperature.[27]

We will discuss the concerted or stepwise nature of the electron transfer and the carbon–fluorine bond breaking during the reduction of the different fluorinated molecules investigated owing to the existing electron-transfer models.[20,28]

Experimental Section

Chemicals. DMF and the different redox mediators were of commercial origin and used as received. *cis*-Perfluorodecalin was obtained from Aldrich. DMSO was distilled before use. DMF (Fluka puriss absolute) was used as received. NBu₄BF₄ (Fluka) was reprecipitated from ethyl acetate and petroleum ether and then was dried under vacuum overnight before use.

Perfluoroalkylphenylcyanides of various lengths were synthesized according to the procedure reported in the literature[29] by reacting until completion (end of reaction was checked by GC-MS) an equimolar mixture of perfluoroalkyliodide and 4-iodobenzonitrile (2 mmol) in hot DMSO in the presence of a 5 molar excess of copper powder (50 μm diameter). After treatment with water and extraction with pentane, the expected products were isolated by flash silica column chromatography. The products, a yellowish oil for **C4** or a white solid for **C6** and **C8**, were obtained with isolated yields of 38 (due to the partial evaporation of the perfluoroalkylhalide), 52, and 51%, respectively, and a purity higher than 95% checked by GC-MS.

Spectral characterizations. ¹H NMR in CDCl₃ (δ, ppm): H$_a$ (Ar, *o*-CF₂) 7.68; H$_b$ (Ar, *o*-CN) 7.75.¹⁹F NMR in CDCl₃ (ppm) for fluorinated carbons from a (adjacent to Ar) to d4, f6, or h8 (CF₃ end of the **C4**, **C6**, and **C8** chain). **C4**: δ_{a4} −112.3; δ_{b4} −123.0; δ_{c4} −126.0; δ_{d4} −81.45. **C6**: δ_{a6} −112.1; δ_{b6} −121.8; δ_{c6} −122.1; δ_{d6} −123.2; δ_{e6} −126.6; δ_{f6} −81.25. **C8**: δ_{a8} −112.0$_5$; δ_{b8} −121.6; δ_{c8} −122.1; δ_{d8-e8} −122.3; δ_{f8} −123.2; δ_{g8} −126.6; δ_{h8} −81.2. MS (*m/z*). **C4**: 321 (M), 302 (M−F), 152 (M−C₃F₇), 102 (M−C₄F₉), 69 (CF₃). **C6**: 421 (M), 402 (M−F), 152 (M−C₅F₁₁), 102 (M−C₆F₁₃), 69 (CF₃). **C8**: 521 (M), 502 (M−F), 152 (M−C₇F₁₅), 102 (M−C₈F₁₇), 69 (CF₃).

Cyclic Voltammetry. The working electrode was a 1 or 3 mm diameter glassy carbon disk. It was carefully polished and rinsed in ethanol before each voltammogram in the direct study. The counter electrode was a platinum wire, and the reference electrode, an aqueous SCE electrode or a AgCl coated silver

wire. Cyclic voltammograms were recorded using a CHI660A potentiostat (CH Instruments, IJ Cambria Scientific, Burry Port, U.K.). Redox catalysis experiments were carried out for each mediator with at least four scan rates, two values of the excess factor (excess factor is the ratio of substrate over mediator concentration), and three mediator concentrations. The given homogeneous rate constants were averages of at least 24 values per redox mediator.

Preparative-Scale Electrolyses. Direct or mediated electrolyses of 10−20 mM solutions of **C6** or **C8** were undertaken under constant current or constant potential in the presence or in the absence of a weak acid (5 equiv of fluorene) in DMF. They were carried out in an undivided cell containing 5 mL of solution. The working electrode was a cylindrical glassy carbon crucible of 20 mm diameter and 20 mm height, and the counter electrode was a soluble anode consisting of a cylindrical magnesium rod of 8 mm diameter. The electrolyses were conducted at constant potential (referred to aqueous SCE, CHI660A potentiostat) or constant current (constant current generator) and controlled by coulometry and cyclic voltammetry at a glassy carbon disk electrode. Aliquots of solution were extracted regularly, passed through silica column chromatography without acidifation, and analyzed by GC-MS in order to check the course of the reaction. Electrolysis of **C6** in the presence of a weak acid (fluorene) showed the formation, after 0.5 C/mol, of traces of a product with a MS signature that we believed assignable to NC−C₆H₄−CF=CF−CF=CF−CF=CF₂ (*M* = 307 g·mol⁻¹). MS (*m/z*): 307 (M), 288 (M − F), 238 (M − CF₃), 218 (M − CF₄H), 207 (M − C₂F₄), 100 (C₂F₄), 81 (C₂F₃). This product was absent at higher electron injection or in the absence of weak acid.

F⁻ ions were titrated by potentiometry at a F⁻ selective electrode (Tacussel PF 4-L) after dilution of 0.1 mL of the electrolysis solution into 10 mL of 1 M acetate buffer (pH = 5.3) + 0.01 M EDTA + 1 M NaCl.

Results and Discussion

Reduction of Perfluoroalkylphenylcyanides. *Direct Study.* The reduction of 3 mM solutions of the perfluoroalkylphenylcyanides **C4**, **C6**, and **C8** at a glassy carbon electrode is presented in Figure 1. These compounds were reduced according to two to four reduction waves. The first reduction step was irreversible and similar in shape and location for the three compounds. Use of scan rates up to 1000 V/s did reveal neither reversibility nor a shoulder of the first wave, and it was unchanged in shape and location upon addition of a weak acid or OH⁻. The first peak potential, E_p, decreased linearly with the logarithm of the scan rate, v (Figure 2a and Table 1 for the slopes of the representative curves). These curves can be regarded as driving force (E_p)−activation (log v) relationships,[20] and an apparent electron-transfer coefficient, $\alpha_{app} = \partial \Delta G^{\neq}/\partial \Delta G°$, could be deduced from the slopes or from the values of the peak width ($E_{p/2} - E_p$) according to[30]

$$\alpha_{app} = \frac{RT \ln 10}{2F} \left(\frac{\partial E_p}{\partial \log v} \right)^{-1} \qquad (3)$$

and

$$\alpha_{app} = \frac{1.85RT}{F(E_{p/2} - E_p)} \qquad (4)$$

The apparent transfer coefficient accounts for the importance of the driving force (the potential) on the kinetics of the
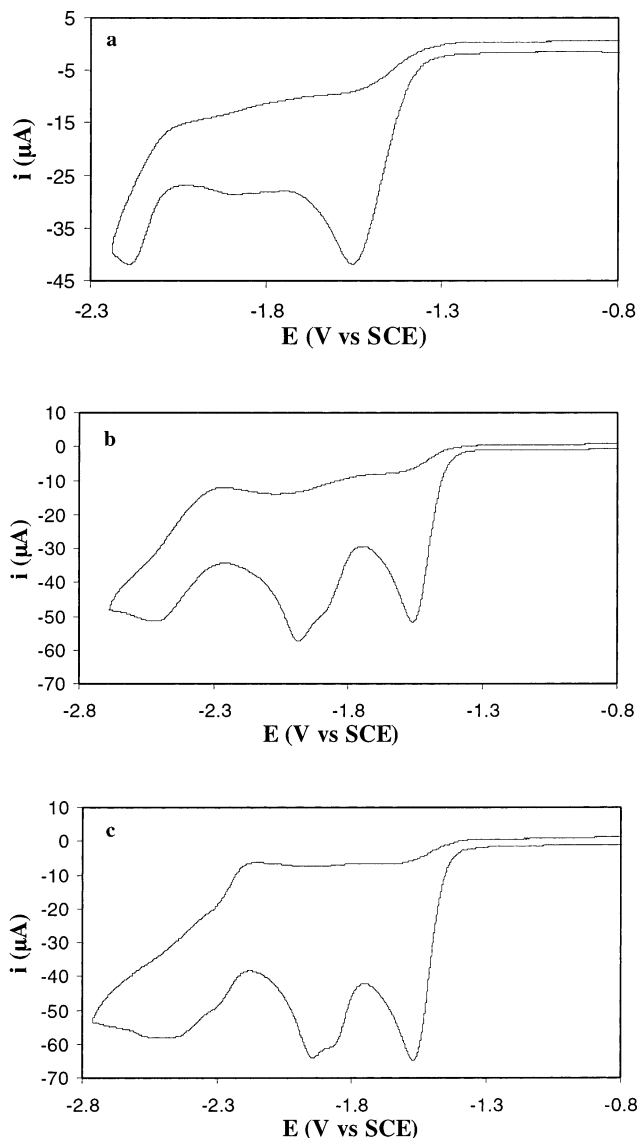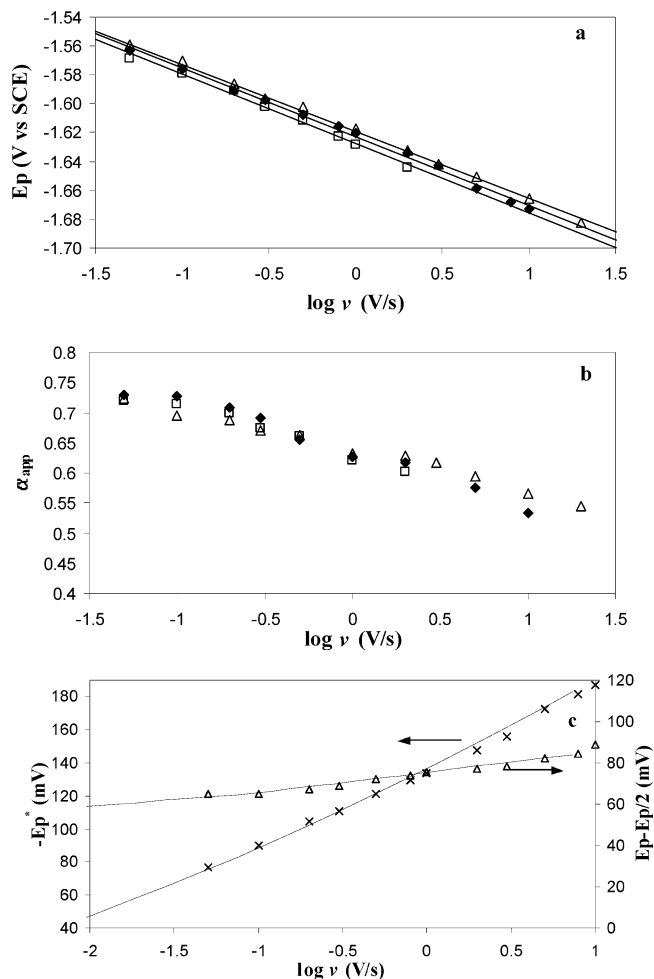
Figure 1. Reduction of (a) **C4**, (b) **C6**, and (c) **C8** in DMF + 0.1 M NBu$_4$BF$_4$ (20 °C) at 0.1 V/s, at a 1 mm diameter glassy carbon disk electrode (20 °C): cyclic voltammograms of 3.1, 3, and 3.1 mM solutions of **C4**, **C6**, and **C8** respectively.

Figure 2. Reduction of **C4**, **C6**, and **C8** in DMF + 0.1 M NBu$_4$BF$_4$ (20 °C): variations of (a) E_p and (b) α_{app} for ($\triangle$) **C4**, ($\blacklozenge$) **C6**, and ($\square$) **C8** with log v; (c) example of the application of the treatment for the deduction of the kinetic parameters of **C6** (symbols, experimental ($\times$) $-E_p^* = -E_{p,exp} + C$ and ($\triangle$) $E_p - E_p/2$; lines, theoretical predictions according to eq 30b: $E_p^* = -(RT/\alpha F)\xi_p^*(v) - RT/2\alpha F \ln(Fv/RT)$).

reduction. Values of α lower than 0.5 indicate that the electrochemical process is kinetically controlled by the electron-transfer (ET) step. The lower the α value, the higher the energy involved in the ET. On the other hand, values higher than 0.5 indicate that the ET is not the rate-limiting step of the reductive process but that it is competing with a following chemical step. A pure control by a following chemical step implies a α value of 1 (E_p decreases by 30 mV per decade of v). Therefore, usually when α is higher than 0.4, it is admitted that the ET and the bond breaking occur sequentially and that a radical anion is formed upon the first ET.[20,28]

The average apparent coefficient transfer values (Table 1) obtained from the heterogeneous reduction of the perfluoro-alkylphenylcyanides ascertain that a radical anion was involved in the process.

The deduction of kinetic and thermodynamic data can be achieved by using a theoretical description of such mixed kinetic control by an ET, characterized by its standard reduction potential, E_S°, its electron-transfer constant, k_S, and its electron-transfer coefficient, α (α close to 0.5), and a following chemical step, characterized by its rate constant, k_C.

Under such circumstances, the peak potential is theoretically defined by[30]

$$E_p = C - \frac{RT}{\alpha F}\xi_p^*(v) - \frac{RT}{2\alpha F} \ln\left(\frac{Fv}{RT}\right) \tag{5}$$

where R is the gas constant, T is the temperature, F is the Faraday constant, $\xi_p^*(v)$ is a function of the scan rate and of the competition between the ET and the following chemical step for the kinetic control, and C is a constant directly related to the ET step given by $C = E_S^\circ + (RT/\alpha F) \ln(k_S/(\alpha D_S)^{1/2})$, with D_S the substrate diffusion constant.

Briefly, the data treatment consists of comparing the experimental dependence of the peak potential and peak half-width on the scan rate with theoretical ones as given in ref 30b. From those variations depicted in Figure 2c, for example, in the case of **C6**, one extracts the value of C and of a parameter describing the competition between the ET and the following chemical step: $k_S^2/k_c^{1/2}D_S$. Those values are reported in the last two columns of Table 1 for the perfluoroalkylphenylcyanides investigated.

Therefore, the complete description of the system requires indirect determinations of two of the four unknown constants (E_S°, D_S, k_S, k_c).

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TABLE 1: Direct Reduction Study

compd	$E_p{}^a$ (V vs SCE)	$\partial E_p/\partial \log v$ (mV/decade)	$\alpha_{app}{}^b$	$\alpha_{app}{}^c$	$E_S^\circ + (RT/\alpha F)$ $\ln(k_S/\alpha D_S){}^d$ (V vs SCE)	$(k_S{}^2/k_c{}^{1/2})$ $D_S{}^e\,(s^{-1/2})$
C4	-1.57^f	47	0.62	0.70	-1.48	1.5
C6	$-1.57_5{}^f$	48	0.61	0.69	-1.48_5	1.5
C8	-1.58^f	48	0.61	0.68	-1.49	1.5
1	-1.50^g	66	0.44	0.43	-1.41	≤ 0.06

^{a} Peak potential at 0.1 V/s and 20 °C. ^{b} Apparent electron-transfer coefficient deduced from $\partial E_p/\partial \log v$ at 0.1 V/s. ^{c} Apparent electron-transfer coefficient deduced from $E_{p/2} - E_p$ at 0.1 V/s. ^{d} Direct study (± 5 mV): E_S°, standard reduction potential; k_S, electron-transfer rate constant; α, electron-transfer coefficient; D_S, diffusion coefficient of the substrate. ^{e} Direct study ($\pm 10\%$): k_c, chemical reaction rate constant. ^{f} In DMF + 0.1 M NBu$_4$BF$_4$. ^{g} In THF + 0.1 M NBu$_4$BF$_4$.

TABLE 2: Diffusion Coefficients Estimation

compd	$V_m{}^a$ (cm^3·mol^{-1})	$D_S/D_M{}^b$	$D_S/D_M{}^c$	$n_e{}^d$
M^e	120^f	1	1	1
C4	226	0.70	0.7 ± 0.02	4.1
C6	272	0.62	0.65 ± 0.02	6.0
C8	318	0.55	0.55 ± 0.02	7.7
1	245^g	0.65	0.65 ± 0.02	3.9

^{a} Molar volume calculated from group increments. ^{b} Apparent diffusion coefficient calculated from Wilke's equation (eq 6). ^{c} Apparent diffusion coefficient: best value obtained from redox catalysis experiments. ^{d} Value of the number of electrons exchanged ($\pm 5\%$). ^{e} **M** = 1,4-diacetylbenzene. ^{f} V_m deduced from available experimental density and group increments. ^{g} From available experimental density.

Estimation of D_S and n_e. The main problem arising from the reduction of compounds that possess several leaving groups comes from the fact that the number of electrons, n_e, exchanged at the first reduction step (first peak) is not known a priori. We have estimated n_e by comparing the reduction peak currents of the substrates to that corresponding to the reversible one electron reduction of a redox mediator, M, namely 1,4-diacetylbenzene, under similar conditions.[31] The difference in the molecular structures of the various substrates and the mediator have been taken into account on the level of their diffusion coefficients by using the empirical Wilke's equation (eq 6). This equation fitted accurately for numerous different compounds the experimental changes in diffusion coefficient with changes in molecular volume V_m
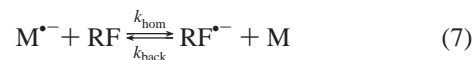
$$D = 7.4 \times 10^{-15} \frac{T}{\eta} \frac{\sqrt{\beta M_s}}{V_m{}^{0.6}} \quad (6)$$

with β, a parameter that takes into account the solvation ability of the solvent, M_s, the solvent molecular weight, and η the solvent viscosity.[32] The diffusion coefficients, D_S, have been deduced from the molar volumes of the perfluoroalkylphenylcyanides, that we have estimated using a group contribution method.[33]

It is striking to notice that when variability in the diffusion coefficients was taken into account, the number of electrons involved (Table 2) was ~4, 6, and 8 for **C4**, **C6**, and **C8**, respectively, indicating that one electron was transferred for each fluorinated carbon atom.

Estimation of E_S°—Redox Catalysis. Redox catalysis is a well-documented process that can be used to determine indirectly the E° of a substrate.[30a,34] It consists of reducing the substrate via a mediator M whose standard potential is more positive than the reduction peak potential of the substrate. Under such conditions, homogeneous electron transfer between M$^{\bullet-}$

and the substrate takes place as the first step according to eq 7 with a homogeneous electron-transfer rate constant k_{hom}. When the substrate radical anion is a reaction intermediate, its decomposition via eq 8 may compete with the backward electron transfer of rate constant k_{back}. However, the system can be kinetically governed by the homogeneous electron transfer when the radical anion does not exist or when its lifetime is too short (fast cleavage rate constant, k_c).

$$M^{\bullet-} + RF \underset{k_{back}}{\overset{k_{hom}}{\rightleftharpoons}} RF^{\bullet-} + M \quad (7)$$

$$RF^{\bullet-} \overset{k_c}{\longrightarrow} R^\bullet + F^- \quad (8)$$

The following electron transfer (reduction of R$^\bullet$ or of any reaction intermediate) can then occur homogeneously by reaction with M$^{\bullet-}$ or RF$^{\bullet-}$ if the latter is stable enough.

The determination of the kinetics of the rate-limiting step of a redox catalysis experiment is based on the comparison of the reduction peak current of the mediator in the absence, $i_p{}^\circ$, and in the presence of the substrate, i_p. Practically, it consists of fitting the experimental curves representing $i_p/i_p{}^\circ$ as a function of $\log v$ with the theoretical curves[35] for different substrate and mediator concentrations and different scan rates.

In the particular case of total redox catalysis (with the strongest electron donor and the lowest scan rates), we have also confirmed the stoichiometry of the electron transfer and the difference between the diffusion coefficients from the height of the peak current corresponding to the irreversible reduction of the mediator (D_M was supposed approximately constant in the series of redox mediators listed in the captions of Figures 3 and 5). More generally, whatever the redox catalysis conditions, the values of n_e and D_S/D_M found to fit the redox catalysis experiments were, for all substrates and redox mediators, in good agreement with those deduced from the direct study. This is illustrated in the case of the mediated reduction catalysis of perfluorohexylphenylcyanide, **C6**, by terephthalonitrile. When imposing $n_e = 6$, the experimental curves were best fitted by taking an apparent substrate diffusion coefficient of 0.65 (Figure 3a).

The experiments were kinetically controlled by the first homogeneous electron transfer, whose rate constant, k_{hom}, did not depend much on the perfluoralkyl chain length (see Supporting Information). This confirmed the similarity of the reductive behaviors of these compounds, as already observed in the direct study.

The values of $\log k_{hom}$ decreased almost linearly with the mediator reduction potential, E_M° (Figure 3b). The apparent homogeneous transfer coefficients deduced from these variations ($\alpha_{hom,app} = -RT/F\ \partial \log k_{hom}/\partial E_M^\circ = 0.72$ for the three compounds) were also in good agreement with the formation of the radical anion of the substrate.[20] The standard reduction potentials, E_S°, of those substrates were obtained by fitting the potential dependence of k_{hom} according to the following Marcus-type equation (Figure 3b):[20,36]

$$\frac{1}{k_{hom}} = \frac{1}{k_{diff}} + \frac{1}{Z^{hom} \exp\left[-\dfrac{F\Delta G_{0,hom}^{\neq}}{RT}\left(1 + \dfrac{E_M^\circ - E_S^\circ}{4\Delta G_{0,hom}^{\neq}}\right)^2 \right]} \quad (9)$$

where k_{diff}, the bimolecular diffusion limit, was taken as 6×10^9 M^{-1} s^{-1}, Z^{hom} was the bimolecular collision frequency taken as 3×10^{11} M^{-1} s^{-1}, and $\Delta G_{0,hom}^{\neq}$ was the intrinsic activation barrier of the homogeneous ET. The best fit of the data was

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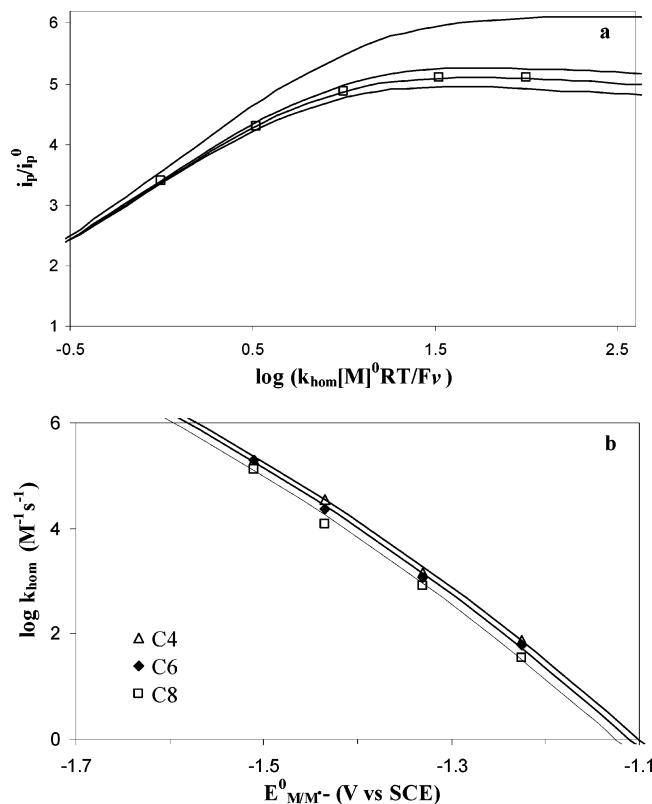
Figure 3. Redox catalysis of **C4**, **C6**, and **C8** in DMF + 0.1 M NBu$_4$-BF$_4$ (20 °C): (a) determination of the limiting rate constant for the mediated reduction of **C6** by terephthalonitrile, with the appropriate abacus [(□) experimental data; (solid lines) abacus for a six electron exchange with, from top to bottom, $D^* = 1$, 0.7, 0.65, and 0.6]; (b) variation of log k_{hom} with the mediator standard potential for (△) **C4**, (◆) **C6**, and (□) **C8**; the mediators used from left to right are terephthalonitrile, *p*-diacetylbenzene, 2-nitroxylol, and 3-nitroxylol.
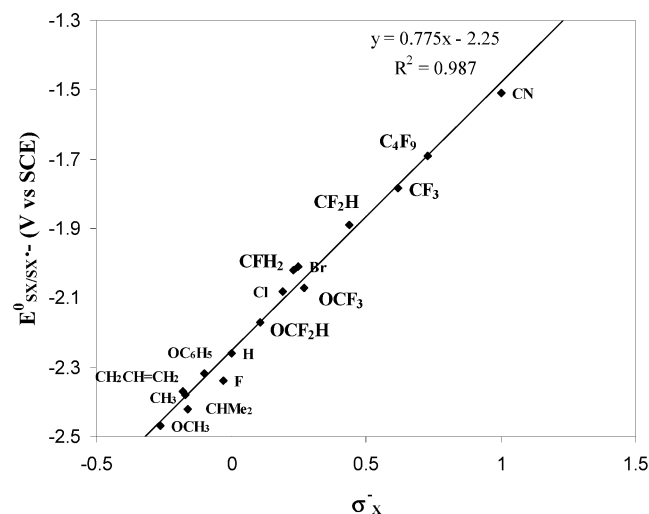
**Figure 4.** Variation of the standard reduction potential of 4-NC−C$_6$H$_4$−X (SX) with σ^- for different X substituents.

obtained with the values of E_S° and the intrinsic barrier collected in Table 3.

The values of the rate constants of the limiting chemical step, k_c, and of the heterogeneous electron transfer, k_s, ensued then from the knowledge of the standard reduction potentials E_S° (Table 3).

Preparative Electrolysis. Electrolyses of perfluorinated substrates give generally poor results because of the reactivity of the products obtained as reported in the literature.[5,16,37] However,
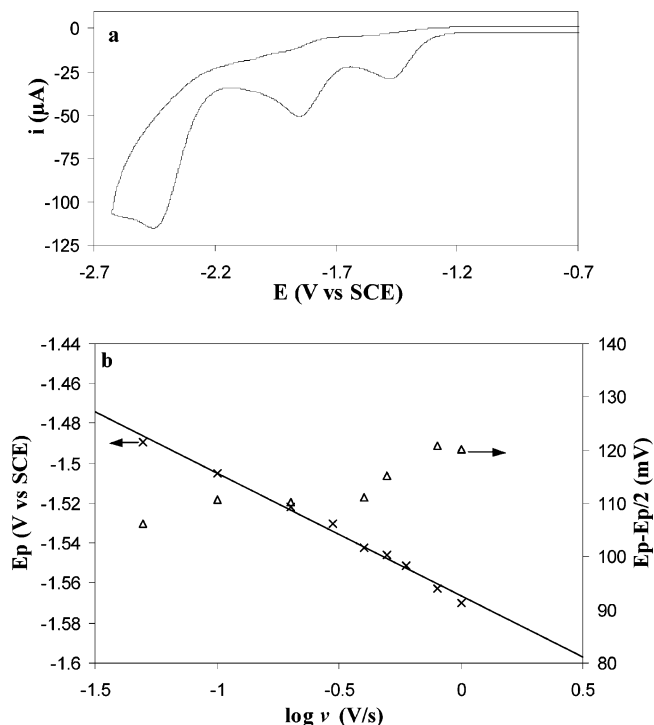
Figure 5. Reduction of 3 mM **1** in THF + 0.1 M NBu$_4$BF$_4$ (20 °C): (a) cyclic voltammogram at 0.1 V/s, at a 1 mm diameter glassy carbon disk electrode; (b) variations of (×) E_p and (△) $E_{p/2} − E_p$ with log v.

TABLE 3: Redox Catalysis Study

compd	$E_S^{\circ a}$ (V vs SCE)	k_c^b (s^{-1})	k_s^c (cm·s^{-1})	$\Delta G^{\neq}_{0,hom}{}^d$ (eV)
C4	−1.68$_5$	1.1 × 10^6	0.1	0.20
C6	−1.69	1.2 × 10^6	0.09$_5$	0.20
C8	−1.70$_5$	1.3 × 10^6	0.1	0.20
1	−1.58	≥4 × 10^7	0.02$_5$	0.27

^{a} Standard reduction potential of the substrate (±10 mV). ^{b} Chemical reaction rate constant (±15%). ^{c} Electron-transfer rate constant (±15%). ^{d} Intrinsic activation energy (±0.01 eV) of the homogeneous ET.

we have performed preparative electrolyses in order to estimate the numbers of electrons exchanged and fluoride anions lost during the reduction and to try to evidence intermediate compounds. The electrolyses were carried out under constant current or constant potential for solutions of **C6** or **C8** in the absence or the presence of a weak acid.

They showed that the starting product was consumed with an average number of electrons exchanged of 6.1 and 7.9 per molecule, respectively, for **C6** and **C8**, which confirmed the number of electrons found or postulated in the direct and indirect mechanistic analysis.

Traces of an intermediate have been detected by GPC-MS during the early stages of **C6** electrolysis in the presence of a weak acid (fluorene). With a parent peak of 307 g, that product could correspond to the perfluorinated polyolefinic compound, NC−C$_6$H$_4$−CF=CF−CF=CF−CF=CF$_2$. It disappeared when the electrolysis was pursued or when the acid was absent; at the end of the electrolysis, no compound could be clearly assigned as an electrolysis product. Possible parasite electro-generation of hydroxide ions from water traces[38] did not lead to the amidation of the cyanide containing starting material, but it could be responsible for the perfluoro-olefinic intermediates' instability.

Fluoride ion determinations showed that the hydrolyzed electrolysis products corresponded to almost complete defluorination (average loss of 11 F$^-$ per **C6** molecule) of the starting

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material. Such a high ratio of n_{F^-}/n_{e^-} confirmed the chemical instability of the electrolysis polyolefinic products upon hydrolysis, as already observed for perfluorinated activated olefins, which are known to be sensitive to nucleophiles such as NH_3[16] or H_2O.[37] Such a phenomenon was certainly too slow to be observed at the time scale of cyclic voltammetry in DMF with low water contents or in the presence of hydroxide ions.

Proposed Reduction Mechanism for C4, C6, and C8. It is interesting to notice that the mechanistic parameters that describe the reduction of perfluoroalkylphenylcyanides (E_S°, standard reduction potentials corresponding to the formation of the substrate radical anion, and k_c, chemical decay rate constants) were quite similar for the different compounds investigated.

In the case of fluoromethylphenylcyanides, the formation of a radical anion through the first electron transfer was attributed to the higher strength of the C–F bond compared to other CH_2–X bonds (X = Cl, Br, or I).[17,20b] The similar values of the standard reduction potentials of **C4**, **C6**, and **C8** express the comparable electron-withdrawing effects of the different perfluoroalkyl chains. However, the E° values for **C4**, **C6**, and **C8** ($E^\circ \approx -1.70$ V vs SCE) were more positive than that of the trifluoromethyl derivative ($E^\circ = -1.785$ V vs SCE),[17] owing to the higher electron-withdrawing effect of the perfluoroalkyl chain.

This effect was confirmed by a Hammett plot[39] of the standard reduction potentials of different para-substituted cyanophenyl derivatives (seven of them were fluorinated). Hammett parameters were available for various fluorine containing substituents.[39,40] All the other standard potential values were obtained directly from selected literature data.[41–43] The best correlation was found with a σ^- coefficient as a consequence of the possible delocalization of the negative charge of the radical anion on the cyano electron-withdrawing group.[44]

When considering all the substituents, we obtained the following correlation (Figure 4):[45]

$$E_{R/R^-}^\circ = 0.775\sigma^- - 2.25 \quad (r^2 = 0.987) \qquad (10)$$

with a slope lower than unity as a consequence of the solvent stabilization of the radical ion.

The closeness of the standard reduction potentials of **C4**, **C6**, and **C8** ($E^\circ \approx -1.70$ V vs SCE) could be explained by the identity of their σ^- values as soon as the perfluoroalkyl chain length possessed more than two carbon atoms ($\sigma^-_{C2} \approx \sigma^-_{C4} \approx 0.72$).

On another hand, the similarity in the radical anion cleavage rate constants ($k_c \approx 10^6$ s^{-1}) indicated that the cleaved bond was not too affected by the perfluoroalkyl chain length. Therefore, the intramolecular dissociative electron transfer accompanying the C–F bond cleavage in the radical anion should be independent of the chain length and should occur at the same distance from the phenylcyanide group that received the extra electron. This suggests that the same C–F bond, adjacent to the aromatic ring, was first cleaved. Moreover, the much faster bond cleavage of a secondary C–F bond than that of a primary one in a CF$_3$ group ($k_{c,CF_3} = 38$ s^{-1})[17] is in agreement with the lowering of the C–F bond dissociation energy (BDE) when replacing fluorine atoms by perfluoroalkyl groups. Such an effect has already been observed in the fluoromethylphenylcyanide series and could be rationalized by application of the intramolecular dissociative electron-transfer model developed by Savéant;[20] its application to the fluorinated substrates investigated in this work will be discussed later.

Owing to (i) the observation of a perfluoalkenylphenylcyanide derivative as an electrolysis intermediate, (ii) the electron

SCHEME 1. Proposed Mechanism for the Reduction of Perfluoroalkylphenylcyanides
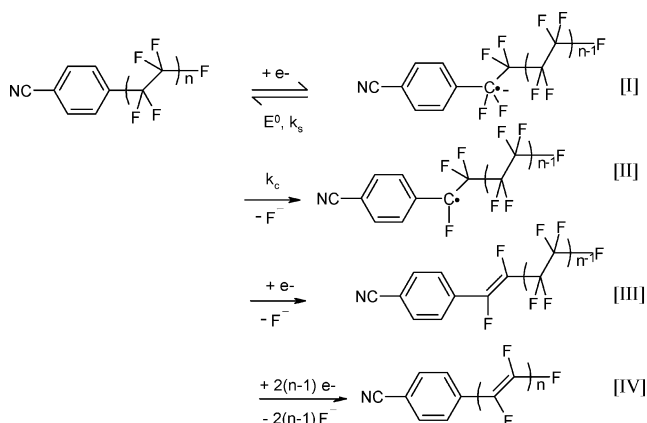

stoichiometry, n_e, found in the kinetic and electrolysis study, and (iii) the general reduction mechanism of vicinal dihaloalkanes into alkenes (one electron transferred per halogenated carbon),[10] we can propose that the first reduction peak of the perfluoroalkylphenylcyanides corresponds to the reduction shown in Scheme 1.

Most likely the radicalar species formed upon the first bond breaking [II] should be easier to reduce than the starting material. Its reduction should lead to the expulsion of a second fluoride anion and formation of a C=C bond [III]. The C–F bond breaking and the electron transfer could be concerted, as for vicinal dihaloalkanes' reduction,[10b–d] or successive, as for perfluoralkenes' reduction.[18] There is a priori no evidence for a privileged path.

As the σ^- value of –CF=CF–CF$_3$ (0.65) is close to that of $-R_f$ (0.72), all but the last olefinic intermediates involved in Scheme 1 should be reduced in the same potential region as that for the starting material. They could be reduced either homogeneously by an internal redox catalysis mechanism (self-catalysis by the radical anion of the starting material when it is stable enough), as it has been proposed for fluorotolunitriles,[17] or heterogeneously by the electrode material (in a succession of ECE steps).

The general trend observed in the reduction of perfluorinated olefins shows the dependence of the E° on the branching and number of perfluoroalkyl substituents on the double bond: the more branched, the more positive the E° of the olefin.[18,19] In the case of perfluoralkylphenylcyanides, the unsaturated derivative, obtained by exchange of one electron per carbon atom (reactions I–IV), is expected to be more difficult to reduce than the starting parent and the reduction should stop after an exchange of one electron and a loss of one F$^-$ per fluorinated carbon atom.

Reduction of Perfluorodecalin 1. We have adopted the same strategy to investigate the reduction of perfluorodecalin **1** as that for **C4**, **C6**, and **C8**. However, any study of perfluorodecalin in solution encounters difficulties, which are due to the poor stability of the solutions. THF and DMF were used as solvents. DMF, which is better for analytical electrochemistry than THF, could not always be used, since perfluorodecalin was poorly soluble in it. In addition, because of the low surface tension of the substrate, DMF solutions of perfluorodecalin were unstable upon bubbling, deaerating, or shaking. These operations tended to gradually decrease the perfluorodecalin content. Therefore, DMF was not thought suitable for a precise determination of the number of electrons exchanged upon direct reduction. To circumvent this drawback, THF, which is the best classical
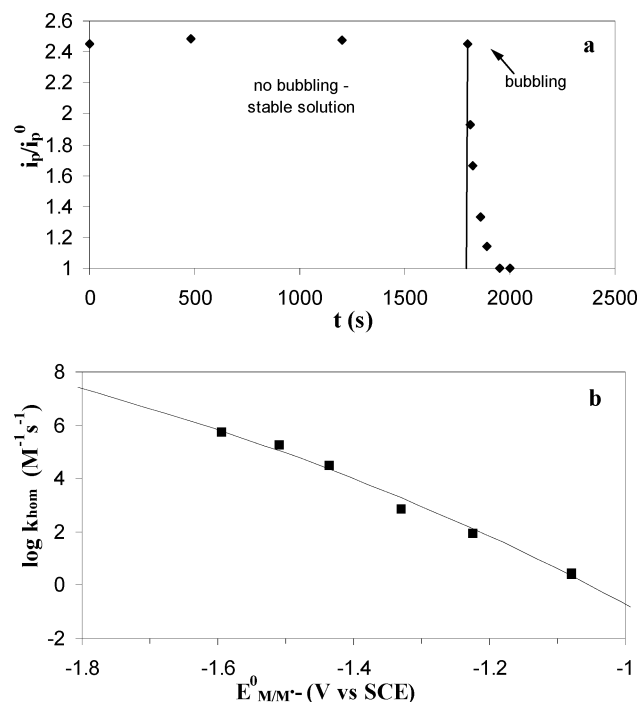
Figure 6. Redox catalysis of **1** in DMF + 0.1 M NBu$_4$BF$_4$ (20 °C): (a) stability of the perfluorodecalin solution in DMF; (b) variation of log k_0 with the mediator standard reduction potential; the mediators used from left to right are phthalonitrile, terephthalonitrile, *p*-diacetylbenzene, 2-nitroxylol, 3-nitroxylol, and nitrobenzene.

solvent of perfluorinated compounds, was used. Cyclic voltammograms obtained in such a solvent were similar in shape and location to those obtained in DMF (Figure 5a). They consisted of three different reduction stages that were reproducible upon repolishing of the electrode. The first peak potential was similar to that observed for **C4**, **C6**, and **C8**. Neither reversibility nor a shoulder could be detected at the level of the first wave for scan rates up to 100 V/s in THF or 1000 V/s in DMF. The shape and position of the voltammogram were unchanged by addition of 1 equiv of HO$^-$ or of a weak acid. From the perfluorodecalin molecular volume and the comparison of the peak current with that of a reversible monoelectronic system (**M** = 1,4-diacetylbenzene), we have estimated an apparent diffusion coefficient (D_S/D_M = 0.65, Table 2), which is in good agreement with literature data,[46] and we have found that four electrons were injected in the first reductive step. In THF, the values of the apparent transfer coefficient deduced from the scan rate dependence of the peak potential (Figure 5b, Table 1, α_{app} = 0.44) or from the peak width (110 mV at 0.1 V/s, Table 1, α_{app} = 0.43) are in favor of the formation of the perfluorodecalin radical anion upon the first kinetically limiting electron transfer.

Indirect analysis by redox catalysis could be performed in DMF, since that method allows the reduction of the substrate in solution instead of at the electrode that is not, in turns, passivated. DMF was preferably used for redox catalysis experiments due to its higher dissociating ability (better ohmic drop compensation that ensures more precise current determinations and allows the use of higher mediator concentrations). The experiment presented in Figure 6a shows how reproducible such redox catalysis experiments were and how stable the studied solutions were when bubbling was prevented. On the other hand, advantage was taken from the poor stability of DMF solutions of perfluorodecalin to change easily the concentration of the substrate.

Redox catalysis experiments were best fitted with an apparent diffusion coefficient of 0.6 and an exchange of four electrons at the first stage. The homogeneous reduction was again controlled kinetically by the first ET for different redox mediators. The apparent electron-transfer coefficient deduced from the variations of the homogeneous electron-transfer rate constant with the mediator standard reduction potential, $E^\circ_{M/M^{\bullet-}}$ ($\alpha_{hom,app}$ = 0.62), indicated that the radical anion of perfluorodecalin was formed with significant reorganization (large $\Delta G^{\neq}_{0,hom}$). From the best fit of these variations (Figure 6b) according to eq 9, we obtained the standard reduction potential corresponding to the perfluorodecalin radical anion formation (E°_1 = −1.58 V, Table 3).

From either direct or indirect study, respectively, in THF and DMF, we have found that more than three electrons were irreversibly injected at the first step of perfluorodecalin reduction.

The electron-transfer rate constant was deduced from E°_1 and the variations of the peak potential and peak width with the scan rate: k_s = 0.025 cm·s^1. It implied the use of a value of 0.43 for the electron-transfer coefficient to fit the direct study results in THF, instead of the classical value of 0.5.[47] If we assume that at the lowest scan rate investigated the system was in a mixed control by the chemical reaction and the electron transfer, we could evaluate a lower limit for the chemical evolution rate of the perfluorodecalin radical anion (k_c > 4 × 10^7 s^{-1}). The existence of the perfluorodecalin radical anion could seem odd, owing to the aliphatic nature of the molecule. However, it is in agreement with the rather high value of the gas-phase electron affinity of cyclic perfluoroalkanes possessing a tertiary carbon atom (E° = −1.58 V vs SCE and EA ≈ 1.3 eV).[21e,22f,24] This value is actually close to that proposed for terephthalonitrile (E° = −1.51 V vs SCE and EA = 1.1 eV), as are the standard reduction potentials of both compounds. Moreover, such positive EA values for perfluorocycloalkanes were confirmed in the solvent phase by their ability to form charge-transfer complexes.[48]

The structure of perfluorocycloalkanes radical anions has been described by EPR spectroscopy,[27] as σ^*-type radical anions.[22a,e] If the σ^* orbital that receives the extra electron has dominant localized C−F character in *n*-perfluoroalkanes, it is not even more the case for cyclic substrates or when increasing the branching of the molecule. In the latter two cases, the σ^* orbital becomes a combination of C−C and C−F orbitals because of both strain energy and the presence of the highly electronegative fluorine atoms that can develop long distance interactions.[49,50] Increasing the number of possible long distance interactions is then expected to lower the σ^* energy and therefore increase the electron affinity (make reduction easier) of the perfluoroalkane. Hence, it has been observed experimentally that cyclic perfluoralkanes possessing a tertiary C−F bond were the most easily reduced perfluoroalkanes.[5,7]

The electrochemical formation of σ^* radical anion has recently been studied in the case of the reduction of disulfides.[28,51,52] It has been demonstrated by electrochemical measurements and theoretical calculations that the formation of σ^* radical anions needed consequent inner reorganization.[28,52] The slowness of heterogeneous and homogeneous ET observed in our work is in agreement with gas-phase data that showed that electron transfer to tertiary perfluorocycloalkanes involved also large reorganization energies (1 eV).[22a−e,53] Those aspects, likely related to the σ^* nature of the perfluorodecalin radical anion, will be discussed in terms of ET theories in the following section.

Reduction of Polyfluorinated Compounds

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SCHEME 2. Proposed Mechanism for the Reduction of Perfluorodecalin (See Written Comments)
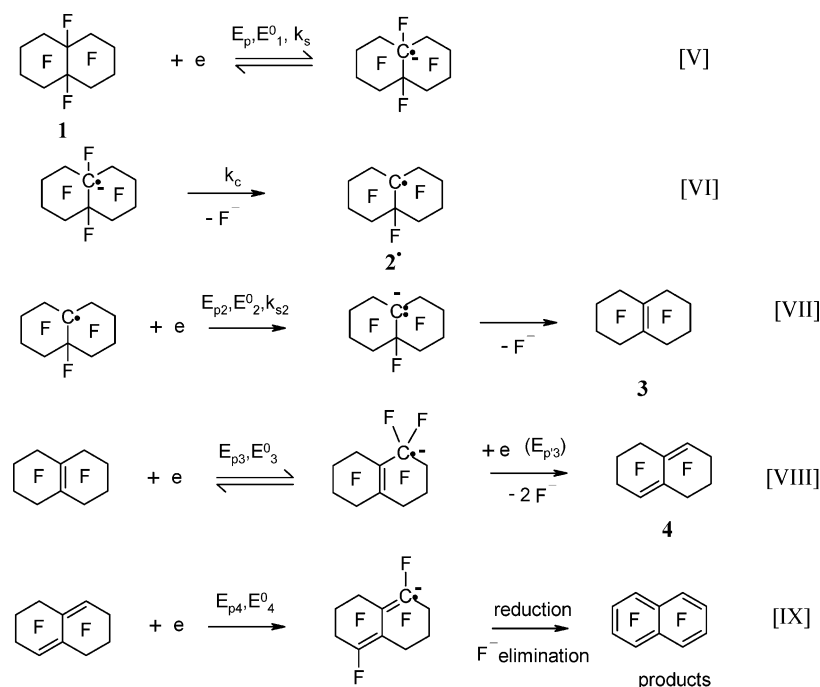
Proposed Reduction Mechanisms. Our results and literature data allowed us to propose a mechanism to explain the reduction of perfluorodecalin (Scheme 2). As for perfluoroalkylphenyl-cyanides, the radical anion, $1^{•-}$, obtained after the first electron transfer ($E_p \approx -1.5$ V [V]) should evolve toward the breaking of a C–F bond. The first broken bond should be a tertiary one, owing to its much lower energy, in good agreement with literature data.[21e,24,54,55] The lower value of the rate constant of the tertiary C–F bond cleavage in the perfluorodecalin anion radical ($k_c > 4 \times 10^7$ s^{-1} (Table 3) [VI]) is compatible with the lifetime of the radical anion of perfluoromethylcyclohexane ($\tau > 10$ μs) in the gas phase[21] or the ESR detection of this anion in a pulsed rigid apolar matrix.[27]

Reduction of the tertiary radical, $2^{•}$, then formed ([VII]) could be compared to that of other tertiary perfluororadicals,[56,57] which is known to occur at quite positive potentials (ca. $E_{p2} \approx 0.55$ V vs SCE)[56b] and should lead to C=C formation by a second C–F bond splitting (most likely for energetic reasons a tertiary one leading to the perfluorinated olefin **3**). This is in good agreement with the detection of the corresponding perfluorinated olefin during UV irradiation of perfluorodecalin in the presence of a suitable electron donor.[9]

The following steps ([VIII]–[IX]) were proposed owing to already known reductive behaviors of perfluorinated olefins in organic solvents.[5,18]

Our investigations of the reduction of the perfluorinated olefin **5** in THF or DMF confirmed the behavior and potential scale observed by Corvaja et al. ($E_{p5} = -1.1$ V vs SCE compared with -1.15 V vs SCE in ref 18a) for perfluoroolefins' reduction.

Then, by analogy with the tetrakis-trifluoromethylethene reduction,[18a] we assumed that the perfluorinated olefin, **3**, formed upon perfluorodecalin reduction was reduced into a radical anion, $3^{•-}$, at a much more positive potential, $\sim E_3^\circ \approx -0.5$ V vs SCE, and then into a dianion at $\sim E_{p'3} \approx -1.1$ V vs SCE. Two C–F bonds were cleaved at this level, leading to the perfluorinated diene, **4**. Since perfluorinated dienes are known to be more difficult to reduce by as much as 1.2 V than the parent alkene,[18a,b,19] we could assume that **4** was reduced at about $E_{p4} \approx -1.7$ V vs SCE. Therefore, a first transfer of four

electrons was expected to occur at the peak potential of -1.5 V vs SCE, leading to the direct formation of the perfluorinated diene **4**. The location of the second peak observed during perfluorodecalin reduction could be in good agreement with the perfluorinated diene reduction at the electrode.

Due to the rather high instability of $1^{•-}$, the electron transfer to $2^{•}$ and **3** should be more reasonably achieved by the electrode rather than by $1^{•-}$ itself; one could then neglect either self-catalysis (formation of $3^{•-}$) or DISP mechanisms (reduction of $2^{•}$).

Application of the Intramolecular Dissociative Electron-Transfer Model

The intramolecular dissociative electron-transfer model of anion radicals' cleavage has been applied to account for the data collected for fluorinated compounds in order to interpret more quantitatively the different trends observed and relate them to the characteristics of the C–F bond. It had been shown previously in the fluorotoluenes series that the presence in the para position of a cyano group lowered the C–F BDE by $\sim$0.20 eV.[17] The dependence of the BDE on the nature of the substituents had already been observed in solution on the benzylic group[58a,59] and interpreted by a Hammett-type relationship;[58b] such effects are much less obvious when BDE values are estimated by low-pressure pyrolysis techniques.[58c] Recently, Savéant[20d] has proposed to relate these differences to possible interactions between the caged fragments issued from the bond cleavage (radical and ion) and he has extended his electron-transfer model to account for such interactions.

This ion–dipole-type interaction is expected to increase with the introduction of electron-withdrawing groups in the radical, increasing the partial positive charge on the formed radicalar atom. As far as fluorinated derivatives are concerned, one should expect to detect such interactions, owing to the high electronegativity of fluorine atoms and the electron-withdrawing ability of perfluoroalkyl groups. We have then used this approach of the intramolecular dissociative ET.

Intramolecular Dissociative Electron-Transfer Model.[20] The model is based on a Marcus-type activation–driving force

TABLE 4: Reduction of Fluorinated Compounds—Application of the Intramolecular Dissociative Electron Transfer Model

compd	$E_S^{\circ\,a}$ (V vs SCE)	$k_c^{\,b}$ (s^{-1})	BDE(C−F)^c (eV)	$E_{R\bullet/R^-}^{\circ\,d}$ (V)	$\Delta G^{\neq e}$ (eV)	$\Delta G_c^{\circ f}$ (eV)	BDE($^{\bullet-}$)^g (eV)	$\Delta G_{0,\text{solv}}^{\neq h}$ (eV)	BDE($^{\bullet-}$)$_{\text{est}}^{\,i}$ (eV)	$\Delta G_0^{\neq j}$ (eV)	$D_P^{\,k}$ (meV)
C4, C6, C8	−1.70	1.2×10^6	4.2_4	0.13	0.40	−0.34	2.4_3	0.19	1.8	0.59	90
ArCH$_2$F	−2.02	7×10^6	4.0_6	−0.56	0.35	−0.85	2.6_0	0.25	2.3_5	0.73	45
ArCHF$_2$	−1.89	4×10^5	4.3_4	−0.08	0.42_5	−0.44	2.5_3	0.25	2.0	0.66	85
ArCF$_3$	-1.78_5	38	4.7_5	0.03	0.66	0.09	2.9_5	0.25	2.0	0.69	14_3
1	−1.58	$\geq 4 \times 10^7$	4.2_9	1.00	$<0.30_5$	−0.18	1.7_2	0.19	<1.2	<0.44	$>10_0$
1$^{\text{homo}\,l}$	−1.58	$\geq 4 \times 10^7$	4.2_9	2.59	$<0.30_5$	−0.18	0.1_2	<0.36		<0.39	

^{a} Standard reduction potential of the substrate. ^{b} C−F$^{\bullet-}$ cleavage rate constant for the first broken bond. ^{c} C−F bond dissociation energy. ^{d} Standard reduction potential of R$^{\bullet}$/R$^-$ from ref 15. ^{e} Free energy of activation using 6×10^{12} s^{-1} for the pre-exponential factor. ^{f} Experimental standard free energy of radical anion cleavage obtained from eq 12. ^{g} Bond dissociation energy of the C−F bond in the radical anion C−F$^{\bullet-}$, from eq 13. ^{h} Solvent reorganization free energy, from eq 16. ^{i} BDE in the radical anion C−F$^{\bullet-}$ deduced from resolution of eq 11. ^{j} Standard free energy of activation obtained from the quadratic Savéant's equation (eq 11) taking into account ion/radical interaction, separated into an internal barrier ($\Delta G_{0,\text{int}}^{\neq} = 1/4(\text{BDE}(^{\bullet-})^{1/2} - D_P^{1/2})^2$ with BDE($^{\bullet-}$) from eq 13) and a reorganization one ($\Delta G_{0,\text{reorg}}^{\neq}$). ^{k} Interaction energy between the caged fragments (radical and fluoride anion). ^{l} Homolytic cleavage of the radical anion.

relationship of the cleavage reaction

$$\Delta G_c^{\neq} = -\frac{RT}{F}\ln\left(\frac{k_c h}{k_B T}\right) = \Delta G_{0,c}^{\neq}\left(1 + \frac{\Delta G_c^{\circ}}{4\Delta G_{0,c}^{\neq}}\right)^2 \quad (11)$$

where $\Delta G_c^{\neq}$ corresponds to the activation energy, ΔG_c° to the free energy, and $\Delta G_{0,c}^{\neq}$ to the intrinsic activation energy of the bond cleavage reaction. The driving force of the cleavage reaction is given by

$$\Delta G_c^{\circ} = \text{BDE(C−F)} + E_{\text{RF/RF}^{\bullet-}}^{\circ} - E_{\text{F}^{\bullet}/\text{F}^-}^{\circ} - T(S_{R\bullet} + S_{F\bullet} - S_{RF}) \quad (12)$$

as a function of the bond dissociation energy BDE(C−F), the standard formation potential of the radical anion $E_{\text{RF/RF}^{\bullet-}}^{\circ}$, the standard oxidation potential of the leaving fluoride anion $E_{\text{F}^{\bullet}/\text{F}^-}^{\circ}$, and an entropic contribution corresponding to the formation of two species starting from one ($\Delta S = 1$ meV K^{-1}).[20]

When the bond cleavage results from an intramolecular dissociative electron transfer, the intrinsic barrier is the sum of an intramolecular contribution (dissociation of the C−F bond in the radical anion C−F$^{\bullet-}$, namely, BDE($^{\bullet-}$))

$$4\Delta G_{0,\text{intra}}^{\neq} = \text{BDE}(^{\bullet-}) = \text{BDE(C−F)} + E_{\text{RF/RF}^{\bullet-}}^{\circ} - E_{R\bullet/R^-}^{\circ} - T(S_{RX} - S_{RX\bullet} + S_{R^-} - S_{R\bullet}) \quad (13)$$

and a contribution from the solvent reorganization

$$\Delta G_{0,\text{solv}}^{\neq} = \lambda_{0,\text{solv}}/4 = \frac{e^2}{4}\left(\frac{1}{D_{\text{op}}} - \frac{1}{D_S}\right)\left(\frac{1}{a_{\text{RF}^{\bullet-}}} + \frac{1}{a_{R\bullet,F^-}} - \frac{1}{d}\right) \quad (14)$$

where $a_{R\bullet,F^-}$ is the radius of the sphere where the charge is located on the leaving group when the bond is broken, d is the distance between the centers of the charges, D_{op} is the optical dielectric constant, and D_S the solvent dielectric constant [$(e^2/4)(1/D_{\text{op}} - 1/D_S)$ was taken empirically as $2.15/4 = 0.537$ eV].[20b]

From all the values that were necessary to use the model, all were known except BDE(C−F) and the standard reduction potentials of the different fluorinated radicals, $E_{R\bullet/R^-}^{\circ}$.

Estimation of BDE(C−F). We have attempted to estimate the BDE of the fluoroalkylphenylcyanides according to the thermodynamic sources used to estimate BDE in *gem*-fluoroethane derivatives[54a,60a] or according to the group increment correlation proposed by Dilling for benzylcyanides.[60b,c]

This should be more reasonable than taking the values proposed by Joshi[54b] (that are likely too low), as we did in a previous study.[17]

In the case of perfluorodecalin **1** we have taken for the BDE the value proposed for a tertiary C−F bond in (CF$_3$)$_3$CF.[54a]

Estimation of the Standard Radical Reduction Potentials, $E_{R\bullet/R^-}^{\circ}$. As already proposed in the same fluoromethylphenylcyanides series (R−CF$_2^{\bullet}$, R−CFH$^{\bullet}$), radicals were reduced at a potential 1.82 V more positive than that of the corresponding fluorinated substrates (R−CF$_3$, R−CF$_2$H, respectively). This approach is unlikely for the reduction of 4-cyanotoluene radical (R−CH$_2^{\bullet}$); in that case, a reduction potential of ~ -0.56 V vs SCE was preferred.[61]

In the case of perfluorodecalin (**1**), the radical reduction potential was estimated from thermodynamic cycles

$$E_{R\bullet/R^-}^{\circ} = \Delta G_{R\bullet}^{\circ\text{f,g}} - \Delta G_{RH}^{\circ\text{f,g}} - 2.3RT/F(\text{p}K_a) + \text{Cst} \quad (15)$$

with the use of the free energies of formation of R$_F^{\bullet}$ and R$_F$H in the gas phase[62a] and from the pK_a of the R$_F^-$/R$_F$H couple.[62b,c] By assuming that the solvation stabilization and the entropic contribution were similar and identical to those observed for CF$_3^{\bullet}$ and CF$_3$H, the constant, Cst, was deduced from the estimated value of $E_{\text{CF}_3^{\bullet}/\text{CF}_3^-}^{\circ} = -0.58$ V vs SCE in DMF.[34f] For the tertiary perfluorinated radical, (CF$_3$)$_3$C$^{\bullet}$, a value of the standard reduction potential $E_{\text{tert}\bullet/\text{tert}^-}^{\circ} = 1.0$ V vs SCE ensued. It was 0.45 V more positive than the reported value of the half-wave reduction potential of the stable perfluoro-2,4-dimethyl-3-ethyl-3-pentyl radical, but this is consistent with the observed slowness of the electron transfer to aliphatic or perfluoroaliphatic radicals.[34f,63]

We have gathered the values of the different energetic terms that could be estimated according to this model in Table 4.

Application of the Model. The intramolecular dissociative electron-transfer model was used to estimate the intrinsic barrier of the cleavage reaction. We assumed that the solvent reorganization energy involved in all the fluorinated compounds under study was constant and equal to the solvation energy of the adduct (R$^{\bullet}$,F$^-$). It corresponded mainly to solvation of the small fluoride anion and was estimated as

$$\Delta G_{0,\text{solv}}^{\neq} \approx 0.537/a_{R\bullet,F^-} \quad (16)$$

where $a_{R\bullet,F^-}$ was obtained by the tangent spheres approximation as

$$a_{R\bullet,F^-} = a_F(2a_{RF}-a_F)/a_{RF} \quad (17)$$

in which a_{RF} was roughly estimated from the molecular volumes.

We then deduced the internal reorganization intrinsic barrier related to the cleavage reaction. In the case of the phenylcyanide derivatives, this value corresponded mainly to the C−F BDE

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in the radical anion. Those estimated values, reported as BDE$_{est}$ in Table 4, were significantly lower than the calculated ones, and the difference increased when the number of fluorine atoms or perfluoroalkyl substituents on the substrate increased. This could be interpreted as a consequence of an increasing interaction between the fluoride anion and the radical in the solvent cage.

We have achieved a more quantitative description of that phenomenon. If changes in the solvent reorganization energy could be neglected,[64] the influence of an interaction between caged fragments could be examined by replacing in relationship 13 the radical anion bond dissociation energy BDE($^{\bullet-}$) by (BDE($^{\bullet-}$)$^{1/2}$ − $D_P^{1/2}$)^2 and in the activation−driving force relationship (eq 11) the driving force of the cleavage reaction, ΔG_c°, by $\Delta G_c^{\circ} - \Delta G_{sp}^{\circ}$, with

$$\Delta G_{sp}^{\circ} = D_P - T\Delta S_{sp}^{\circ} \tag{18}$$

where D_P is the work needed to bring the fragments into the cage formed by (R$^{\bullet}$,F$^-$).[20d] The latter approximate values of D_P are gathered in Table 4. The value for 4-cyanobenzylfluoride was consistent with that obtained for the chloride derivative.[59a] Those obtained for the other fluorinated derivatives were comparable to those reported in the reduction of CCl$_4$[59b] or 4-nitrobenzyl chloride.[59c] That confirmed the influence of the electron-withdrawing substituent on the ion/dipole interaction between the radicalar fragment and the fluoride anion.

In the case of perfluorodecalin, we have only estimated a lower limit for the interaction term. On one hand, owing to the possible partial C−F character of the σ* orbital receiving the extra electron, one could also consider that the mesolytic bond cleavage in the perfluorodecalin radical anion was more homolytic (**1^{homo}** in Table 4, eq 19a) than heterolytic (**1** in Table 4, eq 19b)

$$RF^{\bullet-} \rightarrow R^{\bullet} + F^- \tag{19a}$$

$$^{-\bullet}RF \rightarrow R^{\bullet} + F^- \tag{19b}$$

depending on whether the electron was localized respectively on the F or the R moiety in the radical anion. From a rough thermodynamic consideration, the homolytic radical anion BDE, obtained by replacing in eq 13 $E_{R^{\bullet}/R^-}^{\circ}$ by $E_{F^{\bullet}/F^-}^{\circ}$, was negligible compared to the heterolytic one (Table 4). This argument would be in thermodynamic favor of the homolytic dissociation of the radical anion. However, in such a case, a higher internal reorganization (kinetic disadvantage) would be accounted for in the first electron-transfer step (eq 1a).

On the other hand, we have used the Savéant's model to analyze the dynamics of the ET step corresponding to the formation of the radical anion. The inner reorganization of this step is expected to follow

$$4\Delta G_{0,in}^{\neq} = \lambda_{0,in} = (BDE(C-F)^{1/2} - BDE(^{\bullet-})^{1/2})^2 \tag{20}$$

Maran et al. have shown, in the case of disulfides' reduction, that this relation underestimated the reorganization of loose σ* radical anions. A more accurate description that reproduced the experimental large inner reorganization responsible for the slow heterogeneous ET was obtained by computation of the energy profiles depicting the ET reaction.[52]

In the case of **1**, the inner reorganization energy ($\lambda_{0,in}$) involved in the radical anion formation could be obtained from the homogeneous ET total reorganization energy ($\lambda_{0,hom} = \lambda_{0,in} + \lambda_{0,solv}$) and the solvent reorganization energy ($\lambda_{0,solv}$[65]). Its

value ($\lambda_{0,in} = 0.56$ eV) compared well with that proposed by the Savéant's model ($\lambda_{0,in} = 0.58$ eV) for the heterolytic bond cleavage. This would confirm that, unlike the case of the disulfides, the σ* radical anion of perfluorocycloalkanes has only partial C−F character and is delocalized on the whole molecule due to the electron-withdrawing properties of the perfluoroalkyl groups.[27,49,50]

Conclusion

We have investigated the reduction of polyfluorinated molecules. Due to the great number of possible leaving groups, the estimation of the number of electrons involved in the first stage of reduction was crucial.

Three model compounds, perfluoroalkylphenylcyanides of different alkyl chain lengths, more soluble and stable in DMF solutions than cyclic perfluoroalkanes, were used to define the strategy to be used. It was shown in direct and redox catalysis studies that the analysis needed to take into account the dependence of the diffusion coefficient on the molecular volume of the substrate. For these model compounds, one electron was exchanged per fluorinated carbon atom at the level of the first reduction wave leading to the fluorinated unsaturated derivatives.

Reduction of *cis*-perfluorodecalin involved three steps. We showed that four electrons were exchanged in the first one, leading to the formation of a diene, in agreement with literature data on the electrochemical behavior of perfluorinated olefins.

In the case of *cis*-perfluorodecalin as well as perfluoroalkylphenylcyanides, even if the reduction products have not been isolated, we could assume that the reduction was kinetically controlled by the first electron transfer, which leads to the formation of a radical anion, and the first C−F bond cleavage in the radical anion.

The intramolecular dissociative electron-transfer model of anion radicals' cleavage has been applied to interpret the variation of the cleavage rate constants with the nature of the C−F bond. To use the model, we have first estimated the C−F bond dissociation energies and the standard reduction potentials of the R$^{\bullet}$/R$^-$ systems.

Comparison of the different parameters obtained (standard reduction potentials and cleavage rate constants) with existing thermodynamic values allowed us to observe the effect of lowering the C−F bond dissociation energy on the cleavage rate constant when going from primary to tertiary fluorinated carbons, as expected from the intramolecular dissociative electron-transfer model. To describe the experimental observations, we had to take into account an increasing ion/dipole interaction between the radicalar fragment and the fluoride anion when the number of electron-withdrawing substituents was increased. In the case of *cis*-perfluorodecalin, the radical anion formed upon the first ET is of the σ*-type, explaining the large reorganization energy needed for the ET. Its dynamics could be described by the Savéant's model probably because of the possible delocalization of the extra electron in the perfluorocyclic molecule.

Supporting Information Available: Table of values of the homogeneous electron-transfer rate constant, k_{hom}. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) (a) In cyclohexane, $D_1 \approx 10^{-5}$ cm$^2\cdot$s^{-1} and $D_{cyclohexane} \approx 1.6 \times 10^{-5}$ cm$^2\cdot$s^{-1}; in decalin, $D_1 \approx 0.4 \times 10^{-5}$ cm$^2\cdot$s^{-1} and $D_{decalin} \approx 0.6 \times 10^{-5}$ cm$^2\cdot$s^{-1}.[46b] (b) Choi, H. T.; Lipsky, S. *J. Phys. Chem.* **1981**, *85*, 4089.

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(64) One would expect that the solvent reorganization includes the interaction of the solvent with the dipolar radical. However, one could predict that higher ion/dipole interaction in the (R•/F⁻) adduct will lead to higher dipole/solvent interaction and then to higher $\Delta G^{\ddagger}_{0,solv}$, that is to say to even higher values of D_P.

(65) For a homogeneous ET, see eq 14, $\lambda_{0,solv} = 2.15[1/a_M + 1/a_{RF} - 2/(a_M + a_{RF})] = 0.54$ eV with a_K the molecular radius expressed in angstroms (3.6 and about 4.6, respectively, for M and **1**).[20]