$C_{13}H_{17}O_3$, 40), 219.1001 (M^+ – side chain – H_2, $C_{13}H_{15}O_3$, 53), 189.0925 (M^+ – side chain, CH_3OH, $C_{12}H_{13}O_2$, 22), 187.0732 (M^+ – side chain – CH_3OH – H_2, $C_{12}H_{11}O_2$, 16); ^1H and ^{13}C NMR data are reported in Table I.

(17*S*)-17-Methylincisterol (3): 0.4 mg; spectroscopic properties identical with those of **2**, except for the ^1H NMR spectrum (see Table I).

(17*R*)-17-Ethylincisterol (4): 1 mg; UV (*n*-hexane) λ_{max} 220 nm (ϵ 6200); IR ($CHCl_3$) ν_{max} 1754 cm^{-1}; HRMS, *m/z* (assignment, relative intensities) 360.2728 (M^+, $C_{23}H_{36}O_3$, 50), 329.2557 (M^+ – OCH_3, $C_{22}H_{33}O_2$, 23), 328.2388 (M^+ – CH_3OH, $C_{22}H_{32}O_2$, 33), 317.2073 (M^+ – isopropyl, $C_{20}H_{29}O_3$, 7), 316.2859 (M^+ – CO_2, $C_{22}H_{36}O$, 5), 285.1846 (M^+ – isopropyl – CH_3OH, $C_{19}H_{25}O_2$, 100), 221.1181 (M^+ – side chain $C_{13}H_{17}O_3$, 43), 219.1019 (M^+ – side chain – H_2, $C_{13}H_{15}O_3$, 55), 189.0902 (M^+ – side chain – CH_3OH, $C_{12}H_{13}O_2$, 23), 187.0729 (M^+ – side chain – CH_3OH – H_2, $C_{12}H_{11}O_2$, 14); ^1H and ^{13}C NMR data are reported in Table I.

Identification of $\Delta^{5,7,22}$-Sterols. The crude sterol fraction (310 mg, R_f equals cholesterol by TLC) eluted with petroleum ether/ethyl ether (6:4) was purified by HPLC using a reversed-phase Hibar RP-18 (10 × 250 mm) column with a mobile phase of methanol, thus obtaining four pure compounds, which were identified as (22*E*)-cholesta-5,7,22-trien-3β-ol (82 mg), (22*E*,24*R*)-24-methylcholesta-5,7,22-trien-3β-ol (30 mg), (22*E*,24*S*)-24-methylcholesta-5,7,22-trien-3β-ol (41 mg), and (22*E*,24*R*)-24-ethylcholesta-5,7,22-trien-3β-ol (130 mg) by comparison of their physical and spectral properties with those previously reported.[5,6]

Isolation of 6a–6d. The earlier fractions eluted with ethyl acetate gave 5 mg of an oily residue that was subjected to HPLC with a Hibar Superspher C-18 (4 × 250 mm) column and $MeOH/H_2O$ (95:5) as eluent, thus obtaining pure compounds **6a–6d**. Compound **6a** [0.6 mg; (22*E*)-6β-methoxy-5α-cholesta-7,22-diene-3β,5-diol] and **6c** [0.3 mg; (22*E*,24*S*)-24-methyl-6β-methoxy-5α-cholesta-7,22-diene-3β,5-diol] were identified by comparison of their spectral data with those of authentic samples.

(22*E*,24*R*)-24-Methyl-6β-methoxy-5α-cholesta-7,22-diene-3β,5-diol (6b): 0.1 mg; IR ($CHCl_3$) ν_{max} 3500 cm^{-1}; HRMS, *m/z* (M^+) 444.3622, calcd for $C_{29}H_{48}O_3$ 444.3591; ^1H NMR ($CDCl_3$) δ 0.60 (s, H_3-18), 0.82 and 0.84 (d's, J = 6.5 Hz, H_3-26 and H_3-27), 0.82 (t, J = 7 Hz, H_3-29), 1.00 (s, H_3-19), 1.03 (d, J = 6.5 Hz, H_3-21), 3.18 (br d, J = 5 Hz, H-6), 3.39 (s, OMe), 4.07 (m, H-3), 5.17 and 5.23 (further coupled AB system, J_{AB} = 14 Hz, H-22 and H-23, respectively), 5.42 (br d, J = 5 Hz, H-7).

(22*E*,24*R*)-24-Ethyl-6β-methoxy-5α-cholesta-7,22-diene-3β,5-diol (6d): 0.4 mg; IR ($CHCl_3$) ν_{max} 3500 cm^{-1}; HRMS, *m/z* (M^+) 458.3702, calcd for $C_{30}H_{50}O_3$ 458.3747; ^1H NMR ($CDCl_3$) δ 0.60 (s, H_3-18), 0.79 and 0.84 (d's, J = 6.5 Hz, H_3-26 and H_3-27), 0.81 (t, J = 7 Hz, H_3-29), 1.00 (s, H_3-19), 1.03 (d, J = 6.5 Hz, H_3-21), 3.17 (br d, J = 5 Hz, H-6), 3.39 (s, OMe), 4.05 (m, H-3), 5.03 and 5.17 (further coupled AB system, J_{AB} = 14 Hz, H-23 and H-22, respectively), 5.40 (br d, J = 5 Hz, H-7).

Isolation of 7a–7d. The combined more polar fractions eluted with ethyl acetate gave 9 mg of an oily residue that contained a mixture of polyhydroxysterols. HPLC with a Hibar Superspher C-18 (4 × 250 mm) column and $MeOH/H_2O$ (92:8) as eluent afforded four pure compounds: (22*E*)-5α-cholesta-7,22-diene-3β,5,6β-triol (**7a**; 1.3 mg), (22*E*,24*R*)-24-methyl-5α-cholesta-7,22-diene-3β,5,6β-triol (**7b**; 0.4 mg), (22*E*,24*S*)-24-methyl-5α-cholesta-7,22-diene-3β,5,6β-triol (**7c**; 0.5 mg), and (22*E*,24*R*)-24-ethyl-5α-cholesta-7,22-diene-3β,5,6β-triol (**7d**; 0.7 mg), which were identified by comparison of their spectral data and/or those of their acetyl derivatives with those reported in literature.[11,12]

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Registry No. 1, 125974-95-0; **2**, 125974-96-1; **3**, 126060-08-0; **4**, 125974-97-2; **6a**, 117585-49-6; **6b**, 126060-09-1; **6c**, 125974-98-3; **6d**, 125974-99-4; **7a**, 100667-74-1; **7b**, 516-37-0; **7c**, 100761-25-9; **7d**, 124596-61-8; (22*E*)-cholesta-5,7,22-trien-3β-ol, 22643-62-5; (22*E*,24*R*)-24-methylcholesta-5,7,22-trien-3β-ol, 57-87-4; (22*E*,24*S*)-24-methylcholesta-5,7,22-trien-3β-ol, 57760-53-9; (22*E*,24*R*)-24-ethylcholesta-5,7,22-trien-3β-ol, 19432-13-4.

Outer-Sphere Dissociative Electron Transfer to Organic Molecules: A Source of Radicals or Carbanions? Direct and Indirect Electrochemistry of Perfluoroalkyl Bromides and Iodides

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Abstract: As an example of the general problem posed in the title, the reduction of CF_3Br, CF_3I, $C_6F_{13}I$, and $C_8F_{17}I$ by outer-sphere heterogeneous (glassy-carbon electrodes) and homogeneous (aromatic anion radicals) reagents is investigated, in aprotic solvents containing tetralkylammonium salts, by cyclic voltammetry and preparative-scale electrolysis. A $R_F^•$ chemistry is thus triggered in all cases with the exception of CF_3Br where a mixed $R_F^•/R_F^-$ chemistry is obtained by direct electrochemical reduction or by electron transfer from aromatic anion radicals having a close reduction potential. Quantitative analysis of the reduction kinetics of R_FX (X = Br, I) and of $R_F^•$ led to the following conclusions. R_FX most likely undergoes a concerted electron-transfer–bond-breaking reduction involving a substantial overpotential (ca. 1.5 V for C–Br and 1.0 V for C–I), mainly governed by the C–X bond dissociation energy. $R_F^•$ radicals are strongly stabilized by interaction with the solvent but are nevertheless easier to reduce than alkyl radicals on thermodynamical grounds, exhibiting however a high intrinsic barrier of the same order as for alkyl radicals. Unlike alkyl radicals, but similar to aryl radicals, $R_F^•$ radicals are good H-atom scavengers and do not couple with aromatic anion radicals.

Electron transfer from heterogeneous and homogeneous outer-sphere reagents to frangible organic substrates provides a means of generating either radicals or carbanions according to the reduction characteristics of both the substrate and the radical/carbanion couple. Investigation and rationalization of these characteristics should thus allow one to predict what type of

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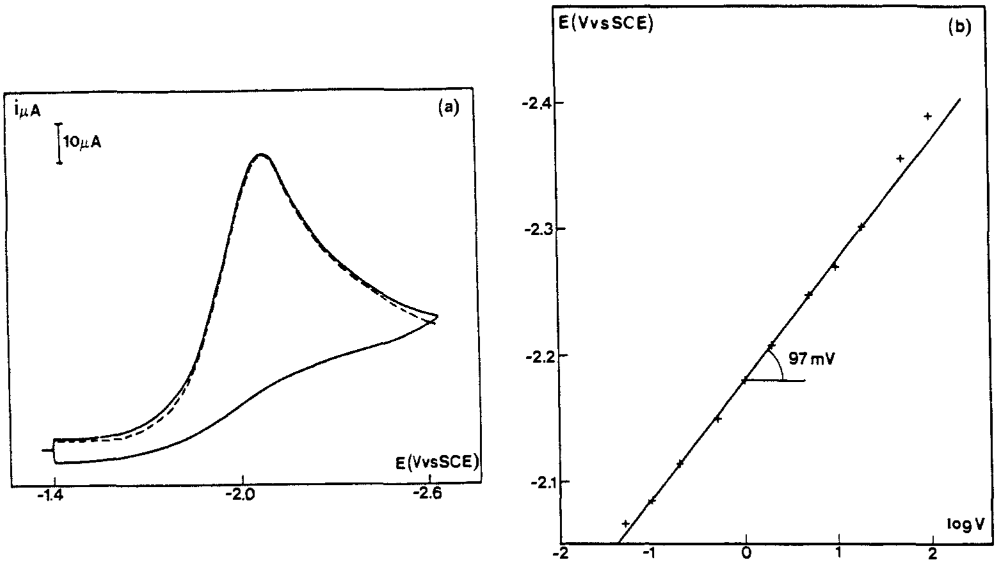

Figure 1. Cyclic voltammetry of CF_3Br, 2 mM at a gc electrode in DMF and 0.1 M NBu_4BF_4 at 25 °C. Graph a shows cyclic voltammogram at 0.2 V/s; full line is the experimental curve; dotted line, simulated curve. Graph b shows variation of the peak potential with the scan rate.

Table I. Reduction Potentials and Number of Electrons per Molecule for the Reduction of CF_3Br and CF_3I at Various Electrodes[a]

compd		gc	Pt	Au	Hg	stainless steel	Ni	Cu
CF_3Br[d]	Ep[b]	-2.07	-1.55	-1.23	-1.25	-1.90	-1.33	-1.18
	n[c]	2.1	1.6	1.7	1.7	1.3	1.2	1.5
CF_3I[e]	Ep[b]	-1.52	-0.95	-0.70	-0.65	-	-	-
	n[c]	1.0	1.2	1.1	1.0	-	-	-

[a] In DMF and 0.1 M NBu_4BF_4. [b] Cyclic voltammetry peak potential (vs aqueous SCE) at 0.2 V/s. [c] Number of electrons per molecule.[17b] [d] At 25 °C. [e] At 5 °C.

ensuing chemistry, radical or carbanionic, would be triggered as a function of the electrode potential in the heterogeneous case and of the standard potential of the electron donor in the homogeneous case. Moreover, comprehension of what happens with outer-sphere reagents, clearly identified as such, also provides a framework for uncovering the possible inner-sphere character of other reagents. The question is of particular relevance to organometallic stoichiometric or catalytic reactions:[1] Is the reactivity of a transition-metal complex toward an organic substrate a result of its redox characteristics or of more intimate chemical (inner sphere) properties is an important issue in many instances?

Direct electrochemistry or indirect electrochemistry, i.e., electrochemical generation of homogeneous electron donors, are valuable tools for obtaining such information. Although the problem posed is of general importance, past investigations in this field have mainly been concerned with the generation of aryl and alkyl radicals, mostly from the parent halides. Aryl radicals are quite easy to reduce, much easier than the parent halides in most cases. In spite of this, an aryl radical chemistry can be triggered electrochemically or by other reductive means as exemplified by the occurrence of many $S_{RN}1$ reactions[2] and of reactions based on H-atom abstraction.[3] An important factor for understanding and mastering the competition with reduction of the aryl radical into the carbanion is the fact that, in dissociative electron transfer to aryl halides, electron transfer and bond breaking are stepwise rather than concerted. Alkyl radicals are much more difficult to reduce than aryl radicals[4] both for thermodynamic and kinetic reasons.[4a] The reduction of the parent alkyl halides is also more difficult[5] than that of the aryl halides again for thermodynamic and kinetic reasons.[5a] It involves concerted rather than stepwise electron transfer and bond breaking.[5,6] As a consequence, the electrochemical reduction of alkyl halides gives rise to a carbanion rather than a radical chemistry in most cases, with the exception of secondary and tertiary alkyl iodides.[4a-c]

In the work described hereafter, we investigated similar problems in the case of perfluoroalkyl halides (R_FX) with the aim of unraveling of the conditions under which a radical or a carbanion chemistry is triggered upon reduction by heterogeneous (inert electrodes) and homogeneous (aromatic anion radicals) outer-sphere electron donors. CF_3Br, CF_3I, n-$C_6F_{13}I$, and n-$C_8F_{17}I$ were selected as examples for this study. Their direct and indirect electrochemistry was investigated in organic solvents (dimethylformamide, DMF; dimethyl sulfoxide, Me_2SO; acetonitrile, MeCN; benzonitrile, PhCN) both by means of microelectrode techniques, viz., cyclic voltammetry, and preparative-scale electrolysis. The results of this investigation are further examples of the general problems evoked earlier. They thus provide guidelines for rationalizing the numerous attempts to introduce perfluoroalkyl groups, by means of either the radical or the

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carbanion, in organic or inorganic molecules by reduction, photolysis or thermolysis of perfluoroalkyl halides or under catalysis by transition-metal complexes.[7-14]

Table II. Peak Potential and Transfer Coefficient for the First Cyclic Voltammetric Reduction Wave of $C_6F_{13}I$ at a gc Electrode

solvent	supporting electrolyte	peak potential at 0.2 V/s[a]	transfer coefficient[b]
DMF	n-Bu_4NBF_4	−1.32	0.28
MeCN	n-Bu_4NBF_4	−1.29	0.28
Me_2SO	n-Bu_4NBF_4	−1.18	0.37
PhCN	n-Bu_4NBF_4	−1.28	0.26
DMF	$LiAsF_6$	−1.27	0.32
MeCN	$LiAsF_6$	−1.38	0.34
Me_2SO	$LiAsF_6$	−0.98	0.48

[a] In V vs SCE. [b] From the peak width using eq 1.

Table III. Respective Production of CF_3H and CF_3D upon Electrolysis of CF_3Br[a] in Me_2SO/D_2O and Me_2SO-d_6/H_2O Mixtures

solvent	% D_2O	% H_2O	% CF_3H	% CF_3D
$(CH_3)_2SO$	5	0	17	83
$(CD_3)_2SO$	0	5	55	45

[a] Saturated solution (0.29 M) at, nominally, −2.0 V vs SCE.[18]

Results

Figure 1a shows a typical cyclic voltammogram obtained with CF_3Br on a glassy-carbon (gc) electrode in DMF at low scan rate (0.2 V/s). A single broad wave is observed at this scan rate as well as at any of the other investigated scan rates between 0.05 and 100 V/s. The variation of the peak potential with the scan rate is shown in Figure 1b. The peak width and the peak potentials showed a good reproducibility and no blocking of the electrode appeared upon repetitive cycling. Since follow-up chemical reactions cannot give rise to such peak-width and peak-potential variations, the rate-determining step appears to be the initial electron transfer. The transfer coefficient, α, can thus be derived either from the peak width, $E^p - E^{p/2}$, or from the variations of the peak potential, E^p, with the scan rate, v.[15,16] α is thus found

$$\alpha = \frac{RT}{F}\,\frac{1.85}{E^{p/2} - E^p} \tag{1}$$

$$\alpha = -\frac{RT}{2F}\,\frac{\partial(\ln v)}{\partial E^p} \tag{2}$$

as equal to 0.30 by both methods.

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(11) (a) Hydroperfluoroalkylation of carbon–carbon double bonds by perfluoroalkyl iodides and bromides in the presence of $CpTiCl_2$[11b] or of perfluoroalkyl iodides in the presence of copper bronzes.[11c] The same reaction was also observed to occur upon anodic oxidation of perfluoro carboxylates in the presence of the olefin.[11d-f] (b) Kitazume, T.; Ischikawa, N. *J. Am. Chem. Soc.* **1985**, *107*, 5186. (c) Coe, P. L.; Milner, N. E. *J. Organomet. Chem.* **1972**, *39*, 395. (d) Brookes, C. J.; Coe, P. L.; Owen, D. M.; Pedler, A. E.; Tatlow, J. C. *J. Chem. Soc., Chem. Commun.* **1974**, 323. (e) Renaud, R. N.; Champagne, P. J. *Can. J. Chem.* **1975**, *53*, 529. (f) Muller, N. *J. Org. Chem.* **1986**, *51*, 263.

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(13) (a) Reaction of perfluoroalkyl halides with carbonyl compounds namely: condensation of R_FI with carbonyl compounds in the presence of calcium,[13c] synthesis of hemifluorinated ketones $R{-}CO{-}R_F$ by reaction of Grignard reagents, R_FMgI, with acyl chlorides,[13b-d] or from perfluoroalkyl iodides and bromides in the presence of transition metal complexes[13e-f] electrochemical trifluoromethylation of carbonyl compounds by CF_3Br[13g-i] synthesis of perfluoro carboxylic acids by reaction of carbon dioxide with Grignard reagents[13j,k] or organozinc derivatives[13l] obtained from perfluoroalkyl iodides, and also by electrochemical reduction of R_FX, in the presence[13m] or in the absence of carbon dioxide.[13n] In the latter case, the solvent, dimethylformamide, is involved in the reaction. (b) Santini, G.; Le Blanc, M.; Riess, J. G. *J. Organomet. Chem.* **1977**, *140*, 1. (c) Moreau, P.; Naji, N.; Commeyras, A. *J. Fluorine Chem.* **1987**, *34*, 421. (d) Naji, N.; Moreau, P. *J. Fluorine Chem.* **1988**, *38*, 19. (e) O'Reilly, N. J.; Maruta, M.; Ishikawa, N. *Chem. Lett.* **1984**, 517. (f) See ref 11b. (g) Leroux, F.; Jaccaud, M. French. Pat. 8507595. (h) Sibille, S.; D'Incan, E.; Leport, L.; Perrichon, J. *Tetrahedron Lett.* **1986**, 129. (i) Andrieux, C. P.; Gelis, L.; Savéant, J.-M. *J. Electroanal. Chem.*, submitted for publication. (j) Moreau, P.; Dalverny, G.; Commeyras, A. *J. Fluorine Chem.* **1975**, *5*, 265. (k) *Ibid.* J. *Chem. Soc., Chem. Commun.* **1976**, 174. (l) Blancou, H.; Moreau, P.; Commeyras, A. *J. Chem. Soc., Chem. Commun.* **1976**, 885. (m) Calas, P.; Commeyras, A. *J. Electroanal. Chem.* **1978**, *89*, 363. (n) Benefice-Malouet, S.; Blancou, H.; Calas, P.; Commeyras, A. *J. Fluorine Chem.* **1988**, *39*, 125.

(14) (a) Synthesis of perfluorosulfinic acids R_FSO_2H by reaction of R_FX with sulfur dioxide under reducing conditions, i.e., in the case of CF_3Br, by zinc in DMF[14b-d] or by electrochemical reduction in dimethylformamide[14e,f] and in the case of long-chain perfluoroalkyl iodides by zinc–copper alloys in dimethyl sulfoxide or zinc alone ine dimethylformamide[13k] and by electrochemical reduction in the same solvent.[13l] (b) Wakselman, C.; Tordeux, M. *Bull. Soc. Chim. Fr.* **1986**, *6*, 1868. (c) Wakselman, C.; Tordeux, M. French. Pat. 2564829. (d) Wakselman, C.; Kaziz, C. *J. Fluorine Chem.* **1986**, *33*, 347. (e) Andrieux, C. P.; Gelis, L.; Jaccaud, M.; Leroux, F.; Savéant, J.-M. French. Pat. 88.09336. (f) Folest, J.-C.; Nedelec, J.-Y.; Perrichon, J. *Synth. Commun.* **1988**, *18*, 1491.

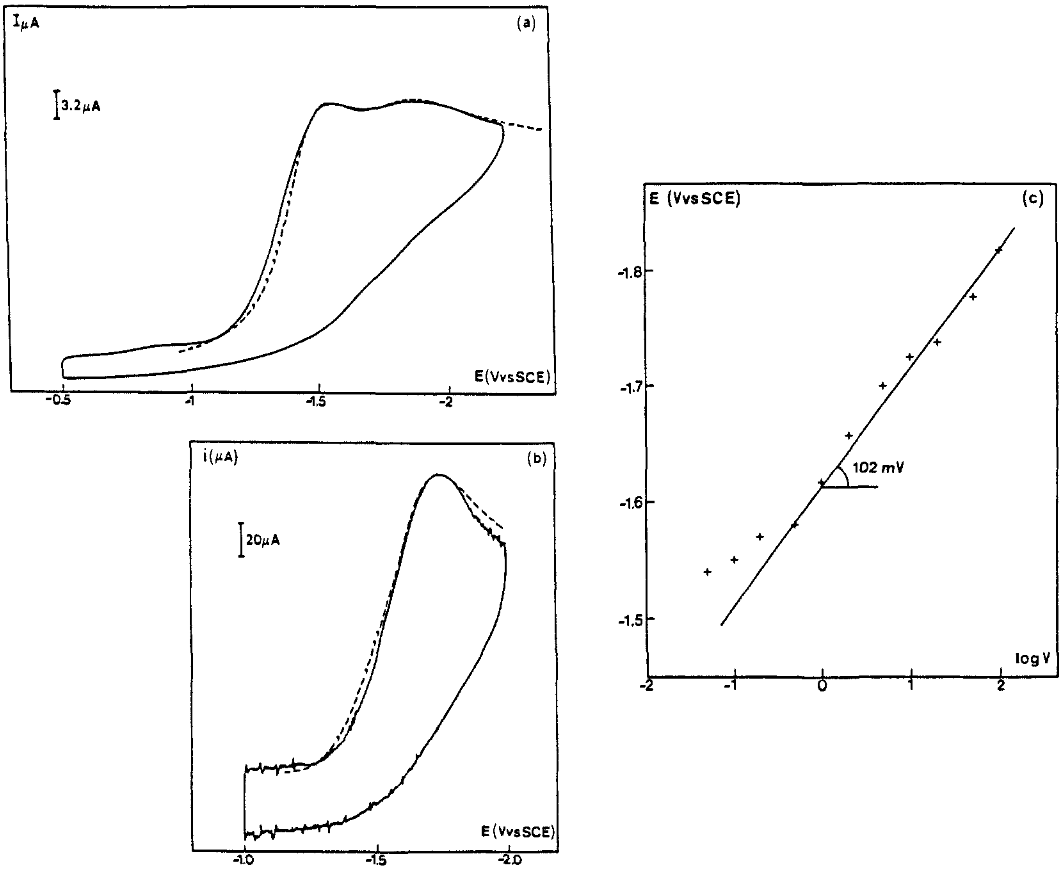

Figure 2. Cyclic voltammetry of CF_3I (2 mM) at a gc electrode in DMF and 0.1 M NBu_4BF_4 at 5 °C as a function of the scan rate: 0.2 (a), 10 (b) V/s; full lines are experimental curves; dotted lines, simulated curves (see text). Graph c shows variation of the peak potential with the scan rate.

Once α is known, it is possible to estimate, from the peak current, i_p, the number of electrons per molecule, n, exchanged in the reaction:[15,16d-f]

$$i_p = 0.496nFSD^{1/2}\,(\alpha Fv/RT)^{1/2}c \qquad (3)$$

(S, electrode surface area; D, diffusion coefficient of CF_3Br). Taking as an approximate estimate of D the value derived from the peak current of the reversible wave of fluorenone in the same medium, n is found equal to 1.9, i.e., very close to 2. We also note that addition of water or of a weak acid such as phenol to the solution does not affect the peak height to any significant extent.

Similar results were obtained on the same electrode in MeCN whereas the wave is less well-defined in Me_2SO, exhibiting a shape that is reminiscent of the interference of adsorption phenomena. Its height corresponds to the exchange of approximately 1.2 electrons per molecule and increases up to a value of 2 e/molecule upon addition of water or of phenol. The latter values is in fact not very meaningful since the application of eqs 1–3 which correspond to a Butler–Volmer rate law is not quite justified in view of the fact that adsorption phenomena affect the shape of the wave.

Typical cyclic voltammograms obtained with CF_3I at a gc electrode in DMF + 0.1 NBu_4BF_4 at 5 °C[17a] are shown in Figure 2. Two closely spaced waves, the second being much smaller than the first, are observed between 0.05 and 2 V/s. They then merge upon raising of the scan rate. At low scan rates, when two distinct waves are observed, the value of α characterizing the first wave was found equal to 0.26 from application of eq 1.

In the range of scan rates where a single wave was observed, α was found equal to 0.28 and 0.30 from the application of eqs 1 and 2, respectively. From the values of α thus determined it was found, by application of eq 3, still approximating the diffusion coefficient by that of fluorenone, that the number of electrons per molecule is close to one at the first wave of the two-wave system obtained at low scan rates and to two for the single wave obtained at higher scan rates. The two waves observed below 2 V/s are less reproducible than the single wave obtained at higher scan rates. The waves tends to flatten out and decrease upon repetitive cycling. Reproducibility was improved by carefully polishing the gc disk after each scan. These observations indicate that the reaction products tend to passivate the electrode surface but also that meaningful data can nevertheless be derived from the first scan.

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(15) Andrieux, C. P.; Savéant, J.-M. *Electrochemical Reactions in Investigation of Rates and Mechanisms of Reactions, Techniques of Chemistry*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. VI/4E, Part 2, pp 305–390.

(16) (a) As discussed elsewhere,[4a,16b,c] even if the rate law governing the electron transfer reaction is not of the Butler–Volmer type[15,16d-f] but of the Hush–Marcus type,[16g,m] i.e., quadratic instead of linear, it can be linearized within the potential range where the corresponding cyclic voltammetric wave develops at a given scan rate. The Butler–Volmer law can thus be applied at each scan rate, the transfer coefficient, α, possibly decreasing as the scan rate is raised. (b) Lexa, D.; Savéant, J.-M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 6464. (c) Andrieux, C. P.; Savéant, J.-M. *J. Electroanal. Chem.* **1989**, *265*, 15. (d) Delahay, P. *Double layer and Electrode Kinetics*; Interscience: New York, 1965; Chapter 2. (e) Matsuda, H.; Ayabe, Y. *Z. Elektrochem.* **1955**, *59*, 494. (f) Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1973**, *44*, 327. (g) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 4966. (h) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 962. (i) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557. (j) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (k) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. (l) Marcus, R. A. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7. (m) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(17) (a) The experimental procedure was different for CF_3Br and CF_3I. In the first case, the experiments were carried out at room temperature and a continuous stream of gaseous CF_3Br was maintained over the solution at room temperature whereas in the second, CF_3I was introduced into the solution and a slight stream of nitrogen maintained over the solution. CF_3I then remains in the solution for periods of time sufficient to perform the cyclic voltammetry experiment provided the temperature is not too high (5 °C in the present case). (b) Determined by combined application of eqs 1 and 3. This is at best a rough estimation since the Butler–Volmer kinetic law on which eqs 1 and 3 are based may well not be strictly applicable in the present case since a chemical catalysis involving an heterogeneous innersphere electron transfer takes place (see the Discussion section).

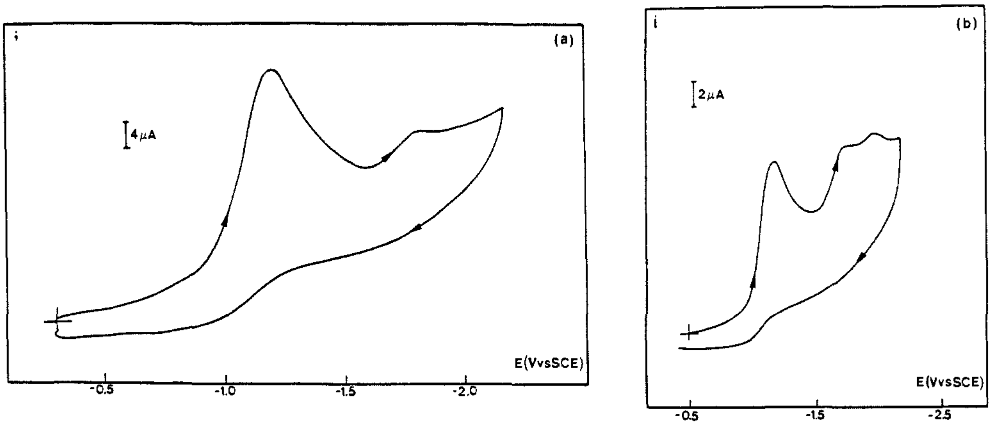

Figure 3. Cyclic voltammetry of $C_6F_{13}I$ at a gc electrode in DMF (a) and Me_2SO (b) and 0.1 M NBu_4NBF_4 at 22 °C. Concentrations are as follows: 1.35 (a) and 0.96 (b) mM. Scan rates are as follows: 0.18 (a) and 0.20 (b) V/s.

A brief investigation of the cyclic voltammetry behavior of CF_3Br and CF_3I at other electrodes was also carried out, showing that considerable positive shifts of the reduction potential as compared to its value on gc can be obtained depending upon the nature of the electrode material (Table I).

The cyclic voltammetry of long chain perfluoroalkyl iodides, namely, $C_6F_{13}I$ and $C_8F_{17}I$, was investigated with the gc electrode in DMF, Me_2SO, MeCN, and PhCN with tetrabutylammonium and lithium as supporting cations. Both compounds exhibit the same behavior. Two cathodic irreversible waves were observed in all cases with a third one in Me_2SO. Typical cyclic voltammograms are shown in Figure 3. While the first wave appeared grossly reproducible, the second and third waves were critically dependent in location and height upon the way in which the electrode surface was polished. The current-potential curves practically disappeared after the first scan if the electrode was not carefully polished between the two scans. The main characteristics of the first wave are summarized in Table II. The apparent number of electrons per molecule was found to be close to 1 in all cases. As in the preceding cases, adsorption appears to play a more important role in Me_2SO than in the other solvents which may be related to the lesser solubility of the starting compounds in this solvent. The second wave appeared to be located in the range −1.8–1.9 V vs SCE, at 0.2 V/s in DMF and Me_2SO, around −2.4 V in MeCN and not detectable in PhCN. (PhCN is significantly easier to reduce than the other solvents.)

Preparative-scale electrolysis and coulometry of CF_3Br were carried out on a carbon electrode in DMF. In these experiments a continuous stream of CF_3Br was passed through the solution. The concentration of CF_3H in the gas phase was determined by gas-phase chromatography by comparison with the peaks obtained in a set of blank experiments carried out with known N_2–CF_3Br–CF_3H mixtures. No trace of C_2F_6 was detected. For a current intensity of 0.1 A on a 20-cm^2 electrode, the production of CF_3H per unit of time thus determined was found to be 5.2×10^{-7} mol/s. Since the expected CF_3H production is 1.04×10^{-6} and 5.18×10^{-7} mol/s for a one and two electron consumption per molecule of CF_3H formed and since CF_3H is the only electrolysis product, we concluded that, two electrons are consumed per molecule of CF_3Br formed, in keeping with the cyclic voltammetry results.

Direct preparative-scale electrolysis of $C_6F_{13}I$ and $C_8F_{17}I$ was found impossible to carry out in all the above-mentioned solvents due to fouling of the electrode surface in keeping with the cyclic voltammetry behavior described above.

Reductive deuteration experiments aimed at determining the fate (further reduction at the electrode followed by protonation and/or hydrogen atom abstraction from the solvent?) of the initially formed $CF_3^\bullet$ radical were carried out in Me_2SO rather than in DMF since perdeuterated Me_2SO is of easier access than perdeuterated DMF. The results obtained upon electrolysis under the same conditions as described above in opposite mixtures, Me_2SO/D_2O on one hand, Me_2SO-d_6/H_2O on the other are listed in Table III. The gas-phase reaction mixtures were analyzed by mass spectrometry using the MS/MS technique described in the Experimental Section.

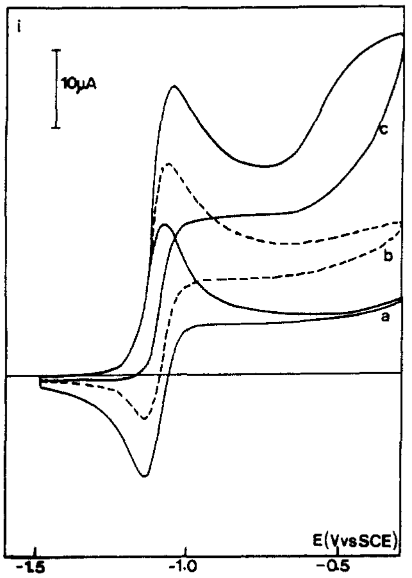

Figure 4. Redox catalysis of the reduction of CF_3I by 3-(trifluoromethyl)nitrobenzene (2 mM) at a gc electrode in DMF and 0.1 M NBu_4BF_4 at 25 °C. Scan rate is 0.1 V/s. CF_3I concentrations (mM) are as follows: 0 (a), 2 (b), 8 (c).

Table IV. Redox Catalysis of the Reduction of CF_3I and CF_3Br by Electrochemically Generated Aromatic and Heteroaromatic Anion Radicals

	catalyst	standard potential (V vs SCE)	rate constant (M^{-1} s^{-1})
CF_3I	1,4-diacetylbenzene	−1.435	2.0×10^7
	9-fluorenone	−1.245	2.3×10^6
	nitrobenzene	−1.08	2.5×10^4
	3-(trifluoromethyl)-nitrobenzene	−0.90	5.4×10^2
CF_3Br	1-cyanonaphthalene	−1.84	1.7×10^7
	4-cyanopyridine	−1.75	6.5×10^6
	1,4-dicyanobenzene	−1.52	4.4×10^4
	1.4-diacetylbenzene	−1.435	6.3×10^3
	9-fluorenone	−1.245	4.5×10^2

In order to investigate the reaction of CF_3Br and CF_3I by homogeneous outer-sphere electron donors, their redox catalytic[15] reduction by a series of aromatic and heteroaromatic anion radicals[16b,19a-d] was carried out by cyclic voltammetry. As illustrated

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[18] In view of the large concentration of CF_3Br the actual electrolysis potential is expected, owing to ohmic drop, to lie in the −1.7 to −1.8 V vs SCE region.

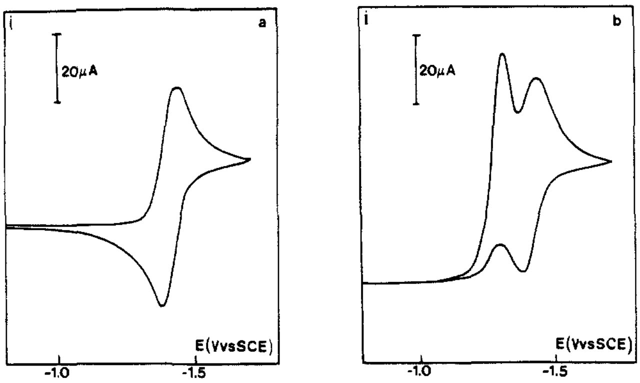

Figure 5. Reduction of CF_3I by the anion radical of 1,4-diacetylbenzene at a gc electrode in DMF and 0.1 M NBu_4BF_4 at 25 °C: an example of "total catalysis". The two graphs show cyclic voltammetry of 1,4-diacetylbenzene (2 mM), in the absence (a) and presence (b) of CF_3I (2 mM). Scan rate is 0.1 V/s.

Table V. Redox Catalysis of the Reduction of $C_6F_{13}I$ in DMF[a] by Aromatic Anion Radicals

catalyst	standard potential (V vs SCE)	rate constant (M^{-1} s^{-1})
9-fluorenone	−1.245	1.0×10^6
nitrobenzene	−1.08	5.1×10^4
4-nitrobenzonitrile	−0.85	1.1×10^4
2-nitrobenzaldehyde	−0.83	5.9×10^3
4-nitropyridine N-oxide	−0.77	2.0×10^3

[a] +0.1 M NBu_4BF_4, temperature = 22 °C.

Table VI. Nitrobenzene Redox Catalyzed Preparative-Scale Electrolysis of $C_6F_{13}I$[a]

solvent	$C_6F_{13}I$[b] consumed, %	$C_6F_{13}H$, %[b,c]	other products
MeCN	40	38	none
DMF	47	42	none
Me_2SO	47	24	A, 21; B, 1[d]
	66	19	A, 40; B, 5[d]
PhCN	86	7	C, 43; D, 7;[d] $C_{12}F_{26}$, 9[e]

[a] $[C_6F_{13}I]$ = 50–70 mM; [nitrobenzene] = 25–35 mM; supporting electrolyte, NBu_4ClO_4; electrolysis potential, −1.25 V vs SCE. [b] Determined by GC. [c] By reference to $C_6F_{13}I$ consumed. [d] See text; C, 4-(perfluorohexyl)benzonitrile; D, 4-(dihydroperfluorohexyl)benzonitrile. [e] Determined after extraction from the carbon electrode surface by (trifluoromethyl)benzene.

in Figure 4, with the example of CF_3I, we start from the reversible cyclic voltammogram of the parent aromatic hydrocarbon or heterocycle, add increasing amounts of the substrate to the solution, and observe the ensuing loss of reversibility of the catalyst wave and increase of its cathodic peak.[15,19] We also note that, given the excess factor, i.e., the ratio of the halide over catalyst concentrations, the increase of the catalyst wave is the larger the smaller the scan rate.[15,19] The various aromatic hydrocarbons and heterocycles used as redox catalysts are listed in Table IV together with their standard potentials. As expected, the more negative its standard potential,[15,19] the larger the increase of the catalyst wave, all the other factors, substrate, concentrations, and scan rate, remaining constant. With CF_3I, for the most negative catalyst, viz., 1,4-diacetylbenzene, the catalytic efficiency is so strong that "total catalysis" [15,19] occurs (Figure 5). Two waves then appear, the first being controlled by the diffusion of the halide, whereas the second reversible wave represents the reduction of the catalyst that has not been consumed in the catalytic process taking place at the first wave.[15,19] For all catalysts, the reaction of CF_3I with the aromatic anion radicals gives rise to a purely catalytic process without the interference of coupling between the $CF_3^\bullet$ radical and the aromatic catalyst, unlike what happens with nonfluorinated alkyl radicals where extensive coupling takes place.[5a,6d] Under the "total catalysis" conditions found with 1,4-diacetylbenzene, it is also possible to determine the stoichiometry of the reaction, i.e., the number, n, of aromatic anion radicals involved in the reduction of CF_3I from:[15,19]

$$\frac{i_p}{i_p^\circ} = 1.365n\frac{[\text{halide}]}{[\text{catalyst}]} \qquad (4)$$

In the framework of the following reaction scheme (P, aromatic hydrocarbon; Q, its anion radical):

Scheme I

$$P + e^- \rightleftharpoons Q \qquad (0)$$

$$Q + CF_3X \xrightarrow{k_1} P + CF_3^\bullet + X^- \qquad (I)$$

$$Q + CF_3^\bullet \xrightarrow{k_2} P + CF_3^-(\xrightarrow{H^+} CF_3H) \qquad (II)$$

$$CF_3^\bullet \xrightarrow{k_3} \text{products} \qquad (III)$$

where $CF_3^\bullet$ is either reduced by the aromatic anion radical or disappears without further consumption of electrons, n = 2 indicates that reaction II predominates over reaction III, n = 1 indicates the opposite, whereas an intermediate value of n would result from comparable values of k_2 [catalyst] and k_3. For CF_3I and 1,4-diacetylbenzene (Figure 5) we found that n = 1. From this result we can infer that n is, a fortiori, equal to 1 for all the other, more positive catalysts, since the rate constant for reduction of $CF_3^\bullet$ is then smaller than for 1,4-diacetylbenzene. Once the stoichiometry is known, the usual procedures[15,19] for determining the rate constant, k_1, of the reaction of the aromatic anion radicals with CF_3I can be applied, leading to the values listed in Table IV.

A similar, although quantitatively different, behavior was found with CF_3Br with the catalysts listed in Table IV. Its detailed description is given elsewhere in the report of a comparative investigation of the reaction of CF_3Br with aromatic anion radicals on one hand and with sulfur dioxide anion radical on the other.[20] Let us recall from the results what is mainly relevant to the present discussion. As found with CF_3I, 1,4-diacetylbenzene and 9-fluorenone anion radicals are not able to reduce $CF_3^\bullet$ (reaction II) competitively with reaction III. Thus n = 1 for CF_3Br also. Total catalysis is found for 1-cyanonaphthalene with n = 1.5, thus indicating a balanced competition between reaction II and III. The variations of the rate constant, k_1, of the reaction of CF_3I and CF_3Br with the various aromatic anion radicals with their standard potential are represented in Figure 6.

Redox catalysis by electrochemically generated aromatic anion radicals was also investigated in the case of $C_6F_{13}I$. It appears as more efficient than in the case of CF_3I in the sense that the same catalyst gives rise to a stronger catalytic current in the first case than in the second. This led us to use several catalysts more positive than with CF_3I (Table V). With nitrobenzene, a "total catalysis" situation is reached in all four solvents as shown in Figure 7 in the case of DMF. The number of electrons per molecule was then found equal to 1. "Total catalysis" was also observed with fluorenone in DMF, and the number of electrons per molecule again found equal to 1. Weaker catalytic currents were obtained with the other three, more positive, catalysts (Figure 7), the rate constant then being determined by the i_p/i_p° vs RTk_1 [catalyst]/$F\upsilon$ working curve procedure.[15,19] The variations of the resulting rate constants with the standard potential of the aromatic anion radical catalysts are shown in Figure 7c.

In an effort to overcome the impossibility of carrying out direct electrolyses of $C_6F_{13}I$, redox catalysis was also used at the preparative scale. The results thus obtained in the four solvents with

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(19) (a) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 3431. (b) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; M'Halla, F.; Savéant, J.-M. *J. Am. Chem. Soc.* **1980**, *102*, 3806. (c) Andrieux, C. P.; Dumas-Bouchiat, J.-M.; Savéant, J.-M. *J. Electroanal. Chem.* **1980**, *113*, 19. (d) Andrieux, C. P.; Savéant, J.-M.; Zann, D. *Nouv. J. Chim.* **1984**, *8*, 107. (e) Savéant, J.-M.; Su, K. B. *J. Electroanal. Chem.* **1984**, *171*, 341.

(20) Andrieux, C. P.; Gélis, L.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 786.

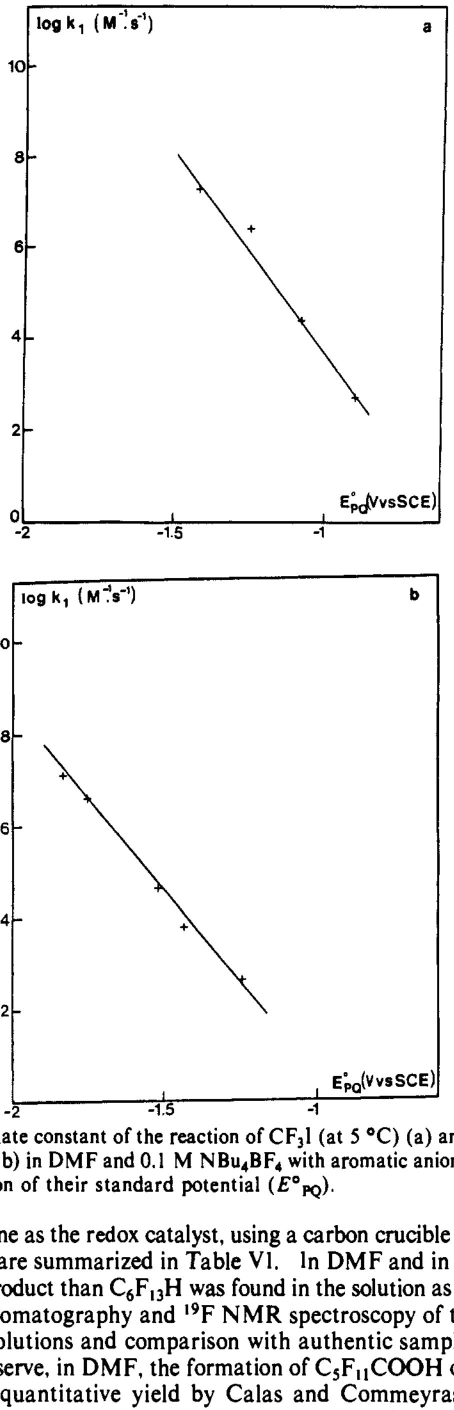
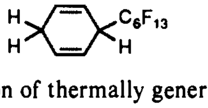


Figure 6. Rate constant of the reaction of CF_3I (at 5 °C) (a) and CF_3Br (at 25 °C) (b) in DMF and 0.1 M NBu_4BF_4 with aromatic anion radicals as a function of their standard potential ($E°_{PQ}$).

nitrobenzene as the redox catalyst, using a carbon crucible working electrode, are summarized in Table VI. In DMF and in MeCN, no other product than $C_6F_{13}H$ was found in the solution as checked by gas chromatography and ^{19}F NMR spectroscopy of the electrolyzed solutions and comparison with authentic samples. We did not observe, in DMF, the formation of $C_5F_{11}COOH$ obtained in nearly quantitative yield by Calas and Commeyras[13n] and deemed this to result from the initial addition of $C_6F_{13}^•$ radicals on DMF. These authors did not obtain $C_6F_{13}H$ whereas its yield reaches 42% in our case. The reduction was however carried out under quite different conditions: direct reduction at the electrode in the presence of LiCl and allylic alcohol in one case[13n] and indirect electrolysis by means of an homogeneous mediator in the other. In Me_2SO, besides $C_6F_{13}H$, two other, yet unidentified products, A and B, were observed by GC and ^{19}F NMR (see the Experimental Section). In PhCN, the yield in $C_6F_{13}H$ is significantly lower than in the three other solvents, and two other products were detected in the solution, namely, 4-(perfluorohexyl)benzonitrile and its dihydro derivative, as results from a ^{19}F NMR comparison with the closely similar compounds, $C_6H_5C_6F_{13}$ and



obtained in the reaction of thermally generated $C_6F_{13}^•$ radicals with benzene.[21]

The possibility that insoluble products could be formed and accumulate at the carbon crucible surface was investigated in the case of benzonitrile with use of (trifluoromethyl)benzene as the recovering solvent. We indeed detected the dimer, $C_{12}F_{26}$, by a gas chromatography comparison with an authentic sample. It was verified that the dimer is totally insoluble in any of the four electrolysis solvents and only slightly soluble in (trifluoromethyl)benzene.

Lastly, the pK_a of CF_3H was determined. This was done in Me_2SO rather than in the other solvents because Me_2SO is stable in sufficiently basic conditions for this determination to be carried out. We used in this connection the same colored pH indicators method as previously described by Bordwell et al.[22] Triphenylmethane (28.5) and acetonitrile (29.2) were found to be the appropriate indicators. We thus found that CF_3H and water have approximately the same pK_a, located between 28.5 and 29.2. This is in fair agreement with the pK_a estimated for CF_3H/CF_3^- couple in DMF (25.5) by an indirect and quite different method.[23]

As discussed in the following the electrochemistry of CF_3I might be affected by the formation of a complex between CF_3^-, which would possibly be formed at the first wave, and the starting material. We took advantage of the preceding pK_a determination to test this possibility. CF_3H (5×10^{-2} M) and hydroxide ions (5×10^{-2} M), generating about 2.5×10^{-2} M CF_3^-, were added to a solution of 2×10^{-3} M CF_3I in Me_2SO. No detectable change of the initial cyclic voltammetric waves of CF_3I was observed upon addition of CF_3^- during the first 30 min after mixing.

Discussion

Let us first discuss the kinetics and mechanism of the reduction of $CF_3^•$ in an attempt to define the conditions leading to a $CF_3^•$ or a CF_3^- chemistry upon reduction of CF_3Br and CF_3I. For this we assume, as will be discussed in details furtheron, that either the dissociative electron transfer to CF_3Br and CF_3I is a concerted process, or if not, that the lifetime of the $CF_3X^{•-}$ anion radical is so short that it has no time to accumulate while $CF_3^•$ undergoes other reactions.[24] Under such conditions, the triggering of a $CF_3^•$ or a CF_3^- chemistry is solely a matter of competition between the rate of electron transfer to $CF_3^•$ from the heterogeneous or homogeneous reagent which serve to generate it from CF_3X and the other reactions it may undergo in the solution. Within this framework we note the following facts:

1. The electrochemical reduction of CF_3Br yields CF_3H quantitatively. The deuterium incorporation experiments show that CF_3H thus formed comes both from H-atom abstraction from the solvent by $CF_3^•$ and from its reduction into CF_3^- followed by protonation. This results from the following discussion.

As in previous similar experiments concerning aromatic halides,[25] we can assume that Me_2SO provides H atoms whereas water provides protons. The relative amount of CF_3D vs CF_3H

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(21) Krespan, C. G. *J. Fluorine Chem.* **1988**, *40*, 129.

(22) (a) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; MacCallum, R. J.; MacCallum, G. T.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (b) Bordwell, F. G. *Pure Appl. Chem.* **1977**, *49*, 963.

(23) (a) From the approximate linear correlation existing between the pK_a of AH and the polarographic half-wave potential of the corresponding of AHgA derivative.[23b] (b) Butin, K. P.; Kashin, A. N.; Beletskaya, I. P.; German, L. S.; Polishuk, V. R. *J. Organomet. Chem.* **1970**, *25*, 11. (c) In the accessible range, i.e., up to 18, pK_a values in DMF[23d-g] are 0.5-1 unit larger than in Me_2SO.[23h] (d) Julliard, J.; Loubinoux, B. *C. R. Seances Acad. Sci., Ser. C* **1967**, *264*, 1680. (e) Julliard, J.; Mallet, A. *C. R. Seances Acad. Sci., Ser. C* **1967**, *264*, 2098. (f) Bréant, M.; Demange-Guérin. *Bull. Soc. Chim. Fr.* **1969**, 2935. (g) Kolthoff, I. M.; Chantooni, M. K.; Smagowski, J. *Anal. Chem.* **1970**, *42*, 1622. (h) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(24) Say a lifetime shorter than 0.1 ns. Then, in the electrochemical case, if the electrode potential at which $CF_3X^{•-}$ is produced from CF_3X is such that any ensuing $CF_3^•$ radical is immediately reduced at the electrode surface, $CF_3^•$ would diffuse back to the electrode surface before having time to undergo first-order or pseudo-first-order reactions with rate constants as large as 10^9 s^{-1}. In the homogeneous case, $CF_3^•$ would not accumulate even if produced with a pseudo-first-order rate constant of 10^9 s^{-1}.

(25) (a) M'Halla, F.; Pinson, J.; Savéant, J.-M. *J. Electroanal. Chem.* **1978**, *89*, 347. (b) M'Halla, F.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1980**, *102*, 4120.

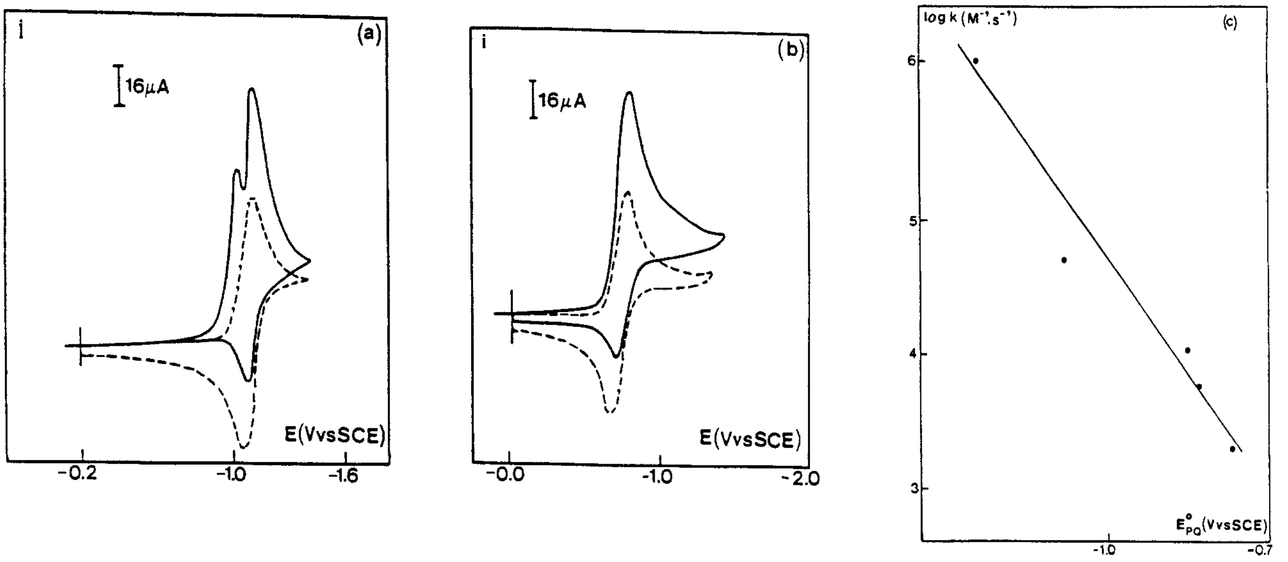

Figure 7. Redox catalysis of the reduction of $C_6F_{13}I$ by electrochemically generated aromatic anion radicals in DMF. The curves of a and b show cyclic voltammetry: (a) nitrobenzene (3.9 mM) in the absence (dotted curve) and presence (solid curve) of $C_6F_{13}I$ (3.9 mM) and (b) 4-nitropyridine *N*-oxide (3.36 mM) in the absence (dotted curve) and presence (solid curve) of $C_6F_{13}I$ (3.36 mM). Scan rate is 0.05 V/s. Graph c shows variation of the electron transfer rate constant with the catalyst standard potential. Temperature is 22 °C.

should thus be a measure of the competition between the D atom abstraction by $CF_3^\bullet$:

$$CF_3^\bullet + SD \rightarrow CF_3D + S^\bullet \qquad (a)$$

(SD, perdeuterated solvent) and its electron-transfer reduction:

$$CF_3^\bullet + e^- \rightarrow CF_3^- \qquad (1 - a)$$

$$CF_3^- + H_2O \rightarrow CF_3H + OH^-$$

in Me_2SO-d_6/H_2O mixtures and, vice versa, of the competition between H atom abstraction by $CF_3^\bullet$:

$$CF_3^\bullet + SH \rightarrow CF_3H + S^\bullet \qquad (a')$$

(SH, solvent) and its electron-transfer reduction:

$$CF_3^\bullet + e^- \rightarrow CF_3^- \qquad (1 - a')$$

$$CF_3^- + D_2O \rightarrow CF_3D + OD^-$$

in Me_2SO–D_2O mixtures. However, unlike the case of aromatic hydrocarbons resulting from the reductive cleavage of aromatic halides,[25] H–D exchange between $CF_3H(D)$ and $D_2O(H_2O)$ may take place in basic (basic because of the production of OH^- or DO^- accompanying the reduction of $CF_3^\bullet$) Me_2SO–water mixtures[26] during the electrolysis time (of the order of 1 h). We have thus to take into account the partial conversion of CF_3D into CF_3H:

$$\underset{(1-b)}{CF_3D} + H_2O \rightarrow \underset{(b)}{CF_3H} + DOH$$

in the first case, and the partial conversion of CF_3H into CF_3D:

$$\underset{(1-b')}{CF_3H} + D_2O \rightarrow \underset{(b')}{CF_3D} + HOD$$

in the second. The relative productions of CF_3D over CF_3H in the first case can thus be expressed as:

$$CF_3D/CF_3H = a(1 - b)/[1 - a(1 - b)] = 0.82$$

In the second case:

$$CF_3H/CF_3D = a'(1 - b') + [1 - a'(1 - b')] = 0.21$$

Thus, $a(1 - b) = 0.45$ and $a'(1 - b') = 0.17$. If we neglect the deuterium/hydrogen isotopic effect in the hydrogen (deuterium) abstraction by $CF_3^\bullet$[26] taking into account that $b'/b = 3.5$,[26] it is found that 56% of the $CF_3^\bullet$ radicals react by H(D) atom abstraction from the solvent and 44% are reduced at the electrode surface. This estimate is certainly rather crude and may change to some extent if the isotopic effect in the H(D) atom abstraction reaction would be taken into account.[26] However we can safely conclude that reduction and H-atom abstraction from the solvent are of comparable importance for the $CF_3^\bullet$ radicals produced upon electrochemical reduction of CF_3Br in Me_2SO.

2. The preceding experiments show that reduction and H-atom abstraction are in balanced competition in the potential region −1.7 to −1.8 V vs SCE.[18] This falls in line with the cyclic voltammetric data for the reduction of CF_3Br and CF_3I. CF_3Br shows a two-electron wave as expected from the more negative value of the peak potential (−2.05 V vs SCE at 0.2 V/s). In contrast, CF_3I exhibits two waves. The first one, which peak potential is located at −1.52 V vs SCE (at 0.2 V/s), corresponds to the uptake of one electron. The latter observation implies that the $^\bullet CH_2N(CH_3)CHO$ radical resulting from the H-atom transfer to $CF_3^\bullet$ is reduced at a more negative potential. That this is indeed the case is confirmed by the results of previous experiments carried out in DMF in which the same solvent radical is produced upon H-atom transfer to the aryl radical showing that the reduction of the DMF radical occurs around −1.95 V vs SCE.[19d]

3. The same trends appear in the reduction of CF_3Br and CF_3I by electrochemically generated aromatic anion radicals, noting that, unlike alkyl radicals, $CF_3^\bullet$ radicals do not couple with aromatic anion radicals. With CF_3I, all the mediators give rise to a one-electron per molecule (one anion radical per molecule of CF_3I) stoichiometry as expected from the values of their standard potentials ranging from −0.90 to −1.435 V vs SCE. In going to CF_3Br, the stoichiometry gradually increases from 1 to 1.5 as the standard potential of the mediator becomes more and more negative, the latter figure being reached at a standard potential of −1.84 V vs SCE.

4. It thus appears that the competition between H-atom transfer to $CF_3^\bullet$ and reduction of $CF_3^\bullet$ is about balanced around −1.8 V vs SCE. It is also in this region that the second reduction wave of CF_3I is observed in cyclic voltammetry. We are thus led to assign this second wave to the reduction of $CF_3^\bullet$ into CF_3^-.

Another possibility should however be discussed: If $CF_3^\bullet$ would be reduced at a potential positive to the reduction potential of CF_3I, the resulting CF_3^- anion would then form a complex with the starting material, CF_3–I–CF_3^-, the reduction of which would be responsible for the second wave. Similar complexes have indeed been obtained from the reaction of $(CF_3)_3C^-$ with $(CF_3)_3CI$.[27] As

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[26] (a) Symons, E. A.; Clermont, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 3127. (b) Symons, E. A.; Clermont, M. J.; Coderre, L. A. *J. Am. Chem. Soc.* **1981**, *103*, 3131.

[27] Farnham, N. B.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2489.

Table VII. Characteristic Parameters of the Reduction of CF_3Br, CF_3I, and $CF_3{}^{\bullet}$ [a]

compd	E^{p} [d,e]	a^{d}	E° [e,g]	$\Delta G_0^{\ddagger}$ [f,g]
CF_3Br [b]	−2.10	0.30	−0.57	0.94
CF_3I [c]	−1.52	0.26–0.30	−0.54	0.75
$CF_3{}^{\bullet}$ [c]	−1.80	0.25	−0.58	0.50

[a] In DMF and 0.1 M NBu_4BF_4 on glassy carbon. [b] At 25 °C. [c] At 5 °C. [d] At 0.2 V/s. [e] In V vs aqueous SCE. [f] In eV. [g] Rough estimation (see text).

indicated in the Results section, there is no change in the cyclic voltammogram of CF_3I upon addition of CF_3^-. If the $CF_3{-}I{-}CF_3^-$ would have been formed, and if its reduction was responsible for the second wave, a decrease of the first wave from an electron stoichiometry slightly less than 2 toward zero and an increase of the second wave from its small initial value up to 2 should have been found. This was not actually observed: the two waves keep the same height with the first corresponding to a 1 e/molecule stoichiometry. The conclusion that the formation of a $CF_3{-}X{-}CF_3^-$ complex does not appear to be significant in the electrochemistry of CF_3I and CF_3Br also falls in line with the observation that linear perfluoroalkyl iodides do not form $R_FIR_F^-$ complexes with R_F^- under the same conditions where $(CF_3)_3CI$ and $(CF_3)_3C^-$ do.[28]

Still another possibility is that the second wave of CF_3I would correspond to the reduction of the $^{\bullet}CH_2N(CH_3)CHO$ radical ($S^{\bullet}$) resulting from the H-atom transfer to $CF_3{}^{\bullet}$ rather than to the reduction of $CF_3{}^{\bullet}$ itself. If $S^{\bullet}$ was easier to reduce than $CF_3{}^{\bullet}$, the first one-electron wave of CF_3I should be followed by two small waves corresponding successively to the reduction of $S^{\bullet}$ and $CF_3{}^{\bullet}$ rather than a single small wave corresponding to the reduction of $CF_3{}^{\bullet}$ in the opposite case.[16c] The latter situation is observed experimentally. This also falls in line with the chemical intuition, based on inductive effects, that $CF_3{}^{\bullet}$ is easier to reduce than $^{\bullet}CH_2N(CH_3)CHO$ and with the fact that the latter is reduced around −1.95 V vs SCE.[19d]

5. In the reduction of CF_3Br by the anion radical of 1-cyanonaphthalene (E°_{PQ} = −1.84 V vs SCE) the electron stoichiometry, 1.5, indicates that $k_2C_P^{\circ}/k_3$ (Scheme I) is approximately equal to 1 (C_P°, catalyst concentration). On the other hand, simulation[4a,16c] of the cyclic voltammograms of CF_3I (Figure 2) in the framework of Butler–Volmer rate law for the first and second electron-transfer steps:

$$\frac{i_1}{FS} = k_1^{f} \exp\left(-\frac{\alpha_1 F}{RT}E\right)[CF_3X]_0 \qquad (5)$$

$$\frac{i_2}{FS} = k_2^{f} \exp\left(-\frac{\alpha_2 F}{RT}E\right)[CF_3{}^{\bullet}]_0$$

(where i_1,i_2 are currents corresponding to the reduction of CF_3X and $CF_3{}^{\bullet}$, respectively; E, electrode potential; S, electrode surface area; α_1,α_2, transfer coefficients; k_1^f,k_2^f, forward electron transfer rate constants for the first and the second steps, respectively; $[CF_3X]_0$,$[CF_3{}^{\bullet}]_0$, concentration of the two species at the electrode surface) leads to the values of α listed in Table VII and to a value of the effective reduction potential of $CF_3{}^{\bullet}$:[4a,16c]

$$E^{*} = \frac{RT}{\alpha_2 F} \ln \frac{k_2^{f}}{(Dk_3)^{1/2}} = E^{p} + 0.78\,\frac{RT}{\alpha_2 F}$$

equal to −1.71 V vs SCE. It follows that the heterogeneous rate constant, $k_2{}^{el}$, at this potential, can be expressed as

$$k_2^{el} = (Dk_3)^{1/2} = Z^{el} \exp\left(-\frac{\Delta G_{el}^{\ddagger}}{RT}\right) \qquad (6)$$

(Z^{el}, heterogeneous collision frequency; $\Delta G_{el}{}^{\ddagger}$, activation free energy of the electrochemical electron transfer at the same potential). On the other hand, at −1.84 V vs SCE:

$$k_2[-1.84] = \frac{k_3}{C_P^{\circ}} = Z^{hom} \exp\left(-\frac{\Delta G_{hom}^{\ddagger}[-1.84]}{RT}\right)$$

(Z^{hom}, homogeneous collision frequency; $\Delta G_{hom}{}^{\ddagger}$, homogeneous activation free energy). At −1.71 V vs SCE, $\Delta G_{hom}^{\ddagger}[-1.71] = \Delta G_{hom}^{\ddagger}[-1.84] - \alpha_2 \times 0.13$ (in V), i.e., since $\alpha_2 = 0.25$ (Table VII); a 0.033-eV increase of the activation free energy and thus a decrease of k_2 by a factor of 0.6 results. Thus:

$$k_2[-1.71] = \frac{k_3 \times 0.6}{C_P^{\circ}} = Z^{hom} \exp\left(-\frac{\Delta G_{hom}^{\ddagger}[-1.71]}{RT}\right)$$

Assuming then that, at the same potential, $\Delta G_{el} \simeq \Delta G_{hom}^{\ddagger}$ owing to the approximate mutual compensation of image and double layer effects:

$$k_3 = \left[\frac{C_P^{\circ} D^{1/2}}{0.6}\,\frac{Z^{hom}}{Z^{el}}\right]^2$$

By taking $D = 10^{-5}$ cm^2 s^{-1}, $Z^{hom} = 3 \times 10^{11}$ M^{-1} s^{-1}, $Z^{el} = 5 \times 10^3$ cm s^{-1} ($C_P^{\circ} = 2 \times 10^{-3}$ M^{-1}), a rough estimation of the rate constant of H atom abstraction by $CF_3{}^{\bullet}$ radical ensures:

$$k_3 = 4.10^5\ \text{s}^{-1}$$

showing that $CF_3{}^{\bullet}$ radicals are fairly good H atom scavengers.

At this point we can thus conclude that the passage from a $CF_3{}^{\bullet}$ to a CF_3^- chemistry takes place around −1.7 V vs SCE in the context of a competition between reduction of $CF_3{}^{\bullet}$ and H-atom transfer from the solvent.[29] The reduction of CF_3I at an inert electrode or by outer-sphere mediators having a more positive potential thus gives rise to a $CF_3{}^{\bullet}$ chemistry. The same is true for the reduction of CF_3Br by outer-sphere reductants having a standard potential positive to −1.7 V vs SCE whereas electrochemical reduction at the foot of reduction wave gives rise to a mixed $CF_3{}^{\bullet}{-}CF_3^-$ chemistry.

It is expected from what precedes that the reduction of the long-chain perfluoroalkyl iodides by outer-sphere reductants having standard potentials positive to the electrochemical reduction wave would produce predominantly an $R_F{}^{\bullet}$ chemistry. This is indeed what is observed since the electron stoichiometry is then 1. Another manifestation of the same is the fact that, when benzonitrile

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(28) Smart, B. E. Personal communication, April 1989.

(29) (a) It is interesting to compare the reduction characteristics of $CF_3{}^{\bullet}$ to those of $CBr_3{}^{\bullet}$. Although in the latter case no value of the reduction potential has been reported, it has been estimated that $CBr_3{}^{\bullet}$ is almost fully reduced by electron donors having an E° as positive as −0.65 V vs SCE,[29b] whereas in the case of $CF_3{}^{\bullet}$, H-atom transfer still balances reduction at a potential as negative as −1.84 V vs SCE. This seems surprising at first sight. However $CBr_3{}^{\bullet}$ and $CF_3{}^{\bullet}$ may well have different H-atom transfer and reduction characteristics and CBr_3^- and CF_3^- have different basicities and different properties toward solvatation. The $CF_3{}^{\bullet}/CF_3^-$ couple is expected to have a standard potential positive to that of the $CBr_3{}^{\bullet}/CBr_3^-$. However, the kinetics of the electron transfer which has been shown here to be quite slow in the first case is likely to be faster in the second. On the other hand, H-atom abstraction by $CBr_3{}^{\bullet}$ is likely to be less efficient than with the $CF_3{}^{\bullet}$ radical.[29c] One thus may conceive that the reduction of $CBr_3{}^{\bullet}$ takes place close to its standard potential, or even at more positive potentials if the electron transfer is fast enough for the follow-up reaction, $CBr_3^- + H^+ \rightarrow CBr_3H$ to interfere in the location of the effective reduction potential. In the case of $CF_3{}^{\bullet}$, as shown here, the electron transfer is slow and abstraction of H atom by $CF_3{}^{\bullet}$ is fast. Follow-up reactions such as $CF_3^- + H^+ \rightarrow CF_3H$ (which is also expected to be less effective than in the case of CBr_3) therefore do not affect the effective reduction potential which is then much more negative to the standard potential (by about 1.2 V) because at the same time charge transfer is slow and H atom abstraction fast. Testing of these possible reasons for the difference between the effective reduction potentials of $CF_3{}^{\bullet}$ and $CBr_3{}^{\bullet}$ should await experimental data allowing dissection of the value found in the latter case into various components. (b) Eberson, L.; Ekström, M. *Acta Chem. Scand. Ser. B* **1988**, *42*, 101. (c) $H{-}CF_3$ and $H{-}CBr_3$ have bond dissociations energies of 106 and 96 kcal/mol, respectively, to be compared with $H{-}OH$ (119) and $H{-}C_6H_5$ (110) which correspond to radicals that are very good H-atom scavengers and with $H{-}CH_2OH$ (94) and $H{-}C(CH_3)_2OH$ (91) which are good H-atom donors.[29d] (d) *Handbook of Chemistry and Physics*, 67th ed.; CRC: Boca Raton, FL, 1986; pp F178, 179.

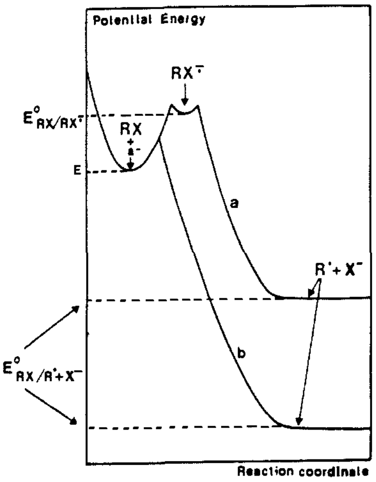
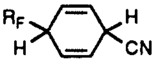


Figure 8. Intermediacy of the anion radical vs concerted bond breaking in the electron transfer to RX. Sketch of the potential energy curves in the two cases are as follows: (a) $\alpha > 0.5$ and (b) $\alpha < 0.5$.

is used as solvent, addition of $R_F^{\cdot}$ on the benzonitrile molecule is observed, leading to

$R_FC_6H_5CN$ and
C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resulting from the disproportionation of the initial addition radical. Formation of the (insoluble) $C_{12}F_{16}$ dimer in the same (poor H-atom donor) solvent also falls in line with the generation of the $R_F^{\cdot}$ radical rather than that of the R_F^- anion. Since the perfluoroalkyl halides are poor electrophiles, the dimer is quite unlikely to result from the attack of R_FI by R_F^-.

Let us now discuss the kinetics of the electrochemical reduction of CF_3Br and its reduction by aromatic anion radicals. A first remark is that the transfer coefficient is small (0.3) as with alkyl bromides (and iodides).[5] In the latter case, this was taken as an indication that electron transfer and bond breaking are concerted:

$$RX + e^- \rightarrow R^{\cdot} + X^-$$

i.e., that the reduction does not go through the anion radical $RX^{\cdot-}$. This conclusion was reached on the following bases. The shape of the wave and its shift with potential indicates, as in the present case, that the rate-determining step is the electron transfer itself rather than a preceding or follow-up reaction. In the framework of a quadratic activation vs driving force relationship (indicated by the variation of the transfer coefficient with the electrode potential[30]), this shows that the standard potential of the rate-determining step is considerably more positive than the potential where the electrochemical reaction takes place. By itself this does not tell us whether or not electron transfer and bond breaking are concerted: we know that the standard potential of the $RX/R^{\cdot} + X^-$ couple fulfills this requirement, but what about the standard potential of the $RX/RX^{\cdot-}$ couple? The latter lies, in fact, in the same region as the effective reduction potential or is even more negative.[31] The standard potential of the $RX/RX^{\cdot-}$ couple thus does not fulfill the above condition and therefore, as sketched in Figure 8, electron transfer and bond breaking are concerted rather than sequential. This falls in line with the finding that a loose $R^{\cdot} + X^-$ adduct rather than a true $RX^{\cdot-}$ anion radical is detected by ESR spectroscopy upon γ irradiation of alkyl halides in apolar or weakly polar solid matrixes at 77 K.[32] In polar solvents, such as those used in electrochemical studies, the interaction between $R^{\cdot}$ and X^- is even weaker. The case of CF_3Br is less unambiguous since the electron withdrawing effect of the fluorine atom lowers the σ^* C–Br orbital where the unpaired electron of the anion radical is located.[33] The electron affinity of CF_3Br in the gas phase is indeed 0.9 ± 0.2 eV, and the $CF_3Br^{\cdot-}$ ion has been detected and shown to have a bond dissociation energy of 0.54 ± 0.2 eV.[34] γ irradiation of CF_3Br with ESR detection of products in similar conditions as above[33] also showed the transient existence of the $CF_3Br^{\cdot-}$ anion radical. It is thus conceivable that the anion radical exists also in our case and that its standard potential is positive to the reduction potential. The intermediacy of $CF_3Br^{\cdot-}$ in the reduction of CF_3Br however appears unlikely under our conditions for the following reasons. One is that the presence of a polar solvent considerably weakens charge–polarizable dipole interaction between Br^- and $CF_3^{\cdot}$. A typical example in this connection is the π anion radical of chlorobenzene for which quantum mechanical calculations predict a ground-state energy about 1 eV lower than $Ph^{\cdot}$ and Cl^-,[35a] whereas its lifetime in polar liquids is certainly smaller than 1 ns.[35b] It follows that the σ radical predicted to exist in the gas phase[35a] has very little chance to appear as a discrete species along the reductive cleavage pathway.

On the other hand, the kinetics of the electrochemical reduction of CF_3Br can be further analyzed in the framework of a Marcus-type quadratic activation–driving force relationship with no starting assumption concerning the concerted or stepwise character of the electron-transfer–bond-breaking process.[36] As seen earlier, the $CF_3^{\cdot}$ radical generated from electron transfer to CF_3Br is easier to reduce than CF_3Br under cyclic voltammetric conditions. The concerted or first step electron transfer to CF_3Br is thus the rate-determining step of the overall reaction. Simulation of the cyclic voltammograms (Figure 1) in the framework of the Butler–Volmer rate law (eq 5) leads to the value of α_1 in Table VII. These data can then be used to estimate the standard potential, E_1°, and the standard activation free energy (intrinsic barrier), $\Delta G_0^{\ddagger}$, of the rate-determining step in the framework of a quadratic activation–driving force relationship which can be applied both in the case where electron transfer and bond breaking are stepwise and in that where they are concerted:[36]

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{E - E^{\circ}}{4\Delta G_0^{\ddagger}}\right)^2 \tag{7}$$

(E, electrode potential; $\Delta G^{\ddagger}$, activation free energy of the forward electron transfer). By taking again $Z^{el} = 5 \times 10^{-3}$ cm s^{-1}, the values of E_1° and $\Delta G_0^{\ddagger}$ listed in Table VII ensue by using the same procedure as previously described.[4a,16c]

Is the value found for $E_1^{\circ} = -0.57$ V vs SCE compatible with concerted and/or stepwise electron transfer and bond breaking? It is interesting, in this connection, to compare it with the value that can be derived from the gas-phase free energies of formation of CF_3Br and $CF_3^{\cdot}$ and the solution free energy of formation of Br^-[37a–c] under the assumption that the free energies of solvation

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(30) (a) The linear variation of the transfer coefficient (symmetry factor), α, with the driving force, or, equivalently, the quadratic character of the activation–driving force relationship have been demonstrated for a number of electrochemical outer-sphere electron transfers to organic molecules[30b] and also, albeit with less precision, in the case of the electrochemical reduction of alkyl halides.[5a] (b) Tessier, D.; Savéant, J.-M. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 57.

(31) The standard potential of the $RBr/RBr^{\cdot-}$ couple is certainly negative to that of $PhBr/PhBr^{\cdot-}$ (since the σ^* orbital of the aliphatic C–Br bond is higher than the π^* orbital of the phenyl group). On the other hand the latter standard potential is in the same region as the reduction potential of RBr.[19a]

(32) Symons, M. C. R. *Pure Appl. Chem.* **1981**, *53*, 223.

(33) (a) Hasegawa, A.; Williams, F. *Chem. Phys. Lett.* **1977**, *46*, 66. (b) Hasegawa, A.; Shiotani, M.; Williams, F. *Faraday Discuss. Chem. Soc.* **1977**, 157.

(34) Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 4360.

(35) (a) Casado, J.; Gallardo, I.; Moreno, M. *J. Electroanal. Chem.* **1987**, *219*, 197. (b) Andrieux, C. P.; Savéant, J.-M. *J. Electroanal. Chem.* **1986**, *205*, 43.

(36) In the case of a stepwise process, Marcus theory can be directly applied to the $CF_3Br/CF_3Br^{\cdot-}$ electron transfer.[16g,m] In the case of a concerted process, Marcus theory is not applicable but Morse-curve modeling of the potential energy surfaces has recently been shown to also lead to a quadratic activation–driving force relationship.[5c]

(37) (a) Benson, S. W. *Thermodynamical Kinetics*, 2nd ed.; Wiley: New York, 1976. (b) Wagman, D. D.; Evans, D. H.; Parker, V. B.; Schumm, R. H.; Halo, I.; Bailey, S. M.; Churney, K. L.; Nuttal, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2. (c) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; Mc Donald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1. (d) Unlike $CH_3^{\cdot}$, $CF_3^{\cdot}$ possesses a pyramidal structure[37c] and most probably a substantial permanent dipole moment with an excess positive charge on the carbon.

of CF_3Br and $CF_3^•$ in DMF are not much different. A value of −1.13 V vs SCE is thus found. In the framework of a concerted pathway, this would amount to a solvation stabilization of $CF_3^•$ vis-â-vis CF_3Br of 0.56 eV. This is not an unreasonable value in view of the electron-withdrawing properties of the fluoro atoms.[37d] In the case of a stepwise process:

$$E^\circ_{CF_3Br/CF_3Br^{•-}} = \Delta G^{f,s}_{CF_3Br} - \Delta G^{f,s}_{CF_3Br^{•-}}$$

where the $\Delta G^{f,s}$s are the free enthalpies of formation in DMF. Thus

$$E^\circ_{CF_3Br/CF_3Br^{•-}} = E^\circ_{CF_3Br/CF_3^•+Br^-} + \Delta G^{0,diss}_{CF_3Br^{•-}}$$

where the latter term is the standard free enthalpy of dissociation of $CF_3Br^{•-}$ in DMF. This has certainly a largely negative value since $CF_3Br^{•-}$, if it exists, is quite unstable in DMF. It follows that $E^\circ_{CF_3Br/CF_3Br^{•-}}$ should be largely negative to the experimental value of the standard potential of the rate-controlling step. This is another reason why the concerted pathway appears more likely than the stepwise pathway.

Still another reason comes from the magnitude of the intrinsic barrier, viz., 0.94 eV, i.e., a reorganization factor of 3.76 eV. This is much too large for an outer-sphere electron transfer leading to $CF_3Br^{•-}$ taking into account solvent reorganization and stretching of the C–Br bond.[33b] In contrast, the magnitude of the intrinsic barrier is in good agreement with the application of the recently developed model of concerted electron-transfer–bond-breaking reactions which predicts that $\Delta G^\ddagger_0$ is the sum of two contributions arising from bond breaking (one fourth of the bond dissociation energy, D) and from solvent reorganization ($\lambda_0/4$) respectively:[5c]

$$\Delta G^\ddagger_0 = \frac{D}{4} + \frac{\lambda_0}{4} \tag{8}$$

$D/4 = 0.77$ eV,[38a] and $\lambda_0/4 = 0.13$ eV,[38b] resulting in $\Delta G^\ddagger_0 = 0.90$ eV as a predicted value to be compared with $\Delta G^\ddagger_0 = 0.94$ eV as derived from the electrochemical data and $\Delta G^\ddagger_0 = 0.83$ eV as derived from the aromatic anion radical data.[39]

We thus conclude that the electrochemical reduction of CF_3Br is more likely to proceed via a concerted electron-transfer–bond-breaking mechanism than through the intermediacy of the $CF_3Br^{•-}$ anion radical. This is a fortiori true for the reduction of CF_3Br by the investigated aromatic anion radicals since the reaction then possesses a lesser driving force than the direct electrochemical reduction.[40]

Since I^- is a better leaving group than Br^-, the concerted electron-transfer–bond-breaking mechanism is even more likely to predominate over the passage through the anion radical in the direct and indirect electrochemical reduction of CF_3I, $C_6F_{13}I$, and $C_8F_{17}I$.

The standard potential of a $CF_3I/CF_3^• + I^-$ couple should not be too different from that of the $CF_3Br/CF_3^• + Br^-$ couple since, as in the case of alkyl iodides and bromides,[5a,c] the difference in the free energies of formation of the halides ions is roughly compensated by the difference in the C–I and C–Br bond energies. From the thermochemical data,[38] it is predicted that $E^\circ_{CF_3I/CF_3^•+I^-}$ be positive to $E^\circ_{CF_3Br/CF_3^•+Br^-}$ by 0.03 V, i.e., equal to −0.54 V vs SCE, assuming that solvation by DMF is about the same for CF_3I and CF_3Br. The easier reductibility of CF_3I vis-â-vis CF_3Br is thus mainly a result of its lesser bond dissociation energy. Indeed, from the preceding value of the standard potential and that of the peak potential, $\Delta G^\ddagger_0$ is found to be (using again eq 7) 0.75 eV whereas a value of 0.65 eV is found for the reaction with the aromatic anion radical.[39] This is to be compared with a theoretical value of 0.72 eV,[38b] as obtained from eq 8. On these bases, a value of 0.34 is predicted for the electrochemical transfer coefficient. The fact that it is somewhat larger than the experimental values (Table VII) is not very surprising in view of adsorption phenomena involved in the electrochemistry of CF_3I especially at low scan rates.

The reduction of $C_6F_{13}I$ is easier, by about 0.2 V, than that of CF_3I whereas the reduction potentials of $C_6F_{13}^•$ and $CF_3^•$ are about the same. This points to a slightly weaker bond dissociation energy in the first case as compared to the second, leading both to a more positive potential and a smaller standard activation free energy.

Let us now turn to the $CF_3^•/CF_3^-$ couple. The standard potential can be derived from the free energies of formation of $CF_3^•$ and CF_3H in the solvent and from the pK_a of the CF_3H/CF_3^- couple[23c] as:[41]

$$E^\circ_{CF_3^•/CF_3^-} \text{ (vs aqueous SCE)} = \Delta G^{f,s}_{CF_3} - \Delta G^{f,s}_{CF_3H} - \frac{RT}{F} \ln \mathrm{p}K_a - 0.43$$

On the other hand, the relative solvation stabilization of $CF_3^•$ vis-â-vis CF_3Br has been estimated to be

$$(\Delta G^{f,s}_{CF_3^•} - \Delta G^{f,g}_{CF_3}) - (\Delta G^{f,s}_{CF_3Br} - \Delta G^{f,g}_{CF_3Br}) = 0.56 \text{ eV}$$

(the $\Delta G^{f,g}$ values are the gas-phase free enthalpies of formation). Assuming that the solvation stabilization of CF_3Br and CF_3H are about the same it follows that:[37]

$$E^\circ_{CF_3^•/CF_3^-} = -0.58 \text{ V vs aqueous SCE}$$

On the other hand, at the reduction potential (−1.71 V vs SCE), the heterogeneous rate constant can be derived from eq 6:

$$k_2^{el}[1.71] = 2 \text{ cm s}^{-1} \text{ and thus } \Delta G^\ddagger_{el}[-1.71] = 0.188 \text{ eV}$$

With use of the above value of E°, application of eq 7 then leads to $\Delta G^\ddagger_0 = 0.62$ eV. A predicted value of α of 0.27 ensues. As for the first reduction wave of CF_3I, it is somewhat larger than the experimental values. As in the case of alkyl radicals, charge transfer to perfluoroalkyl radicals appears as requiring a rather large reorganization free energy arising most probably from both solvent reorganization and geometrical reorganization ($CF_3^•$ is pyramidal[37d] whereas $CH_3^•$ is flat but CF_3^- is likely to be flatter than CH_3^- owing to electron displacement on the F atoms and charge repulsion).

While glassy carbon electrodes and electrochemically generated aromatic anion radicals appear, from what preceeds, to function as outer-sphere reagents giving rise to a concerted electron-transfer–bond-breaking reduction of R_FX, this is obviously not the case with the various metallic electrodes in which the cyclic voltammetry of CF_3Br and CF_3I were investigated (Table I). Significant to dramatic decreases of the reduction potential (as large as 0.8–0.9 V for Cu, Hg, and Ni) are observed, indicating the involvement of the metal in an inner-sphere process, presumably $X^•$ or X^+ abstraction. Let us recall in this connection that an example of the reduction of CF_3Br by an inner-sphere homogeneous reagent, the sulfur dioxide anion radical, has been described and showed to involve $Br^•$ abstraction.[20]

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(38) (a) *Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca Raton, FL, 1980. (b) From the Marcus dielectric continuum model as in ref 5c.

(39) This value was obtained according to the following procedure: an average value of log k_1 for the middle of the E°_{PQ} range, −1.54 V vs SCE, was derived from the experimental data (Figure 6, Table IV) by linear regression. The activation free enthalpy ΔG^* was then obtained from $\Delta G^* = (RT/F) \ln (Z^{hom}/k_1)$ where Z^{hom}, the homogeneous collision frequency was taken as equal to 3×10^{11} M^{-1} s^{-1}. ΔG_0^* was then derived from eq 7 replacing $E - E^\circ$ by $E^\circ_{PQ} - E^\circ$, i.e., −1.54 − (−0.57) eV. A similar procedure was used for CF_3I.

(40) (a) We note, en passant, that the passage through the anion radical rather than the occurrence of an electron-transfer–bond-breaking process is not strictly speaking an intrinsic property of the starting molecule. The first mechanism is favored by a large driving force and vice versa for the second (Figure 8).[19c] Of course, due to the limitations of the driving force range in which meaningful kinetic determinations can be carried out, most of the real systems will fall in one category or in the other. Borderline cases are however conceivable in which a change of mechanism could occur upon varying the driving force.

(41) (a) For the estimation of the term −0.43 corresponding to the aqueous SCE, see ref 41b–f. (b) Marcus, Y. *Pure Appl. Chem.* **1985**, *57*, 1103. (c) *Ibid.* 1129. (d) Trasatti, S. *Pure Appl. Chem.* **1986**, *58*, 955. (e) Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 339. (f) *Ibid.* 2985.

$R_F^•$ radicals behave similarly to aliphatic alkyl radicals as to their generation mechanism from the parent bromide or iodides which involves a concerted electron-transfer–bond-breaking reaction and the intrinsic slowness of their reduction. They are however much better H atom scavengers, and they do not couple with aromatic anion radicals whereas $R^•$ radicals do. It is noteworthy that $R_F^•$ radical do not react with aromatic anion radicals even when the standard potential of the latter is much more positive than the $R_F^•$ reduction potential. These features are in fact interrelated: the lack of reactivity of $R_F^•$ toward aromatic anion radicals derives both from their more facile reducibility and from the fact that they easily scavenge H atoms from the solvent. In these respects $R_F^•$ bear some similarity with aryl radicals.

Experimental Section

Chemicals. MeCN, DMF, Me_2SO, and nitrobenzene were from commercial origin and distilled before use. PhCN (Aldrich, Gold Label), NBu_4BF_4 (Fluka), CF_3Br (Atochem), CF_3I (Aldrich), CF_3H (Atochem), C_2F_6 (Atochem), $C_6F_{13}I$ (Aldrich), $C_6F_{13}H$, $C_{12}F_{26}$ (Atochem), and Me_2SO-d_6 (Spin et Techniques), as well as the various redox catalysts, were used as received.

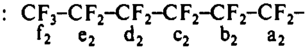
Cyclic Voltammetry. It was carried out in a thermostated cell with a platinum counter electrode and an aqueous SCF reference electrode. In most cases, the working electrode was a glassy carbon (Tokai Corp.) disk of 0.03-cm² surface area. It was carefully polished before each run with a 1-μm diamond paste and ultrasonically rinsed in absolute ethanol. The other working electrodes were disks of the various metals (Table I) and a hanging mercury drop (attached on a gold disk). In the case of CF_3Br, the gas was diluted with N_2 (by means of an Alphagaz mass flow regulator), and the mixture flowed into the cell. The concentration of CF_3Br in the solution was adjusted on the basis of its solubility in the solvent (e.g., 40 g in 1 kg of DMF determined by weighing). For example, 2 mM CF_3Br in DMF corresponds to a 90 cm³/mn N_2 flow and to a 0.676 cm³/mn CF_3Br flow. In the case of CF_3I a cool (5 °C) stock solution was prepared from pure CF_3I by weighing and diluting in the usual way.

Preparative-Scale Electrolyses. They were carried out in a cylindrical glassy-carbon (Carbone Lorraine V25) crucible of 70-mm diameter and 50-mm height serving as working electrode with 100 mL of solution in the cathodic compartment. The counter electrode was a platinum wire separated from the cathodic compartment by a glass frit (porosity = 4) or a Nafion membrane. The same procedures as in cyclic voltammetry was used for setting the concentration of CF_3Br. The gaseous mixture resulting from electrolysis was analyzed by gas chromatography with a catharometer detector (IG 11 Delsi instrument with a 2.5-m neutral alumine column treated with 3% tetramethylsilane containing 2% 112 Alcatel oil). In the case of $C_6F_{13}I$, the electrolysis mixtures was analyzed by gas chromatography with a flame-ionization detector (Girdel 30 Delsi Instrument with a 4-m 3% SE 30 Chromosorb W 100/120 column). In both cases the ^{19}F NMR analysis of electrolyzed solution was carried out on a 250-MHz Brücker instrument in $CDCl_3$; chemical shifts are reported in parts per million relative to fluorotrichloromethane as internal standard. Negative values are upfield from the standard.

Mass Spectroscopy Analysis of Deuterium Incorporation Experiments. The electrolyses in D_2O–Me_2SO and H_2O–Me_2SO-d_6 mixtures were carried out with CF_3Br saturated solutions. Direct mass spectroscopic analysis of the solution (CF_3Br, CF_3H, and CF_3D) was not possible since CF_3H and CF_3D are too frangible for their mass peaks to be detected (the heaviest detectable fragment is $CF_3^•$). We thus used an MS/MS technique quite similar to that described in ref 26; the loss of HF (20), F (19), and DF (21) was analyzed at the 51 (CF_2H) and 52 (CF_2D) *m/e* peaks.

^{1}H and ^{19}F NMR Data. CF_3Br: δ −61.4. Electrolysis of a DMSO solution of $C_6F_{13}I$, besides the signals corresponding to $C_6F_{13}H$, shows two new ^{19}F signals observed at δ −117.8 and −162.2:

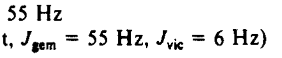
$C_6F_{13}I$:



$$\underset{f_1}{CF_3}-\underset{e_1}{CF_2}-\underset{d_1}{CF_2}-\underset{c_1}{CF_2}-\underset{b_1}{CF_2}-\underset{a_1}{CF_2I}$$

δ_{a_1} −59.8; δ_{b_1} −113.9, δ_{c_1} −121.6; δ_{d_1} −123.2; δ_{e_1} −126.0; δ_{f_1} −80.0.

$C_6F_{13}H$:

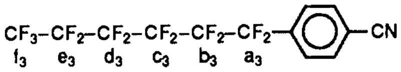


$$\underset{f_2}{CF_3}-\underset{e_2}{CF_2}-\underset{d_2}{CF_2}-\underset{c_2}{CF_2}-\underset{b_2}{CF_2}-\underset{a_2}{CF_2}-H$$

δ_{a_1} −139.0; δ_{b_2} −129.0, δ_{c_2} −122.0; δ_{d_2} −123.4; δ_{e_2} −126.0; δ_{f_2} −81.0; J_{H-F} = 55 Hz

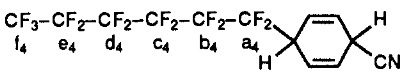
δ_H 5.90 (tt, J_{gem} = 55 Hz, J_{vic} = 6 Hz)

Electrolysis of a PhCN solution, besides the signals of $C_6F_{13}I$ and $C_6F_{13}H$, showed the signals of



(C)

δ_{a_3} −112.4; δ_{b_3} −119.7; δ_{c_3} −120.0; δ_{d_3} −121.3; δ_{e_3} −124.7; δ_{f_3} −81.7.



(D)

δ_{a_4} −120.1 (J_{H-F} = 14 Hz); δ_{b_4} −119.7; δ_{c_4} −120.0; δ_{d_4} −121.3; δ_{e_4} −124.7; δ_{f_4} −81.7.

Conclusions

The most important conclusions of the present study concern the conditions to be fulfilled for triggering, upon reduction of the corresponding bromides and iodides by outer-sphere electron donors, a $R_F^•$ or a R_F^- chemistry. The effective reduction potential of $R_F^•$ radicals is the result of the intrinsic thermodynamic and kinetic characteristics of the $R_F^•/R_F^-$ couple and of their H atom scavenger reactivity toward the solvent. Overall, on inert electrodes, it is close to the potential required for their generation from the corresponding bromides and significantly more negative than that required in the case of iodides. Electrolysis at this generation potential thus triggers a $R_F^•$ radical chemistry in the second case and a mixed $R_F^•/R_F^-$ radical–carbanion chemistry in the first. Indirect electrochemistry using aromatic anion radicals as mediators triggers an $R_F^•$ chemistry in both cases except, in the case of CF_3Br, for mediators having a standard potential very close to its reduction potential where again a mixed $CF_3^•/CF_3^-$ chemistry takes place. Overall, the triggering of an $R_F^•$ chemistry by reduction of R_FX (X = Br, I) appears more accessible than that of an R_F^- chemistry using heterogeneous outersphere reductants (electrolysis at a potential much beyond a reduction wave is difficult, making constant current conditions preferred in practice).

These conclusions might be modified in the case of inner-sphere heterogeneous or homogeneous reductants or by the presence of cations strongly interacting with the R_F^- carbanions such as Mg^{2+}. In the latter case, a carbanionic organometallic-type intermediate is expected which might explain the better reactivity toward carbonyl compounds of R_F^- generated[13h] in the presence of Mg^{2+} than in that of tetraalkylammonium cations.[13g,i]

The reduction of all investigated R_FX by heterogeneous (glassy-carbon electrodes) and homogeneous (aromatic anion radicals) outer-sphere electron donors most likely involves concertedness of electron transfer and bond breaking. Approximate estimates of the $R_FX/R_F^• + X^-$ standard potentials reveal that the reduction cleavage of the R_FX bond involves substantial overpotentials of the order of 1.5 V for the C–Br bond and 1.0 V for the C–I bond. The bond dissociation energy appears as the main factor governing the intrinsic barrier of the reductive cleavage.

The same kind of rough estimates of the $R_F^•/R_F^-$ standard potential indicates that $R_F^•$ radicals are stabilized by interaction with nucleophilic solvents such as DMF, significantly more than aliphatic alkyl radicals. In spite of this, they are easier to reduce than $R^•$ radicals on thermodynamic grounds as expected from the F-electron withdrawing stabilization of R_F^- as compared to R^- which also manifests itself by a much lesser basicity. The intrinsic barrier of the $R_F^•/R_F^-$ couple is however of the same order of magnitude as that of the $R^•/R^-$ couple. $R_F^•$ radicals appears as much better H-atom scavengers than $R^•$ radicals, resembling thus more aryl radicals from this viewpoint. For this reason and also because of their lesser reducibility they do not couple with aromatic anion radicals like aryl radicals and unlike aliphatic alkyl radicals.

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