# Dissociative Electron Transfer. Autocatalysis and Kinetic Characteristics of the Electrochemical Reductive Cleavage of the Carbon–Halogen Bond in Alkyl Halides Giving Rise to Stable Radicals and Carbanions

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Abstract: The electrochemistry of two benzylic type chlorides giving rise to stable radicals (R·) and carbanions (R⁻) is investigated by means of cyclic voltammetry. A remarkable autocatalysis process is demonstrated involving the carbanion as electron-transfer catalyst

$$RX + 2e^- \longrightarrow R^- + X^-$$

$$R^- + RX \longrightarrow 2R\cdot + X^-$$

$$R\cdot + 1e^- \longrightarrow R^-$$
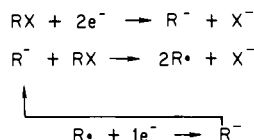
showing that, besides their basic and nucleophilic properties, such carbanions can act as redox reagents. Activation–driving-force free energy relationships characterizing the electrochemical and homogeneous reduction of the starting halide are investigated taking advantage of the fact that all the characteristic standard potentials, R·/R⁻, R·/R⁺, RX/(R· + X⁻), and RX/(R⁻ + X⁻), could be determined experimentally. The following points are discussed on these grounds: intermediacy of RX⁻· anion radical vs. concerted electron transfer-bond breaking reduction and nature of the reoxidation reaction.

Part of the current interest in the kinetic study of electrochemical electron transfers stems from the fact that it is a convenient means for investigating activation–driving-force free energy relationships characterizing electron-transfer reactions. A continuous variation of the driving force can indeed be simply obtained by changing the electrode potential. In this respect, the main successful attempts, in the organic field, have concerned thus far the experimental testing of several aspects of the Hush–Marcus theory[2] in cases where the one-electron-transfer product is chemically stable within the time scale of the experiments. The effect of solvent polarization,[3] the relationship between heterogeneous and homogeneous charge transfer kinetics,[4] and the variation of the transfer coefficient with the potential[5] have been investigated in this connection.

Regarding the electron transfer reactions involving concomitant bond cleavage, the reduction of alkyl halides (RX) appears as one of the simplest examples, among organic molecules, where such a process is suspected to occur. Although this is still a matter of investigation, there is evidence that a discrete RX⁻· anion radical does not exist in the case of simple alkyl halides.[6-10] Furthermore,

as discussed in the following, even if a discrete RX⁻· anion radical exists but requires a highly exergonic electron transfer to be formed, a direct electron-transfer–bond-cleavage pathway may prove more effective within the range of electrochemically accessible activation free energies.

Although a large amount of work has been devoted to the electrochemical reduction of these compounds,[12] a clear-cut picture of the reaction mechanism has not emerged so far. This is essentially due to the extreme reactivity of the intermediates generated upon electron transfer, RX⁻· (if it exists, vide supra), R·, and R⁻. Fast surface and/or volume chemical reactions[13] are then expected to follow the initial electron-transfer step, which makes the use of the standard microelectrolytic kinetic techniques, such as cyclic voltammetry, of little help for unravelling the reaction mechanism. Also, the high reactivity of the alkyl radicals makes possible chemical interaction with the electrode material. This is obviously the case with mercury which has been often used as electrode.[12] On the other hand, there have been relatively few studies of the distribution of products at inert electrodes and no attempt to use its variations with the experimental parameters as a tool for establishing the reaction mechanism which seems

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(6) In the case of simple aliphatic halides, low-temperature γ irradiation coupled with ESR characterization of the resulting species[7a] has shown that loose adducts rather than covalently bonded anion radicals are formed upon electron transfer.[7b-f] These are expected to cleave into R· and X⁻ upon raising the temperature.[7a,f] RX⁻· radicals do exist at low temperature in the case of trifluoromethyl halides.[8a,b] Ab initio quantum chemical calculations gave conflicting results in the case of CH₃Cl⁻·: one[9a] predicts the existence of a discrete anion radical while another[9b] is in agreement with the formation of a loose complex between CH₃· and Cl⁻. In the case of CF₃Cl⁻· no discrete anion radical is predicted to exist[9c] at variance with the experimental findings. Pulse radiolysis investigations also indicate the absence of discrete anion radicals for simple aliphatic halides.[10] This is also true for unsubstituted benzyl halides,[10c] while nitro- and cyano-substituted benzyl halides give rise to discrete anion radicals.[11]

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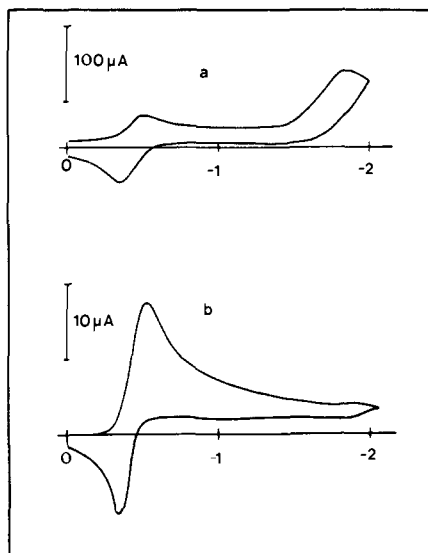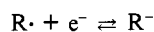(13) Savéant, J. M. *J. Electroanal. Chem.* **1980**, *112*, 175; **1983**, *143*, 447.

Figure 1. Cyclic voltammetry of **1** (1.0 mM) in CH_3CN + 0,1 M NBu_4ClO_4 at 20 °C. Sweep rate: (a) 10 V s^{-1}; (b) 0.2 V s^{-1}. Silver wire quasireference electrode.

the only viable route in view of the high reactivity of the reduction intermediates.[14]

In the present report we describe a cyclic voltammetric investigation of the reduction of 9-chloro-9-{α-(9-fluorenylidene)-benzyl}fluorene and 9-chloro-9-mesitylfluorene in acetonitrile (compounds **1** and **2**; see structures below). They possess the

(1)   (2)
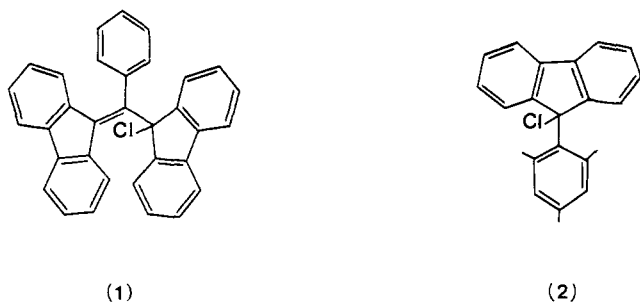
advantage of giving rise to both chemically stable R· and R$^-$ species, the electrochemical characteristics of which can be determined independently.[15]   Whenever the reduction pathway involves a discrete RX$^-$· anion radical rapidly cleaving into R· and X$^-$ or a concerted electron-transfer–bond-breaking process leading directly to R· and X$^-$, R· is formed very close to the electrode surface, if not at the electrode surface.   Provided it accepts electrons more easily than the starting RX, which is the case with the two above compounds,[16] R· will be reduced at the electrode surface:

$$R· + e^- \rightleftarrows R^-$$

before having time to undergo any other reaction.   In these cir-

Figure 2. Cyclic voltammetry of **2** in CH_3CN + 0.1 M NBu_4Cl at 20 °C. Sweep rate (V s^{-1}) and RX concentration (mM): (a) 0.05, 0.5; (b) 0.1, 0.9; (c) 0.5, 5; (d) 0.5, 0.5; (1) experimental curve (SCE reference electrode); (2) simulated curves corresponding to the kinetic characteristics given in the text.

cumstances the R·/R$^-$ couple should be able to act as an homogeneous redox catalyst[17–25] for the electrochemical reduction of

(17) Homogeneous redox catalysis of the electrochemical reduction of aliphatic halides by aromatic anion radicals has been previously described.[18a–c] However, unlike the case of aromatic halides,[19] alkylation of the catalyst competes with, and in several cases completely prevails over, nonbonded electron transfer.[18d] The question thus arises whether the alkylation reaction proceeds either by electron transfer followed by coupling of R· with the aromatic anion radical

$$ArH + e^- \rightleftarrows ArH^-$$

$$ArH^- · + RX \rightarrow ArH + R_, + X^-$$

$$ArH^- · + R· \rightarrow ArHR^-$$
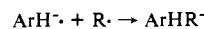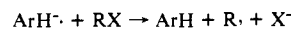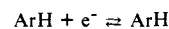
or along a direct SN2 reaction

$$ArH^- · + RX \rightarrow ArHR^- + X^-$$

A stereochemical investigation of the problem in the case of anthracene anion radical and secondary octyl halides has shown that the relative participation of the SN2 pathway is quite small for X = I, Br, Cl, not exceeding 11% of the total alkylation reaction.[18e] On the other hand, cobalt(II),[20] cobalt(I),[21] iron(I),[22a] and "iron(0)"[22b] complexes react with aliphatic halides to yield the corresponding alkyl–metal complexes. In most cases, however, these reactions have been shown not to involve outer-sphere electron transfer but to rather proceed along atom transfer[20a,c] or SN2[21b,22a] mechanisms. The very rough correlation between the rate constant and the driving force (±3 orders of magnitude dispersion in rate constants) observed with these complexes together with other reducing agents[23b] does not actually indicate that the same outer-sphere electron-transfer mechanism proceeds in all cases. It merely reflects the general tendency of the reactivity to increase with the reducing power of the reagent as expected intuitively (the nucleophilic reactivity is anticipated to roughly parallel the reducing power). A more precise analysis of the activation–driving-force relationships clearly shows that these are not the same, e.g., aromatic anion radicals (outer-sphere electron transfer) and iron(I) porphyrins (inner-sphere mechanism): for the same value of the standard potential the latter are more reactive than the former toward n-butyl halides by several orders of magnitude.[22a] In several cases where an alkyl–metal complex is formed, catalysis of the R–X reductive bond cleavage has been observed upon further addition of electron to the complex.[21e,22b,c] It thus involves a "chemical" catalysis scheme rather than a purely redox scheme.[24]

(14) (a) As an example of this approach see the investigation of the reduction mechanism of carbon dioxide in aprotic media.[14b–d]   (b) Gressin, J. G.; Michelet, D.; Nadjo, L.; Savéant, J. M. *Nouv. J. Chim.* **1979**, *3*, 545.   (c) Amatore, C.; Savéant, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 5021.   (d) Amatore, C.; Nadjo, L.; Savéant, J. M. *Nouv. J. Chim.* **1984**, *10*, 566.

(15) (a) Merz, A.; Tomahogh, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 938. (b) Andrieux, C. P.; Merz, A.; Savéant, J. M.; Tomahogh, R. *J. Am. Chem. Soc.* **1984**, *106*, 1957. (c) the R·/R$^-$ couple exhibits a Nernstian diffusion controlled behavior showing no significant adsorption of R· on the electrode (platinum).

(16) (a) In spite of previous opposite conclusions,[16b] there is so far no example where R· has been demonstrated to be more difficult to reduce than RX when the electrode material is inert toward the reaction intermediates.[16c] (b) Breslow, R.; Grant, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 7745. (c) Bard, A. J.; Merz, A. *J. Am. Chem. Soc.* **1979**, *101*, 2959.
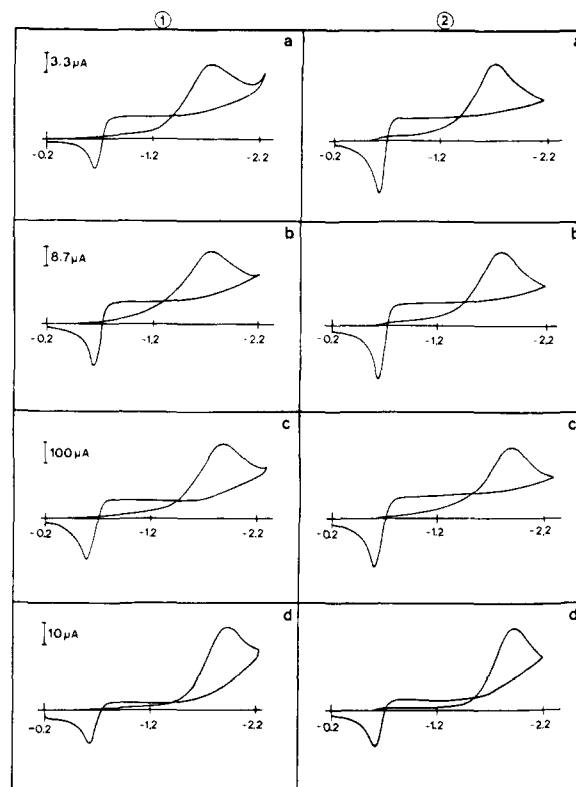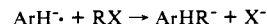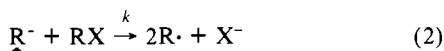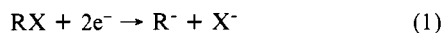
RX giving rise to an *autocatalytic* process:

$$RX + 2e^- \rightarrow R^- + X^- \qquad (1)$$

$$R^- + RX \xrightarrow{k} 2R\cdot + X^- \qquad (2)$$

$$R\cdot + e^- \rightleftarrows R^- \qquad (3)$$

As described hereafter, this is indeed what happens with **1** and **2**. With the latter compound it was possible to carry out a quantitative analysis of the autocatalytic mechanism leading to the determination of the rate constant of reaction 2. With the same compound it was also possible to derive the value of the standard potential of the $RX + e^- \rightleftarrows R\cdot + X^-$ reaction from previous data obtained by pre-dissociation homogeneous redox catalysis of its electrochemical reduction.[15b,25] We could therefore, in this case, investigate the activation–driving-force relationship characterizing the reductive cleavage of an alkyl halide by using a measured value of the standard potential whereas this is usually possible only on the basis of estimated E° values.[23]

Results

Figure 1 shows typical voltammograms of the reduction of **1** obtained at 0.2 and 10 V s^{-1}. At the lower sweep rate, a two-electron single wave is observed at a potential practically identical with that of the reduction of R· into R$^-$.[15] The reoxidation of R$^-$ into R· is observed upon scan reversal. At the higher sweep rate, a first reversible wave appears at the potential of the R·/R$^-$ couple while a second irreversible and broad wave is observed at much more negative potentials.

With **2** (Figure 2), the same two-wave system is also observed. However, the first cathodic wave is much smaller and a remarkable trace crossing appears upon scan reversal indicating that a reducible species is produced during the anodic scan.

These observations suggest that the autocatalytic process sketched in the introduction (reactions 1–3) is taking place. Figure 3 (0%) shows the theoretical dimensionless voltammograms that are expected for such an autocatalytic reaction scheme as a function of the kinetic dimensionless parameter $\lambda = RTkC^\circ/Fv$ (k is the rate constant of reaction 2, C° the bulk concentration of RX, and v the sweep rate); λ is a measure of the competition

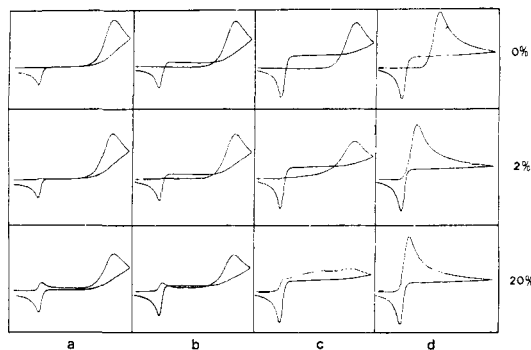**Figure 3.** Theoretical cyclic voltammograms for an autocatalytic mechanism (eq 1–3) for 0%, 2%, and 20% of R· as impurity in the starting material. The values of the dimensionless kinetic parameter $\lambda = RTkC^\circ/Fv$ are (a) 0, (b) 2×10^{-2}, (c) 2×10^{-1}, (d) 15.

between the rate-determining step of the autocatalytic process (reaction 2) and diffusion. The rate of the latter process is an increasing function of the sweep rate while that of the former increases with RX concentration since it is a second-order reaction. The whole voltammetric pattern is actually a function of two other parameters characterizing the direct reduction of RX at the electrode surface (reaction 1), the transfer coefficient, α, and a dimensionless parameter

$$\Lambda = k_S^{ap}(RT/FvD)^{1/2} \exp\{(\alpha F/RT)(E^\circ_{RX/R\cdot+X^-} - E^\circ_{R\cdot/R^-})\}$$

which besides the sweep rate and the diffusion coefficient depends upon the apparent standard rate constant, k_S^{ap}, of the electrochemical electron-transfer reaction.[26] In the simulated curves

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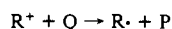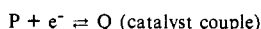
(21) (a) Schrauzer, G. N.; Windgassen, R. J.; Kohnle, J. *Chem. Ber.* **1965**, *98*, 3324. (b) Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341. (c) Eckert, H.; Ugi, I. *Angew. Chem.* **1975**, *87*, 847. (d) Clark, D. W.; Hush, N. S.; Woolsey, I. S. *Inorg. Chim. Acta* **1976**, *19*, 129. (e) Lexa, D.; Savéant, J. M.; Soufflet, J. P. *J. Electroanal. Chem.* **1979**, *100*, 159. (f) Puxeddu, A.; Costa, G.; Marsich, N. *J. Chem. Soc., Dalton Trans.* **1980**, 1489.

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(25) (a) Ferrocene and substituted ferrocenes as well as quinoid anion radicals have been shown to catalyze the electrochemical reduction of **1** and **2** without the formation of addition product with the substrate at potential very positive (up to 2 V) to the substrate wave.[15b] The catalytic reaction scheme is, however, different, involving the predissociation of the halide into the carbocation and the halide ion:

$$P + e^- \rightleftarrows Q \text{ (catalyst couple)}$$

$$RX \rightleftarrows R^+ + X^-$$

$$R^+ + Q \rightarrow R\cdot + P$$

(26) (a) The system is described by the following set of dimensionless partial derivative equations, initial and boundary conditions

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} - \lambda ac$$

$$\tau = 0, y > 0, \text{ and } y = \infty, \tau > 0; a = 1, b = c = 0$$

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} + 2\lambda ac; \quad \frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} - \lambda ac$$

$$y = 0, \tau \geq 0; \frac{\partial a}{\partial y} + \frac{\partial b}{\partial y} + \frac{\partial c}{\partial y} = 0, b = c \exp\left\{\frac{F}{RT}(E - E^\circ_{R\cdot/R^-})\right\};$$

$$\psi = \Lambda \exp\left\{-\frac{\alpha F}{RT}(E - E^\circ_{R\cdot/R^-})\right\} a$$

with

$$\psi = 2\left(\frac{\partial a}{\partial y}\right)_0 - \left(\frac{\partial c}{\partial y}\right)_0$$

where a, b, and c are the concentrations of RX, R·, and R$^-$, respectively, normalized toward the bulk concentration of RX, C°; $\tau = RTt/Fv$, $y = x(RT/FvD)^{1/2}$ (t = time; x = distance to the electrode surface) are the dimensionless variables of time and space. $-(F/RT)(E - E^\circ_{R\cdot/R^-})$ is the dimensionless potential variable with $E = E_i - vt$ (E = electrode potential, $E^\circ_{RX/R\cdot+X^-}$ and $E^\circ_{R\cdot/R^-}$ are the standard potential of the RX/(R· + X$^-$) and R·/R$^-$ couples, respectively, E_i = initial potential of the scan). $\psi = I/FC^\circ(FvD/RT)^{1/2}$ is the dimensionless current (I = current density, D = diffusion coefficient (assumed to be the same for all three species). The above system was solved numerically by using an explicit (Schmidt) finite difference method.[26c] It actually suffices to solve the system consisting of the first and third partial derivative equations since $\partial(a + b + c)/\partial\tau = \partial^2(a + b + c)/\partial y^2$ and thus

$$b_0 = 1 - (a_0 + c_0) \text{ and } \Lambda =$$
$$k_S^{ap} (RT/FvD)^{1/2} \exp\{(\alpha F/RT)(E^\circ_{RX/R\cdot+X^-} - E^\circ_{R^0/R^-})\}$$

(b) We assume that in eq 1, RX + e$^-$ → R· + X$^-$ is the rate-determining step, R· being immediately reduced into R$^-$ at the electrode surface since the R·/R$^-$ standard potential is largely positive to the reduction potential. We treated the kinetics of the direct reduction of RX assuming a Volmer–Butler law:

$$I/F = k_S^{ap} \exp\{(\alpha F/RT)(E - E^\circ)\}\{RX\}_0$$

with a transfer coefficient, α, independent of the electrode potential. Although this is likely not to be true over an extended potential range as developed in the Discussion section, this is a sufficient approximation within the restricted potential range where the second wave occurs. (c) "The Mathematics of Diffusion", Crank, J., Ed.; Oxford University Press: London, 1964.

of Figure 3, α was taken as equal to 0.25 and Λ was rather arbitrarily maintained constant and equal to 1.8×10^{-9}. It actually varies with the sweep rate and this effect will be taken into account later on. For the moment, this is sufficient to draw a qualitative picture of the effects of the autocatalytic process on the cyclic voltammograms.
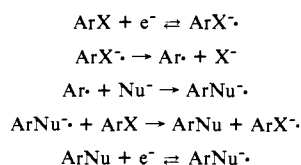
For the lowest values of λ, corresponding to small k's and C^0's and high sweep rates, there is no effect of the autocatalytic process. The intrinsic characteristics of the direct reduction of RX are then reflected by the second cathodic wave. When λ increases, the autocatalytic reaction interferes more and more. A characteristic feature of the involvement of reaction 2 is then the appearance of trace crossings upon scan reversal: the R· radicals that are continuously formed through reaction 2 are reduced into R⁻, even during the anodic scan, owing to the fact that the R·/R⁻ standard potential is well positive to the RX reduction potential.[27] At the same time the RX reduction wave is also affected—it shifts positively and is less and less drawn-out. For the smallest values of λ, the reduction of RX occurs entirely at the potential of the R·/R⁻ couple, giving rise to a "reversible" wave which involves the passage of two electrons on the cathodic side and one on the anodic side.

This behavior matches qualitatively what was observed with compounds 1 and 2, more closely, however, in the second case than in the first. It actually appears that some R· radicals are present as an impurity in the starting halide. They probably come from the slow dissociation of RX into R⁺ and X⁻, the reaction being pulled by the conversion of the very reducible R⁺ ($E°_{R^+/R·} = +0.79$ and +0.75 V vs. SCE for 1 and 2, respectively)[15] into R· by adventitious reducing impurities, The lowest parts of Figure 3 show the predicted effect of the presence of 2% and 20% R· in the starting halide, respectively. The curves obtained at high values of λ, where no autocatalysis occurs, show now, in addition to the irreversible RX direct reduction wave, the reversible R·/R⁻ wave with a height corresponding to the starting amount of R·. Upon increasing λ the same general trends as before are observed, the "reversible" 2e/1e behavior being reached at values of λ that are the smaller the bigger the starting amount of R·. This falls in line with the cyclic voltammetric behavior of both 1 and 2 and with the observation that it was more difficult to get rid of R· as impurity in the first case than in the second.

In order to quantitatively test the validity of the autocatalysis mechanism we therefore used compound 2 with tetrabutyl-ammonium chloride as supporting electrolyte so as to minimize the amount of R· present in the starting material. A satisfactory agreement between the experimental and calculated[26] voltammograms was obtained for several values of the sweep rate and of the RX concentration (Figure 2). It was obtained for the following values of the various kinetic parameters:

$$k = 8.10^2 \text{ M}^{-1} \text{ s}^{-1}, \ \alpha = 0.25, \ k_S^{ap} \exp\{(\alpha F/RT)E°_{RX/R·+X^-}\} = 5.9 \times 10^{-11} \text{ cm s}^{-1}$$

(27) (a) Trace crossing has been previously observed and quantitatively interpreted[27b] in electrochemically induced SRN₁ aromatic substitution,[27c] corresponding to the following reaction scheme:

$$ArX + e^- \rightleftarrows ArX^{-·}$$
$$ArX^{-·} \rightarrow Ar· + X^-$$
$$Ar· + Nu^- \rightarrow ArNu^{-·}$$
$$ArNu^{-·} + ArX \rightarrow ArNu + ArX^{-·}$$
$$ArNu + e^- \rightleftarrows ArNu^{-·}$$

which, in the case where the Ar Nu/Ar Nu⁻· standard potential is positive to the ArX reduction potential, is formally similar to what occurs in the present case. (b) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1980**, *107*, 59. (c) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 423. (d) Another example of an autocatalytic process also giving rise to trace crossing is the reductive cleavage of diarylethanes substituted in the 1 and 2 positions by nucleofugic groups.[27e] Upon reduction it gives rise to the anion radical of the corresponding diarylethylene which is able to transfer electrons to the starting compound homogeneously. Although the problem was not treated quantitatively, the proposed mechanism is likely to be the origin of the observed cyclic voltammetric behavior. (e) Martigny, P.; Simonet, J. *J. Electroanal. Chem.* **1977**, *81*, 407.

Table I. Peak Characteristics of the Anodic Oxidation R· + X⁻ − e⁻ → RX for 2 in the Presence of Cl⁻ [a]

sweep rate (V s⁻¹)	ΔE_p[b] (mV)	$E_{p,a}$[c] measured[e]	$E_{p,a}$[c] predicted[d]
0.05	av 52	0.538	0.543
0.10		0.552	0.551
0.20		0.559	0.560

[a] 0.72 M NBu₄Cl. [b] Peak to half-peak potential separation. [c] In V vs. SCE. [d] On the basis of $E_{p,a} = E°_{R^+/R·} - 0.78(RT/F) + (RT/2F) \ln [(RT/F)(k_a/v)]$ with $E°_{R^+/R·} = 0.75$ V, $k_a = 1.6 \times 10^8$ M⁻¹ s⁻¹.[15b] [e] $\partial E_p/\partial \log v = -40$ mV in average.

Another point of interest concerns the reoxidation reaction. As seen on Figures 1 and 2, R⁻ is first reoxidized into R·, giving rise to a one-electron Nernstian wave in agreement with the fact that the R· radical is chemically stable. R· is itself oxidized at a more positive potential, giving rise to a one-electron wave which is irreversible in the presence at stoichiometric, or more, amount of Cl⁻.[15] Table I summarizes the main features of this anodic wave for compound 2 in the presence of 0.72 M chloride ions. It is seen that the peak characteristics are close to those of a rapid electron transfer followed by a fast and irreversible first-order chemical reaction (EC reaction scheme) with a slight participation of the electron-transfer step to the kinetic control.[28] It suggests that the reoxidation mechanism involves the reoxidation of the R· radical into the R⁺ carbocation followed by the reaction of the latter with chloride ions:

$$R· - e \rightleftarrows R^+$$
$$R^+ + Cl^- \xrightarrow{k_a} RCl$$
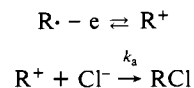
This is further confirmed by the good agreement between the measured peak potential values with those that can be predicted on the basis of this EC mechanism with use of previously determined values of $E°_{R^+/R·}$ and k_a[15b] (Table I).

Discussion

In the case of compound 2, we can obtain the value of the standard potential for the reductive cleavage reaction $E°_{RX/R·+X^-}$ from that of $E°_{R^+/R·}$ (+0.75 V vs. SCE) and that of the dissociation constant of the R⁺ + Cl⁻ ⇌ RCl reaction (2.5×10^{-9} M) which have been previously determined.[15b] Thus

$$E°_{RX/R·+X^-} = 0.246 \text{ V vs. SCE}$$

Using the value of $E°_{R·/R^-} = 0.69$ V vs. SCE[15b] one can also obtain the standard potential for the overall reaction RX + 2e⁻ ⇌ R⁻ + X⁻;

$$E°_{RX/R^-+X^-} = -0.222 \text{ V vs. SCE}$$

The peak potential obtained at 1 V s⁻¹ is −1.970 V vs. SCE, showing that the electrochemical reduction is an extremely irreversible process. Although the exact values of the standard potentials in the case of 1 are not known, the same is likewise qualitatively true. There is thus ample room for redox homogeneous catalysis[24] by solution reversible redox couples.

This has been observed first by using very positive redox couples which catalyze the reaction leading to the R· radical

$$RX + e^- \rightleftarrows R· + X^-$$
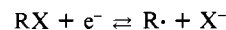
along a predissociation mechanism involving the prior formation of the carbocation.[15b,25a]

The analysis of the cyclic voltammetric data described in the preceding reaction showed another example of redox mediation. The catalyst couple R·/R⁻ is much more negative than the above couples, and catalysis involves a direct electron transfer to the RX molecules yielding the two-electron product R⁻. This is an autocatalytic process in the sense that one of the reduction products, R⁻, is the redox catalyst (reaction 2). Furthermore, it is an "avalanche" type catalysis since two molecules of catalyst are

(28) Nadjo, L.; Savéant, J. M. *J. Electroanal. Chem.* **1973**, *48*, 113.

regenerated each time one molecule of catalyst reacts with one molecule of substrate.

Another interesting point in this connection is that the "carbanionic nucleophile" R⁻ reacts with the electrophile RX by an outersphere electron-transfer mechanism. R· radicals, which are chemically stable in the present case, are thus produced in the solution while they cannot survive at the electrode surface. Indeed, as mentioned in the introduction and more completely discussed in the following, the RX + e⁻ → R· + X⁻ reaction is likely to proceed in a concerted electron-transfer–bond-breaking manner. In the potential region where the electrochemical reduction occurs, R· thus produced at the electrode surface is immediately reduced before having time to diffuse toward the solution since the R·/R⁻ standard potential is much more positive. The species which diffuse towards the solution is thus the carbanion R⁻. The reaction of the latter with incoming molecules of RX then produces R· radicals within the diffusion layer. These diffuse back toward the electrode surface where they are reduced into R⁻, and the catalytic cycle starts again. In cases where the R· radicals would be less stable chemically, yielding, for example, dimerization and H atom transfer disproportionation products, an interesting situation may occur which throws some light on the longly debated question of whether the reaction products, in cleavage reactions, derive from the R· radicals or the R⁻ carbanions.[12] It is very possible that the overall product distribution is controlled by the chemistry of the R· radicals rather than by (or together with) that of the R⁻ carbanions in spite of the fact that the latter are exclusively produced at the electrode surface as a consequence of the extreme instability, if not the inexistence, of the RX⁻· anion radical. For example, in cases where the functional carbon bears a hydrogen atom, the occurrence of RH and R(−H) should be rationalized taking a priori into consideration that they may derive both from the direct attack of R⁻ on RX or form a prior electron transfer leading to two R· radicals that may then undergo H atom transfer disproportionation.

Let us now discuss more closely the intrinsic kinetic features of the electrochemical reduction on the example of compound **2** for which the characteristic standard potentials are known. These are derived from experiments where the sweep rate is large enough for the kinetic interference of the autocatalytic reaction to be negligible. A first observation is the strikingly low value of the transfer coefficient ($\alpha = 0.25$). This is not a special feature of compound **2**. Recent investigation of the electrochemical reduction of primary, secondary, and tertiary butyl iodides and bromides at inert electrodes also indicates low values of the transfer coefficient, around 0.3 and 0.2 for the iodides and bromides, respectively.[29]

A first possible explanation is that, in the context of a RX + e⁻ ⇌ R· + X⁻ concerted electron-transfer–bond-breaking process, the transfer coefficient varies with the electrode potential. In this context, since the reduction potential is much more negative (the peak potential is −1.97 V vs. SCE at 1 V s⁻¹) than the standard potential of the RX/(R· + X⁻) couple (+0.246 V vs. SCE), a value of α significantly lower than 0.5 is indeed expected. Let us use the Marcus activation–driving-force free-energy relationship[2a] to test quantitatively this possibility. Although the Marcus theory was originally devised for outer-sphere electron transfers not involving bond breaking, it has been shown that it can be approximately applied also to proton and other atom transfer reaction.[2d,30] Then, the activation free energy of the forward electrochemical reaction, $\Delta G^{\ddagger}_{el}$, is given as a function of the driving force $F(E - E^{\circ}_{RX/R·+X^-} - \phi_r)$ and the standard activation energy, $\Delta G^{\ddagger}_{0,el}$, by

$$\Delta G^{\ddagger}_{el} = \Delta G^{\ddagger}_{0,el}\left(1 + F\frac{E - E^{\circ}_{RX/R·+X^-} - \phi_r}{4\Delta G^{\ddagger}_{0,el}}\right)^2 \quad (4)$$

where E is the electrode potential, E° the standard potential of

(29) Andrieux, C. P.; Gaillardo, I.; Savéant, J. M.; Su, K. B., submitted.
(30) (a) Agmon, N. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 388. (b) Murdoch, J. R. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 297.

Table II. Treatment of the Cyclic Voltammetry Data by Nonlinear and Linear Activation–Driving-Force Free-Energy Relationships

activation–driving-force free-energy relationships	$\xi_p{}^a$	ϵ^b	$\Delta G^{\ddagger}_{0,el}$		α^c
			eV	kcal	
electron transfer, Marcus[2a]	175.7	1.11	25.6	0.272
electron transfer, Rehm–Weller[33]	137.9	0.87	20.1	0.133
	84.75				
atom transfer, Marcus, Agmon, Levine[34]	160.0	1.01	23.3	0.204
linear, Volmer–Butler[35]	131.8	0.83	19.2	0.25

$^a \xi_p = -(F/RT)(E - E^{\circ}_{RX/R·+X^-} - \phi_r)$. $^b \epsilon = 4\Delta G^{\ddagger}_0/RT$. $^c \alpha = -d(\Delta G^{\ddagger}/F)/dE$. For the question of two possible definitions of α see ref 5b.

the RX + e⁻ ⇌ R· + X⁻ reaction, and ϕ_r the potential at the reaction site vis-à-vis that of the solution (usually considered as located in the outer Helmoltz plane). The heterogeneous forward rate constant $k(E)$ is then given by

$$k(E) = Z_{el} \exp(-\Delta G^{\ddagger}_{el}/RT)$$

where Z_{el} is the heterogeneous collision frequency.[4] In the potential region of the voltammetric wave, the RX + e⁻ → R· + X⁻ reaction can be considered to proceed irreversibly from left to right. Under these conditions, the dimensionless equation of the voltammogram is obtained by a simple extension of the theory corresponding to the Volmer–Butler kinetics[28] leading to

$$\frac{\psi}{1 - I\psi} = \Lambda^{\circ} \exp\left\{-\frac{\epsilon}{4}\left(1 - \frac{\xi}{\epsilon}\right)^2\right\} \quad (5)$$

where

$$\xi = -\frac{F}{RT}(E - E^{\circ}_{RX/R·+X^-} - \phi_r), \quad \psi = I/FC^{\circ}(FvD/RT)^{1/2}$$

$$\Lambda^{\circ} = Z_{el}/(FvD/RT)^{1/2}, \quad \epsilon = 4\Delta G^{\ddagger}_{0,el}/RT,$$

$$\text{and } I\psi = \pi^{-1/2}\int_{-\infty}^{\xi}\psi(d\eta)(\xi - \eta)^{-1/2}\,d\eta$$

With the following numerical values—$Z_{el} = 2 \times 10^3$ cm s⁻¹, $D = 5 \times 10^{-6}$ cm s⁻¹,[4] $v = 1$ V s⁻¹, $E_p = -1.97$ V, $E^{\circ} = 0.246$ V, $\phi_r = -0.075$ V—[32] the numerical computation of the above equation according to previously described procedures[28,31] gave the results shown in Table I. It is seen that there is a good agreement between the predicted (0.272) and experimental (0.25) values of the transfer coefficient. Other nonlinear activation–driving-force free-energy relationships, namely the Rehm–Weller equation for electron transfer[33]

$$\Delta G^{\ddagger}_{el} = F\left(\frac{E^{\circ}_{RX/R·+X^-} - \phi_r}{2}\right) + \left\{\left(F\frac{E^{\circ}_{RX/R·+X^-} - \phi_r}{2}\right)^2 + \Delta G^{\ddagger 2}_{0,el}\right\}^{1/2} \quad (6)$$

and the Marcus–Agmon–Levine equation for atom transfer[34]

$$\Delta G^{\ddagger}_{el} = F(E - E^{\circ}_{RX/R·+X^-} - \phi_r) + \frac{\Delta G^{\ddagger}_{0,el}}{\ln 2}\ln\left[1 + \exp\left\{-\frac{F(E - E^{\circ}_{RX/R·+X^-} - \phi_r)\ln 2}{\Delta G^{\ddagger}_{0,el}}\right\}\right] \quad (7)$$

were also tested as to the comparison between the experimental and predicted values of α (Table II). Although all three treatments

(31) (a) Matsuda, H.; Ayabe, Y. *Z. Elektrochem.* **1955**, *59*, 494. (b) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1977**, *85*, 27.
(32) ϕ_r was calculated by using the Frumkin procedure[32b] assuming that the reaction site is located in the outer Helmoltz plane with use of the double layer capacitance data for platinum in acetonitrile. (b) Delahay, P. "Double Layer and Electrode Kinetics-Interscience"; New York, 1965. (c) Petrii, O. A.; Khomchenko, I. G. *J. Electroanal. Chem.* **1980**, *106*, 277.
(33) (a) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(34) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) Agmon, N.; Levine, R. D. *Chem. Phys. Lett.* **1977**, *52*, 197.

Table III. Treatment of the Kinetics of the $R^- + RX \rightarrow 2R\cdot + X^-$ Electron Transfer by Nonlinear and Linear Activation–Driving-Force Free-Energy Relationships[a]

activation–driving-force free-energy relationship	$\dfrac{\Delta G^{\ddagger}_{hom}, E^{\circ}_{R\cdot/R^-} - }{E^{\circ}_{RX/R\cdot+X^-}}$	$\Delta G^{\ddagger}_{0,hom}$[c]	$\Delta G^{\ddagger}_{iso,RX/R\cdot+X^-}$[d]	$\Delta G^{\ddagger}_{0,el,RX/R\cdot+X^-}$[e]
electron transfer, Marcus[2a]		0.914	1.378–1.728	1.11
electron transfer, Rehm–Weller[32]	0.506	0.729	1.008–1.358	0.87
atom transfer, Marcus, Agmon, Levine[33]	−0.936	0.890	1.330–1.680	1.01
linear, Polyani[35]		0.740	1.030–1.380	0.83

[a] Free energies in eV. [b] Activation free energy and driving force of the reaction. [c] Standard activation free energy of the reaction. [d] Isotopic activation free energy of the $RX/(R\cdot + X^-)$ couple. [e] Electrochemical standard activation free energy of the $RX/(R\cdot + X^-)$ couple.

led to comparable values of the standard free energy of activation, $\Delta G^{\ddagger}_{0,el}$ (20 kcal/mol), a much better fit was obtained for α with the first and third laws than with the second.

Another possibility is that of a linear relationship (Volmer–Butler type)[35] with a transfer coefficient equal to 0.25 whatever the electrode potential. This would lead to a comparable value of $\Delta G^{\ddagger}_{0,el}$ (Table II).

Since we have measured the rate constant of the homogeneous electron transfer $R^- + RX \rightarrow 2R\cdot + X^-$ and we known the driving force of the reaction, i.e., $E^{\circ}_{R\cdot/R^-} - E^{\circ}_{RX/R\cdot+X^-} = -0.936$ V (from the above determined values of $E^{\circ}_{RX/R\cdot+X^-}$ and $E^{\circ}_{R\cdot/R^-} = -0.69$ V),[15b] we can compare the electrochemical and homogeneous free energies of activation in the framework of the various activation–driving-force relationships considered above (Table III). Taking as homogeneous collision frequency, 3.5×10^{11} M^{-1} s^{-1},[4] the homogeneous activation free energy, $\Delta G^{\ddagger}_{hom}$, is found to be 0,506 eV (11.7 kcal/mol). By using the homogeneous counterparts of eq 4, 6, and 7 ($E - E^{\circ} - \phi_r$ is replaced by $E^{\circ}_{R\cdot/R^-} - E^{\circ}_{RX/R\cdot+X^-}$) and the linear Polyani relationship[36]

$$\Delta G^{\ddagger}_{hom} = \Delta G^{\ddagger}_{0,hom} + \alpha(E^{\circ}_{R\cdot/R^-} - E^{\circ}_{RX/R\cdot+X^-})$$

the series of values of the standard homogeneous free energy of activation, $\Delta G^{\ddagger}_{0,hom}$,[37] given in Table III was obtained. Furthermore

$$\Delta G^{\ddagger}_{0,hom} = \frac{\Delta G^{\ddagger}_{iso,RX/R\cdot+X^-} + \Delta G^{\ddagger}_{iso,R\cdot/R^-}}{2}$$

where the two $\Delta G^{\ddagger}_{iso}$'s are the isotopic free energies of activation of the two redox couples. Investigation of the cyclic voltammetry of the $R\cdot/R^-$ couple as a function of the sweep rate showed that a Nernstian behavior is obtained up to at least 10 V s^{-1}. It follows that its electrochemical standard free energy of activation is less than 0.225 eV. According to Marcus,[2a] $\Delta G^{\ddagger}_{iso}$ is twice $\Delta G^{\ddagger}_{0,el}$ whereas according to Hush[2b] they are equal. This is not a settled question neither from the theoretical nor from the experimental viewpoint.[4,19a,38] Thus a maximal estimate of $\Delta G^{\ddagger}_{iso,R\cdot/R^-}$ is 0.45 eV. On the other hand, $\Delta G^{\ddagger}_{iso,R\cdot/R^-}$ should be larger than the corresponding quantity for highly delocalized aromatic hydrocarbon/anion radical couples, i.e., larger than 0.10 eV.[4] We can thus, using the above relationship, bracket the value of $\Delta G^{\ddagger}_{iso,RX/R\cdot+X^-}$ as shown in Table III. Comparison of the last two entries of Table III shows that the electrochemical standard activation free energy is smaller than the homogeneous isotopic activation free energy. This is not unexpected since both the large electric field at the electrochemical reaction site and the image force effects are anticipated to facilitate the bond cleavage process.

A pretty consistent picture of the heterogeneous and homogeneous dissociative electron transfer to the investigated aliphatic halides thus emerges from the preceding analysis. It involves either a nonlinear activation–driving-force free-energy relationship of the Marcus or the Marcus–Agmon–Levine type (the Rehm–

Weller relationship appears not to fit the experimental data) with an α value close to 0.5 at the standard potential or a linear relationship with a constant α equal to 0.25. The latter case would imply that the potential energy surface of the products be steeper (by a factor of 3) than that of the reactants at the intersection point and that the ratio of the slopes remains the same over a potential range encompassing the standard potential and the actual reduction potential, i.e., wider than 2.2 V. It is not impossible that the slopes of the two potential energy surfaces be different since that of the reactant essentially involves the stretching of a C–Cl bond while that of the products corresponds to a weak induced dipole charge interaction between R· and Cl$^-$ giving rise to a shallow energy minimum.[39] It is, however, unlikely that the slopes at the intersection point would remain the same over such an extended range of energy. A nonlinear activation–driving-force relationship thus appears more likely, noting, however, that there is no reason why the slopes of the potential energy surfaces should be the same for a zero driving force and that anharmonicity may interfere especially concerning the product potential energy surface. A way of getting more information about this problem would be to investigate the experimental variations of α with the electrode potential in a similar manner as already described for outer-sphere simple electron transfer.[5] It requires the investigation of the largest possible range of sweep rates. The present example is not very convenient in this connection since the autocatalysis process interferes below 1 V s^{-1}. An experimental study of the problem on the example of simple saturated aliphatic halides is presently underway.

Within this framework it is now possible to discuss more precisely the question of the existence and possible intermediacy of the $RX^-\cdot$ anion radical in the reduction reaction. So far we have assumed a concerted electron-transfer–bond-breaking pathway. If the $RX^-\cdot$ anion radical was an intermediate in the reduction, let us estimate a maximum limit of the $\Delta G^{\ddagger}_{0,el}$ as a solvent reorganization energy. The negative charge is likely to be delocalized over the fluorenyl ring. Let us assume, to obtain the maximum limit, that it is entirely located on the chlorine atom. Using its Van der Waals radius, 1.80 Å, we find $\Delta G^{\ddagger}_{0,el} = 0.45$ eV, i.e., $\epsilon = 71$.[2a,3,4] Using the same procedure as previously to predict the value of the transfer coefficient that should be observed on the 1 V s^{-1} voltammogram in the context of Marcus theory, we find $\alpha = 0.42$ which is clearly inconsistent with the experimental value (0.25). This shows that the concerted electron-transfer–bond-breaking pathway is much more likely to be followed under our experimental conditions.

Figure 4 gives a picture of the potential energy surfaces for compound **2**, in the context of Marcus theory.[39] The hatched zone represents the experimental window provided by the cyclic voltammogram at 1 V s^{-1} from a potential corresponding to one tenth of the peak current (lower curve) up to the peak potential (upper curve). The dotted line curve represents a possible location of the potential energy surface of the anion radical, $RX^-\cdot$. It shows that $RX^-\cdot$ may exist as a discrete species while not being an intermediate in the reduction process. It would, however, correspond to a species very unstable toward dissociation into R· and

(35) (a) Butler, J. A. V. *Trans. Faraday Soc.* **1924**, *19*, 729. (b) Butler, J. A. V. *Trans. Faraday Soc.* **1924**, *19*, 734. (c) Erdey-Gruz, t.; Volmer, M. *Z. Phys. Chem.* **1930**, *150A*, 203.

(36) (a) Evans, M. D.; Polyani, M. *Trans. Faraday Soc.* **1936**, *32*, 1340. (b) Evans, M. D.; Polyani, M. *Trans. Faraday Soc.* **1938**, *34*, 11.

(37) I.e., the value that $\Delta G^{\ddagger}$ would have if the two couples had the same standard potentials.

(38) Peover, M. E.; Powell, J. S. *J. Electroanal. Chem.* **1969**, *20*, 427.

(39) In addition to the stretching of the C–X bond, the reaction coordinate also contains a component representing the solvent polarization which is expected to be more important for the products than for the reactants.

(40) (a) Faure, D.; Lexa, D.; Savéant, J. M. *J. Electroanal. Chem.* **1982**, *140*, 285. (b) Lexa, D.; Savéant, J. M. *Acc. Chem. Res.* **1983**, *16*, 235.
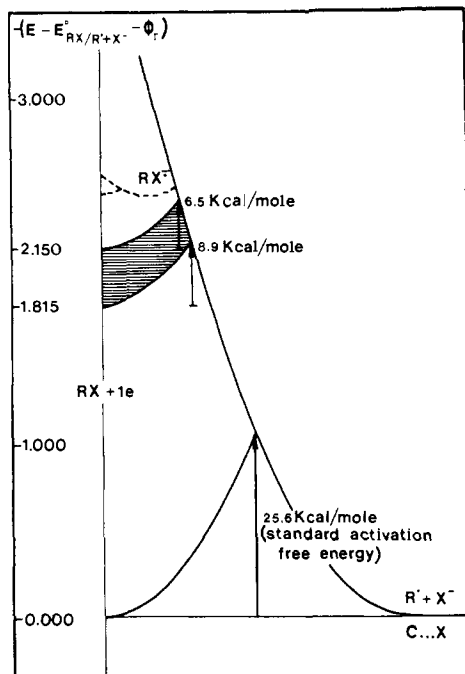
Figure 4. Representation of the potential energy surfaces for the electrochemical reduction (hatched zone, 1 V s⁻¹, cyclic voltammetry) for compound **2** in the context of Marcus theory (RX + e⁻ → R· + X⁻).

X⁻, involving a driving force of at least −2.2 eV (51.3 kcal), i.e., a dissociation constant of 7×10^{37} M.

So far we have assumed that the rate-determining process of the overall RX + 2e⁻ → R⁻+X⁻ is the bond cleavage assisted transfer of one electron leading to R· and X⁻, R· being further reduced into R⁻. Since the latter reaction has a large driving force (−1.28 V at the peak of the cyclic voltammogram), the question may be raised of the possibility that the transfer of the second electron is concerted with the transfer of the first and the bond cleavage. Analysis of the electrochemical data in the same way as above does not lead to a clear-cut answer: the α predicted by the Marcus relationship (0.23) is much too large as compared to the experimental value (0.125 for a two-electron process) but the α's deriving from the Marcus–Agmon–Levine and the Rehm–Weller relationships (0.16 and 0.09, respectively) are compatible

with the experimental value. This possibility is, however, unlikely since the introduction of two electrons in a molecule where the C–X bond is only moderately stretched would result in a very large Coulombic repulsion barrier. It is thus more likely that the second electron enters the system when, the bond being almost broken, it retains the characteristics of the R· radical.

Lastly, it is worth discussing the mechanism of the reverse reaction, i.e., the oxidation of R⁻ + X⁻ back into RX. R⁻ is first reversibly reoxidized into R· without interference of the halide ions. Then R· is reoxidized first into R⁺ which reacts with the halide ion regenerating the starting alkyl halide:

RX

R⁺ + X⁻ ⇌ R· + X⁻
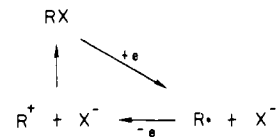
The reoxidation pathway is thus not the exact reverse of the reduction pathway. This is not an unprecedented situation. The same occurs in the electrochemistry of vitamin B_{12} derivatives:[38] the reduction of a strongly liganded cobalt(II) complex into the cobalt(I) complex is a one-electron transfer involving the breaking of a cobalt axial ligand bond (analogous to the RX + e⁻ → R· + X⁻ in the present case) whereas the reoxidation reaction involves first the oxidation of the cobalt(I) complex into a cobalt(II) complex weakly bound with the solvent (analogous to R·-e⁻ → R⁺) and then the coordination by the strong ligand (analogous to R⁺ + X⁻ → RX),

Experimental Section

9-Chloro-9{α-(9-fluorenylidene)}benzylfluorene (**1**) and 9-chloro-9-mesitylfluorene (**2**) were prepared as described in a previous paper.[15b] The procedures for solvent and supporting electrolyte purification are also described there. Due to the extreme hygroscopy of tetrabutylammonium chloride, stock solutions were prepared at the vacuum line and diluted to the desired concentrations. The working electrode was a bright platinum disk of about 0.08 cm² surface area. The other electrodes, cell, and instrumentation were the same as previously described.[15b]

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Communications to the Editor

Configuration Entropy of the Alanine Dipeptide in Vacuum and in Solution: A Molecular Dynamics Study[†]

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The configurational entropy of biopolymers is an important contribution to their free energy and thus can play an essential role in determining their structure and function.[1–3] In many cases

it is appropriate to separate the configurational entropy into two parts, i.e., that contributed by the presence of several accessible minima and that contributed by the flexibility in each of the minima. Evaluation of the latter is the focus of this paper; the former can be obtained by summing over the results for each of the minima with the appropriate statistical weights. Harmonic treatments have been used for the configurational entropy of biopolymers.[3–6] To introduce anharmonicity, the results of

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