Passage from Concerted to Stepwise Dissociative Electron Transfer as a Function of the Molecular Structure and of the Energy of the Incoming Electron. Electrochemical Reduction of Aryldialkyl Sulfonium Cations

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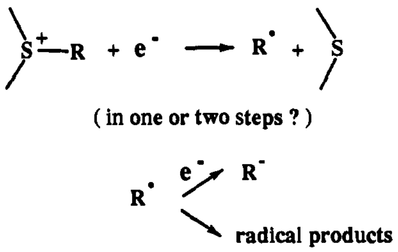
Abstract: The electrochemical reductive cleavage of the carbon–sulfur bond in the title compounds offers the example of a reaction where the concerted or stepwise character of the electron-transfer–bond-breaking process is a function of molecular structure. As with the reductive cleavage of the carbon–halogen bond in benzyl halides and of the nitrogen–halogen bond in aromatic *N*-halosultams, the two main factors governing the nature of the mechanism are the LUMO energy and the bond strength in the starting molecule: the higher the former and the weaker the latter, the greater the tendency for the concerted mechanism to prevail over the stepwise mechanism and vice versa. Consistently with the effect of these two mechanism-governing factors, two borderline cases were identified where the reaction passes from the concerted pathway to the stepwise pathway upon increasing the driving force by raising the scan rate and thus shifting the reduction potential toward negative values. The reasons for possible variations of the concerted or stepwise character of the mechanism of reductive cleavages upon changing the mode of electron injection are discussed.

The electrochemical reduction of sulfonium salts has been the object of several studies in the past from which the reaction mechanism in Scheme 1 has emerged.[2,3] The radical resulting from the initial reductive cleavage reaction may give rise to various products not involving further consumption of electrons or, in most cases, be further reduced to the carbanion, which is eventually converted into the corresponding hydrocarbon. The starting sulfonium cation plays the role of the acid in the latter reaction when the medium does not contain additional acids, as when the reaction is carried out in unbuffered aprotic solvents and when at least one carbon bonded to the sulfur bears at least one hydrogen. Half of the starting sulfonium cation is then converted into the corresponding ylid, and the overall reaction follows consequently a one electron per molecule stoichiometry (Scheme 2).[4]

Previous electrochemical studies indicate that the most stable radical is formed upon reductive cleavage as, for example, phenacyl, detected under the form of acetophenone, in phenacyldiethyl and phenylmethyl sulfonium salts;[4b–d] cyanomethyl in the dimethylcyanomethyl sulfonium cation;[5a] benzyl in the benzyldimethyl sulfonium cation, as detected by means of a radical trap;[4b] and methyl, isopropyl, benzyl, *p*-cyanobenzyl, phenacyl, and $\cdot CH_2(Ph)C{=}C(CN)_2$ in the corresponding phenylmethyl and 1-naphthylmethyl sulfonium salts, as attested by the formation of the phenylmethyl and 1-naphthylmethyl sulfides, respectively, identified by comparison of their anodic cyclic voltammetric peak potentials with those of authentic samples.[3] The same conclusion may also be drawn from the study of the reduction of an extended series of phenylalkyl sulfonium salts by potassium in graphite in tetrahydrofuran.[6]

Scheme 1



As in other one-electron reductive cleavage reactions, the question arises of whether the electron-transfer and bond-breaking steps are successive or concerted (Scheme 3). In the first case, the first reaction in Scheme 1 is an elementary step, whereas, in the second, it is merely the balanced equation of a two-step reaction going through a transient neutral radical intermediate. Previous investigations of the discrimination between the two pathways and of the factors that govern the occurrence of one or the other in electrochemical reactions have been restricted to carbon–halogen bond cleavage and, more recently, nitrogen–halogen bond cleavage.[7] These studies revealed that the two main governing factors are the energy of the low-lying orbital (such as a π^* orbital) in which the incoming electron can be transitorily located and the strength of the cleaving bond in the starting molecule. High orbital energies and weak bonds favor the concerted mechanism over the stepwise mechanism and vice versa.

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(1) (a) Université Denis Diderot. (b) Eastman Kodak Co.

(2) (a) For a review, see: ref 2b. (b) Chambers, J. Q. Organic Sulfur Compounds. In *Encyclopedia of Electrochemistry of the Elements, Organic Section*; Bard, A. J., Lund, H., Eds.; Dekker: New York, 1978; Vol. XII, pp 329–502.

(3) (a) Saeva, F. D.; Morgan, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4124. (b) Saeva, F. D. *Tetrahedron* **1986**, *42*, 6123. (c) Saeva, F. D. *Top. Curr. Chem.* **1990**, *156*, 61.

(4) (a) The role of ylid formation has been pointed out in early polarographic studies of phenacyldiethyl and phenylmethyl sulfonium salts.[4b–d] Ylid formation during the reduction in aprotic solvents has been taken advantage of for synthetic purposes, making them react with carbonyl compounds.[4e,f] (b) Savént, J.-M. *C. R. Hebd. Seances Acad. Sci.* **1963**, *257*, 448. (c) Savént, J.-M. *C. R. Hebd. Seances Acad. Sci.* **1964**, *258*, 585. (d) Savént, J.-M. *Bull. Soc. Chim.* **1967**, 481. (e) Shono, T.; Mitani, M. *Tetrahedron Lett.* **1969**, 687. (f) Shono, T.; Akazawa, T.; Mitani, M. *Tetrahedron* **1969**, 687.

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(6) Beak, P.; Sullivan, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 4450.

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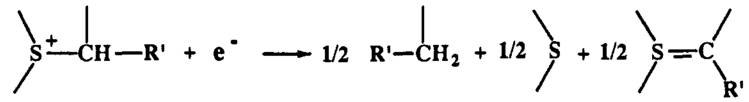
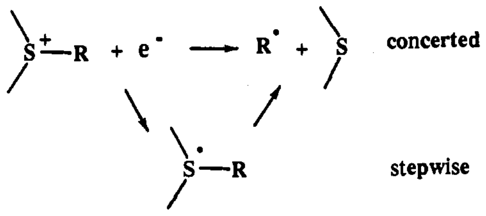
Scheme 2



Scheme 3



The work described below is aimed at unraveling the nature of the mechanism, concerted or stepwise, in the electrochemical reductive cleavage of an entirely different type of bond, namely, the carbon–sulfur bond in sulfonium cations. The following series of alkylmethylaryl sulfonium cations (Scheme 4) were investigated for the purpose of examining the possible changes in mechanism as a function of the molecular structure. The variation of the aryl group and of the cleaving alkyl group is aimed at modifying the energy of the π^* orbital and of the bond strength. It was noted, in a previous study of the phenyl and 1-naphthyl derivatives of the series,[3a,b] that the cyclic voltammetric peak potentials were very sensitive to the nature of the cleaving radical, and it was inferred from this observation that the reductive cleavage was likely to follow the concerted pathway. As shown in Scheme 4, this conclusion is partly correct: the reduction of several sulfoniums in the series does follow the concerted mechanism, but others are reduced according to the stepwise mechanism. The set of sulfonium cations shown in Scheme 4 also provided an opportunity to investigate the possible passage from the concerted to the stepwise mechanism as the driving force of the reaction increases according to previous predictions.[8,9] As with all irreversible cyclic voltammetric reduction waves, an increase of the scan rate shifts the reduction potential, e.g., the peak potential, toward more and more negative values, thus offering a larger and larger driving force to the reaction. The passage from one mechanism to the other as the driving force changes is illustrated in terms of potential energy surfaces in Figure 1, where the reaction coordinate is a combination of the breaking bond length and of the solvent reorganization coordinate.

Results and Discussion

Figure 2 shows a typical example of the cyclic voltammetric behavior of the sulfonium salts investigated in this work. The first cathodic peak corresponds to an irreversible one-electron reduction.[10] At more negative potentials, one notices the presence of an irreversible wave followed by the reversible one-electron wave of *p*-tolunitrile (identified by comparison with an authentic sample). The second irreversible wave corresponds to the reduction of the ylid. It is indeed the same as the irreversible wave appearing after addition of an equimolar amount of hydroxide ions (Figure 2b). It is also observed that the first peak doubles in height upon addition of a strong acid (Figure 2c). The reduction, in the absence of acids or bases, thus corresponds to the set of reactions represented in Scheme 2 with expulsion of the 4-cyanobenzyl group, as attested by the fact that the anodic wave appearing upon scan reversal after the first reduction is the same as the oxidation wave of methylphenyl sulfide (Figure 2a).

Similar behaviors were found with all the sulfonium cations investigated. With the anthracenyl derivatives, expulsion of the methyl radical in **1c** and of the 4-cyanobenzyl radical in **3c** is attested by the fact that the anodic wave observed upon scan reversal after the first cathodic peak is the same in both cases as well as by the fact that the reversible one-electron wave of *p*-tolunitrile is observed on the reduction side with **3c**. We may thus conclude that for all members of the series the reductive cleavage occurs as depicted in Scheme 1 and that, in the absence of acids or bases, the overall stoichiometry is as represented in Scheme 2.

The determination of the concerted or stepwise character of the cleavage mechanism requires a closer examination of the characteristics of the first cathodic peak as a function of the scan rate. In order to cover an extended range of scan rates, 0.05–1000 V/s, three glassy carbon electrodes of decreasing diameter were used successively: a 3-mm-diameter disk between 0.05 and 10 V/s; a 1-mm-diameter disk between 5 and 100 V/s; and a 0.35-mm-diameter disk between 50 and 1000 V/s, as described in the Experimental Section. This strategy allowed minimization of the ohmic drop over the whole range of scan rates, as was checked with the reversible one-electron wave of anthracene (Figure 3). Careful polishing of the electrode surface after each run allowed a reproducibility on the order of 1 mV for the peak widths and 1–4 mV for the absolute values of the peak potentials.

Figures 4–7 show the variations of the peak potential, E_p, and of the peak width, $E_{p/2} - E_p$, with the scan rate, v, in the range 0.05–1000 V/s measured at 20 °C. We found that these variations were the same after addition of a stoichiometric amount of perchloric acid, which suppresses the formation of the ylid and accordingly raises the peak current up to a two electron per molecule stoichiometry. The peak potentials of all the compounds in the series at 0.1 V/s are listed in Table 1. The peak potentials and the peak widths corrected from ohmic drop using the data obtained with anthracene (Figure 3) are also shown in Figures 4–7.

The easiest mechanism diagnosis is made with **1c**: the slope of the $E_p - \log v$ plot, $\partial E_p/\partial \log v$, is constant over almost the whole range of scan rates, with a value close to 29 mV per unit, the theoretical value characterizing an "EC" mechanism in which the rate-determining step is a first-order chemical step ("C") following a fast electron-transfer step ("E").[10b,c] This is confirmed by the fact that the peak width, $E_{p/2} - E_p$, is also constant, with a value close to the theoretical value, 47 mV, characteristic of the same mechanism and kinetic situation.[10b,c] We may therefore conclude that the reduction of **1c** follows the stepwise mechanism and that the initial electron transfer is fast enough and/or the followup cleavage slow enough for the latter to be the rate-determining step. One has to go to the highest scan rate, 1000 V/s, to detect the beginning of a mixed kinetic control where electron transfer starts to interfere with the followup reaction. These conclusions are further confirmed by the observation that, using an ultramicroelectrode of 10-μm diameter (see the Experimental Section), the reduction wave starts to show chemical reversibility above 10 000 V/s. Simulation of the cyclic volta-

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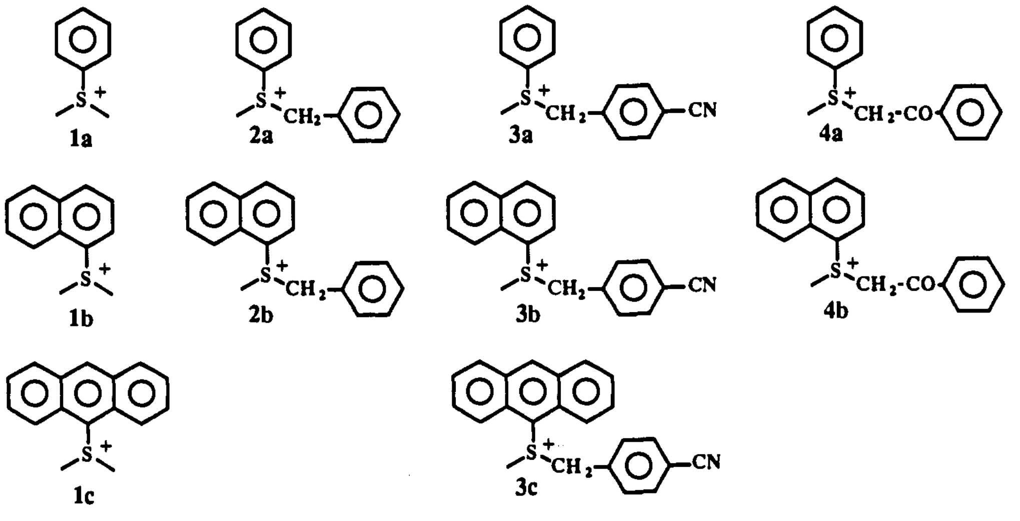
[8] Andrieux, C. P.; Merz, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1985**, *107*, 6097.

[9] (a) Evidence for the occurrence of a similar phenomenon has been reported in the homogeneous reduction of phenyltriphenylmethyl sulfide by electrochemically generated aromatic anion radicals.[9b] (b) Severin, M. G.; Farnia, G.; Vianello, E.; Arevalo, M. C. *J. Electroanal. Chem.* **1988**, *251*, 369.

[10] (a) The electron stoichiometry was determined by reference to the one-electron reversible wave of ferrocene ($i_p = 0.446FSC^0D^{1/2}(Fv/RT)^{1/2}$) taking into account that the wave is irreversible ($i_p = 0.496FSC^0D^{1/2}(\alpha Fv/RT)^{1/2}$) with a transfer coefficient that is derived from the peak width: $\alpha = 1.85(RT/F)/(E_{p/2} - E_p)$.[10b,c] i_p is the peak current, E_p and $E_{p/2}$ the peak and half-peak potential, respectively, S the electrode surface area, C^0 the substrate concentration, D its diffusion coefficient, and v the scan rate. (b) Andrieux, C. P.; Savéant, J.-M. In *Electrochemical Reactions, 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. (c) Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1973**, *48*, 113.

Scheme 4



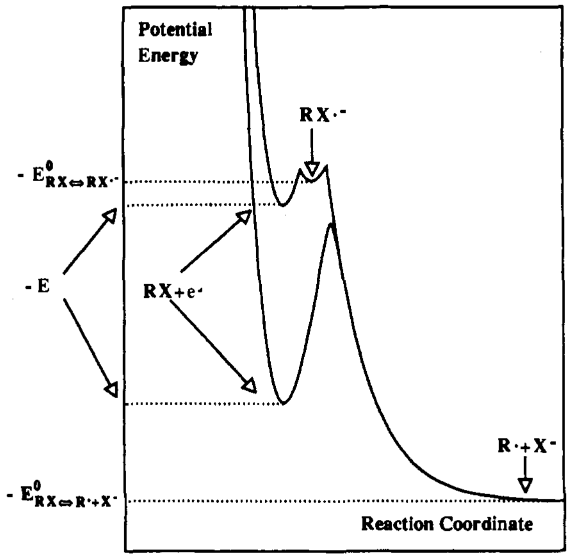


Figure 1. Passage from the concerted to the stepwise mechanism upon increasing the driving force, i.e., shifting the electrode potential, E, negatively. For sulfonium cations, X = >S⁺.

mmograms obtained in the range 1000–60 000 V/s (Figure 8) leads to the following values of the parameters characterizing the electron-transfer and followup cleavage step: standard potential $E^\circ_{>S-R^+/>S-R^\cdot} = -1.20$ V vs SCE; transfer coefficient $\alpha = 0.5$; standard rate constant of electron transfer uncorrected from double layer effects $k_S^{ap} = 3$ cm/s; rate constant of the followup cleavage step $k_{>S-R^\cdot \rightarrow >S+R^\cdot} = 3 \times 10^4$ s^{-1}, taking 1.5×10^{-10} F and 900 Ω for the double-layer capacitance and the uncompensated cell resistance, respectively. We note that the standard potential for the injection of one electron into **1c** is considerably positive, by 600 mV, compared to that of anthracene (Figure 3), indicating that there is strong interaction between the π^* orbital of the anthracenyl group and the orbitals of the sulfur atom.

Passing from **1c**, vertically in Scheme 4, to **1b** and, horizontally, to **3c**, two similar behaviors are met: $\partial E_p/\partial \log v$ and, accordingly, $E_{p/2} - E_p$ vary more with the scan rate and have larger values. The value of $E_{p/2} - E_p$ however remains much below that of a rate-determining electron-transfer step with a transfer coefficient of 0.5, 94 mV,[10b,c] indicating that we are still dealing with an "EC" mechanism even if the electron-transfer step participates more significantly in the mixed control of the kinetics and, as expected, more and more as the scan rate is increased.[10b,c] There are two reasons for this larger participation of the electron-transfer step in the kinetic control of the reaction when passing from **1c** to **1b**. One is that electron transfer is slower since, the charge being spread over a smaller volume, the solvent reorganization energy is bigger. The other is that the cleavage rate constant is larger essentially because the LUMO energy in the >S· radical is higher.[11] From **1c** to **3c**, the main factor is the acceleration of the cleavage mainly due to a decrease of the bond strength passing from the methyl to the 4-cyanobenzyl group.[11] For both **1b** and **3c**, no reversibility of the cyclic voltammetric wave was detected up to 800 000 V/s, implying that $k_{>S-R^\cdot \rightarrow >S+R^\cdot} \geq 4 \times 10^7$ s^{-1}.

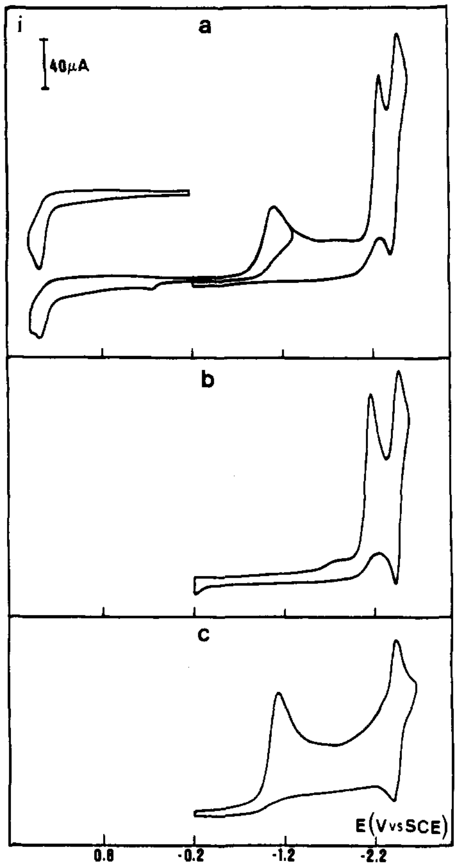


Figure 2. Cyclic voltammetry of methylphenyl-4-cyanobenzylsulfonium trifluoromethanesulfonate (1.5 mM) at a glassy carbon electrode (a) in acetonitrile with 0.1 M n-Bu$_4$NBF$_4$, (b) after addition of 1.5 mM Me$_4$NOH, and (c) after addition of 1.5 mM ClO$_4$H. Scan rate 0.5 V/s. Inset in part a shows cyclic voltammetry of phenylmethyl sulfide at the same scan rate.

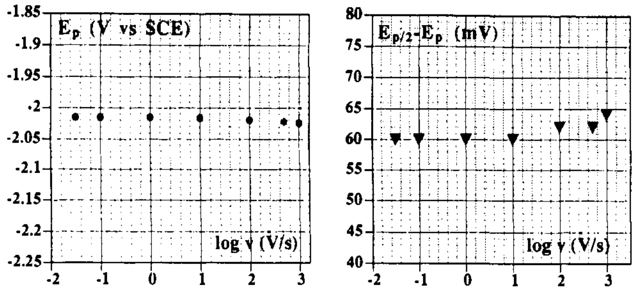


Figure 3. Cyclic voltammetry of anthracene in acetonitrile + 0.1 M n-Bu$_4$NBF$_4$. The peak potential and the peak width vary with the scan rate.

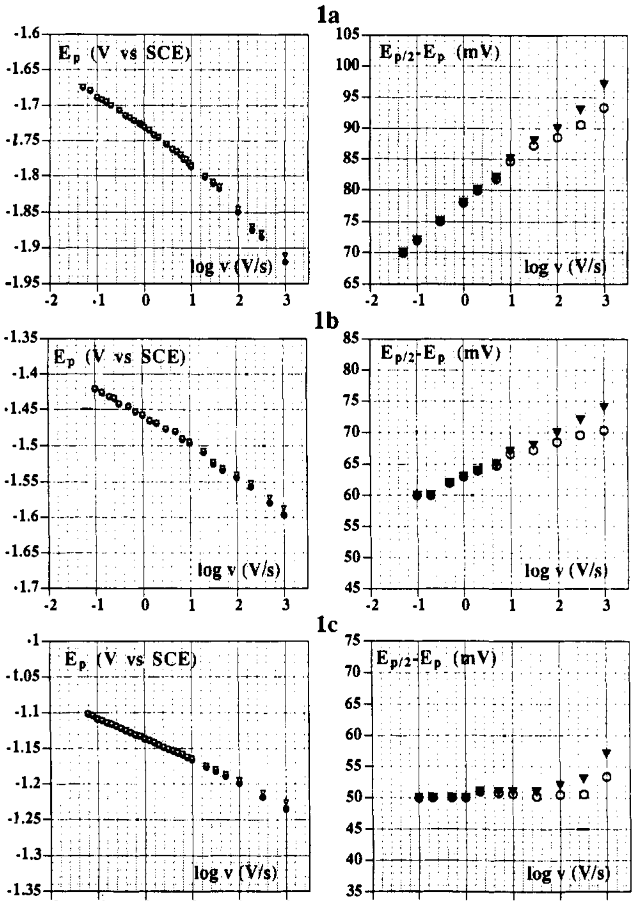
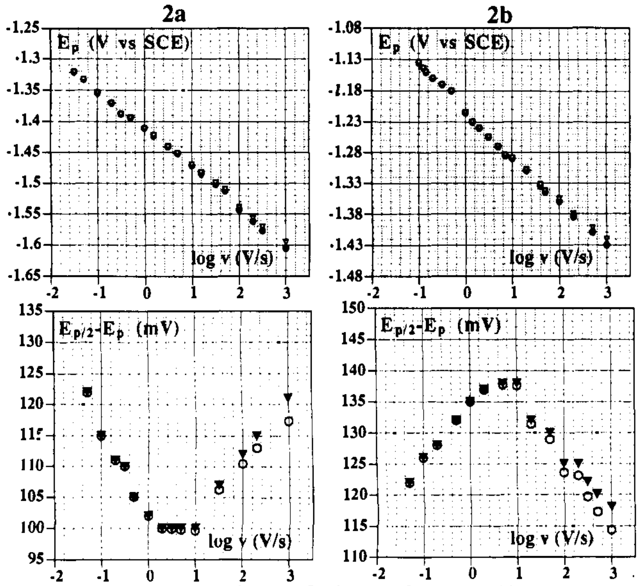
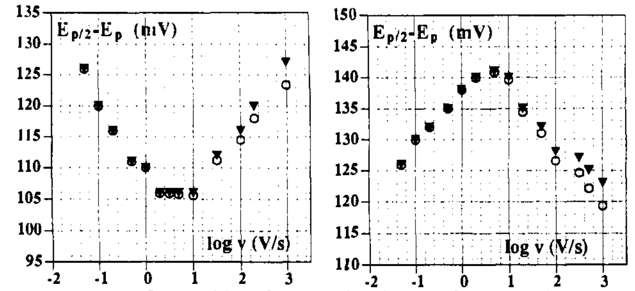


Figure 4. Cyclic voltammetry of compounds **1** in acetonitrile + 0.1 M n-Bu$_4$NBF$_4$ and variations of the peak potential (● raw data, ▽ corrected from ohmic drop) and the peak width (▼ raw data, ○ corrected from ohmic drop) with the scan rate.

Going from **1b** to **1a**, $\partial E_p/\partial \log v$ and, in a parallel fashion, $E_{p/2} - E_p$ vary more with the scan rate and have larger values. The values of $E_{p/2} - E_p$ at low scan rates remain however much below that of a rate-determining electron-transfer step with a transfer coefficient of 0.5, 94 mV, indicating that we are still dealing with an "EC" mechanism even if the electron-transfer step participates more significantly in the mixed control of the kinetics and, as expected, more and more as the scan rate is increased. At the highest edge of the scan rate range, complete kinetic control by the electron-transfer step is practically reached. The reasons causing this increased participation of the electron-transfer step in the kinetic control of the reaction are again a smaller rate constant of electron transfer due to a larger solvent reorganization energy and an acceleration of the cleavage due the increase of the >S· radical LUMO energy. Again, no reversibility of the cyclic voltammetric wave could be detected up to 800 000 V/s, implying that $k_{>S-R\cdot \to >S+R\cdot} \geq 4 \times 10^7$ s^{-1}.



In the absence of acid (one-electron peak)



After addition of perchloric acid (two-electron peak)

Figure 5. Cyclic voltammetry of compounds **2** in acetonitrile + 0.1 M n-Bu$_4$NBF$_4$ and variations of the peak potential (● raw data, ▽ corrected from ohmic drop) and the peak width (▼ raw data, ○ corrected from ohmic drop) with the scan rate.

We may thus conclude from the preceding observations that with **1a**, **1b**, **1c**, and **3c** the reduction follows the stepwise mechanism. Although the rate constants of the initial electron-transfer and followup cleavage steps vary from one of these sulfoniums to the other, the fact that the peak potential at a given scan rate shifts negatively from **1c** to **1b** and to **1a** as well as from **3c** to **1c** is essentially the result of the negative shift of the standard potential $E^\circ_{>S-R+/>S-R\cdot}$, which is a measure of the increase of the LUMO energy.

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(11) (a) As appears in the following equation, the driving force of the radical cleavage reaction is governed by three main factors:

$$\Delta G^\circ_{>S-R\cdot/>S+R\cdot} = D_{>S-R+/>S\cdot++R\cdot} + E^\circ_{>S-R+/>S-R\cdot} - E^\circ_{>S\cdot+/>S} + T\Delta S$$

where $\Delta S = \bar{S}_{>S-R^+} - \bar{S}_{>S\cdot^+} - \bar{S}_{R\cdot}$ (the $\bar{S}$ are the subscript partial molar entropies) does not vary much from one compound to the other.[7a,d,11d] The activation–driving force relationship may be modeled by the quadratic equation

$$\Delta G^\ddagger_{>S-R\cdot/>S+R\cdot} = \Delta G^\ddagger_{0,>S-R\cdot/>S+R\cdot}\left(1 + \frac{\Delta G^\circ_{>S-R\cdot/>S+R\cdot}}{4\Delta G^\ddagger_{0,>S-R\cdot/>S+R\cdot}}\right)^2$$

with an intrinsic barrer given by the following expression.

$$4\,\Delta G^\ddagger_{0,>S-R\cdot/>S+R\cdot} = D_{>S-R+/>S\cdot++R\cdot} + E^\circ_{>S-R+/>S-R\cdot} - E^\circ_{>S\cdot+/>S} + T\Delta S$$

where $\Delta S = \bar{S}_{>S-R^+} - \bar{S}_{>S-R\cdot} - \bar{S}_{>S\cdot^+} + \bar{S}_{>S}$ is small and about constant from one compound to the other.[11d] Since the two factors $E^\circ_{>S-R+/>S-R\cdot}$ and $E^\circ_{>S\cdot+/>S}$ nearly compensate for each other when the two remaining groups on sulfur change,[11d] the main factor governing the intrinsic barrer is the bond dissociation energy. (b) As discussed latter on, there is some increase of the bond dissociation energy and some positive shift of the sulfide standard potential upon going up vertically in Scheme 4, giving rise to opposite effects on $\Delta G^\circ_{>S-R\cdot/>S+R\cdot}$, but the main effect in the passage from **1c** to **1b** is the negative shift of $E^\circ_{>S-R+/>S-R\cdot}$, which is a measure of the increase in energy of the sulfonium LUMO. (c) As discussed further on, the LUMO energy decreases to some extent from **1c** to **3c**, but this is largely compensated by the decrease of the bond dissociation energy. (d) Savéant, J.-M. *J. Phys. Chem.*, in press.

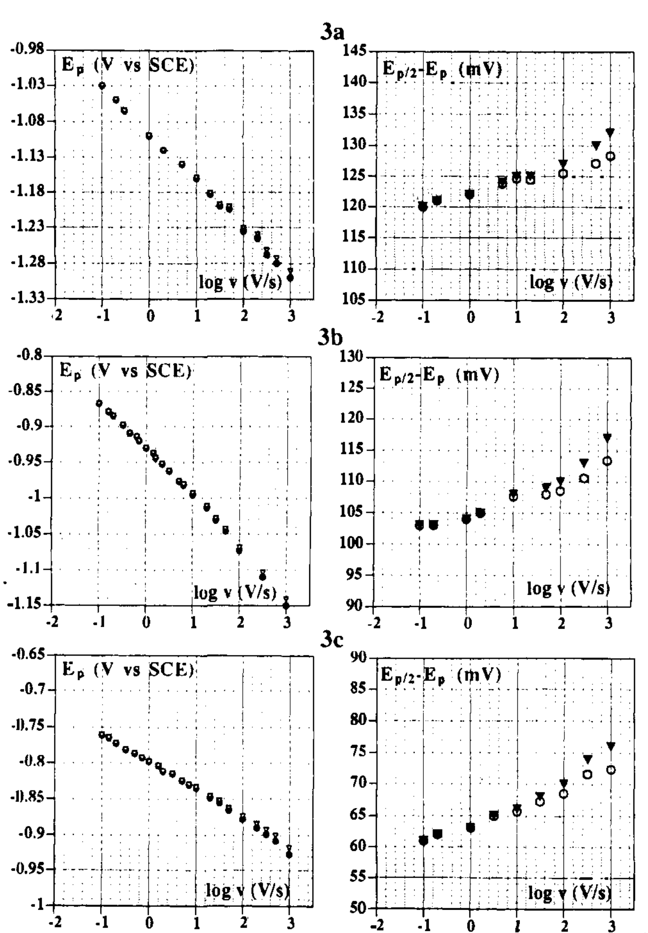

Figure 6. Cyclic voltammetry of compounds **3** in acetonitrile + 0.1 M n-Bu_4NBF_4 and variations of the peak potential (● raw data, ▽ corrected from ohmic drop) and the peak width (▼ raw data, ○ corrected from ohmic drop) with the scan rate.

For these reasons, the standard potential $E^\circ_{>S-R^+/>S-R\cdot}$ for **3c** cannot be derived rigorously from its peak potential values. It is however interesting, for the following discussion, to estimate approximately how positive it is to the $E^\circ_{>S-R^+/>S-R\cdot}$ of **1c**. The difference in standard potentials between these two compounds is certainly smaller than the difference between their peak potentials at the same scan rate (≈300 mV) because the cleavage is faster in the case of **3c** than in that of **1c**. From the peak width variations of **3c** (Figure 6), it can be seen that kinetic control by the electron-transfer step is practically achieved at the highest edge of the scan rate range with a transfer coefficient value of approximately 0.6. It follows, since the electron-transfer standard rate constant should be approximately the same as for **1c** (k_S^{ap} = 3 cm/s), that the standard potential of **3c** is ≈50 mV negative to its peak potential at 1000 V/s, i.e., equal to −0.97 V vs SCE, 230 mV more positive than the standard potential of **1c**. The latter figure is a measure of the inductive effect of the R group, from methyl to 4-cyanobenzyl, at the level of $>S-R^+$ and/or $>S-R\cdot$.

An entirely different situation is met when going to the upper right-hand corner of Scheme 4, i.e., to **3a**, **3b**, **4a**, and **4b**. The E_p–log v slopes and peak widths do not vary much with the scan rate and are much larger than in the preceding cases, indicating that the kinetic control is by an electron-transfer step in the framework of either a concerted or a stepwise mechanism. The ensuing values of the transfer coefficient (symmetry factor), α, are given in Figure 9. They are all below 0.5 and are even less with the phenyl than with the naphthyl derivative. This is an indication that the reduction potential is more negative than the standard potential of the rate-determining step, which accords with the occurrence of the concerted mechanism and not the stepwise mechanism. The difference with 0.5 is however not very large, calling for a confirmation of the mechanism from the analysis of other parameters of the electrochemical reduction. As noted earlier, the peak potentials of **3a** and **4a** are much more positive than that of **1a**, and the same is true for **3b** and **4b** as compared to **1b**. Comparing, for example, **3a** and **1a**, the difference is 620 mV at the highest edge of the scan rate range, where kinetic control is by electron transfer in both cases. In the case of **3b** and **1b**, the difference is 450 mV. If the reduction of **3a** and **3b** was to follow the stepwise mechanism, their peak potentials at these scan rates would be expected to be controlled by electron transfer, i.e., expressed by the following equation.[10b]

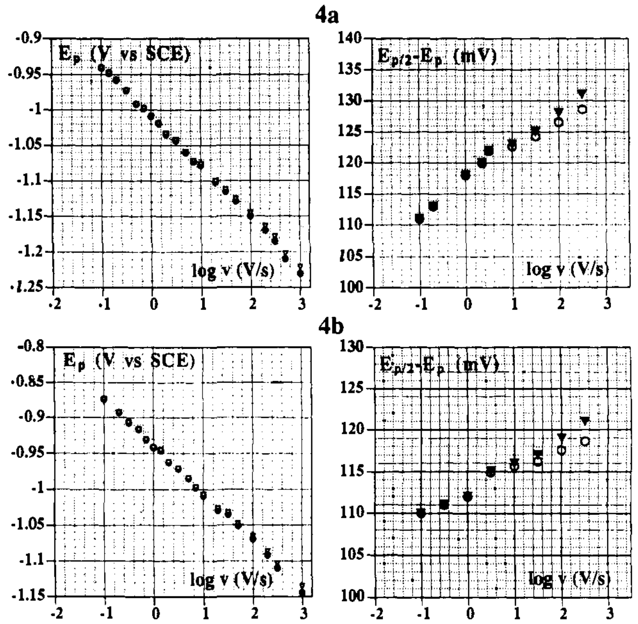

Figure 7. Cyclic voltammetry of compounds **4** in acetonitrile + 0.1 M n-Bu_4NBF_4 and variations of the peak potential (● raw data, ▽ corrected from ohmic drop) and the peak width (▼ raw data, ○ corrected from ohmic drop) with the scan rate.

$$E_p = E^\circ_{>S-R^+/>SR\cdot} - 0.78\frac{RT}{\alpha F} + \frac{RT}{\alpha F}\ln\left[\frac{k^{ap}_{S,>S-R^+/>SR\cdot}}{(\alpha F v D/RT)^{1/2}}\right]$$

where $k^{ap}_{S,>S-R^+/>SR\cdot}$ is the apparent standard rate constant of electron transfer (uncorrected from double-layer effects), α, the transfer coefficient, v the scan rate, and D the diffusion coefficient. Since $k^{ap}_{S,>S-R^+/>SR\cdot}$ is approximately the same for **3a** and **1a** and for **3b** and **1b**, respectively, the difference between the peak potentials would be essentially governed by the differences in standard potentials. The peak potentials of **3a** and **3b** should thus be ca. 230 mV more positive than those of **1a** and **1b**, i.e., much less than experimentally observed. The location of the peak potentials of **3a** and **3b** is thus incompatible with the stepwise mechanism, leading to the conclusion that the reduction of these two sulfoniums follows the concerted mechanism. The same is true for **4a** and **4b**, which have characteristics almost identical to those of **3a** and **3b**.

Table 1. Peak Potentials of the First Cathodic Cyclic Voltammetric Wave

	sulfonium									
	1a	**1b**	**1c**	**2a**	**2b**	**3a**	**3b**	**3c**	**4a**	**4b**
E_p (V vs SCE) at 0.1 V/s	−1.69	−1.42	−1.11	−1.35	−1.14	−1.03	−0.87	−0.76	−0.94	−0.87

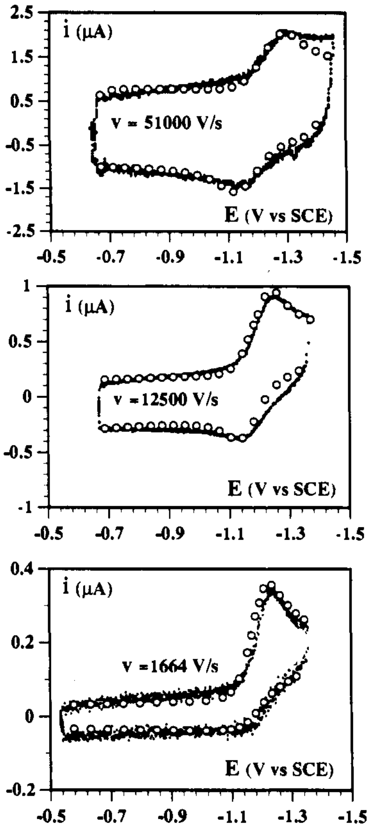

Figure 8. High scan rate cyclic voltammetry of compound **1c** in acetonitrile + 0.1 M *n*-Bu$_4$NBF$_4$, at a 10-μm-diameter ultramicroelectrode: points, experimental data; full lines, simulation.

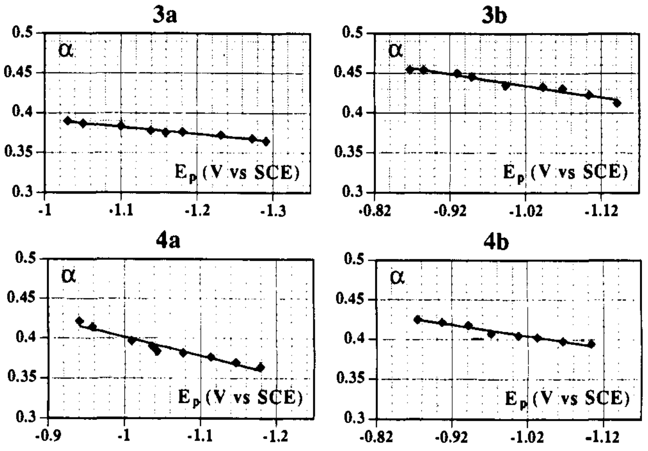

Figure 9. Values of the transfer coefficient (symmetry factor), derived from the peak widths for the four sulfoniums undergoing concerted reductive cleavage.

For these four sulfoniums we may estimate the bond dissociation energy in the sulfonium cation, $D_{>S-R^+\to>S^{\cdot+}+R^\cdot}$, from the values of the peak potential by application of the dissociative electron transfer quadratic model.[7,12] The peak potential and the bond dissociation energy are indeed related through the following equations.

$$\Delta G^{\ddagger}_{>S-R^+/>S+R^\cdot} = \frac{RT}{F}\ln\left[A\left(\frac{RT}{\alpha FVD}\right)^{1/2}\right] - 0.78\frac{RT}{F} \quad (1)$$

(A is the pre-exponential factor, D the diffusion coefficient, v the scan rate)

$$\Delta G^{\ddagger}_{>S-R^+/>S+R^\cdot} = \Delta G^{\ddagger}_{0,>S-R^+/>S+R^\cdot}\left(1 + \frac{E_p - E^{\circ}_{>S-R^+/>S+R^\cdot}}{4\Delta G^{\ddagger}_{0,>S-R^+/>S+R^\cdot}}\right)^2 \quad (2)$$

with

$$\Delta G^{\ddagger}_{0,>S-R^+/>S+R^\cdot} = (D_{>S-R^+\to>S^{\cdot+}+R^\cdot} + \lambda_0)/4 \quad (3)$$

(λ_0 is the solvent reorganization factor). On the other hand, the standard potential of the dissociative electron transfer reaction may be related to the bond dissociation energy according to

$$E^{\circ}_{>S-R^+/>S+R^\cdot} = -D_{>S-R^+\to>S^{\cdot+}+R^\cdot} + E^{\circ}_{>S^{\cdot+}/>S} - T(\bar{S}_{>S-R^+} - \bar{S}_{R^\cdot} - \bar{S}_{>S^{\cdot+}}) \quad (4)$$

An approximate estimate of the bond dissociation energy may then be obtained by using the simplified method described in ref 7c (see Figure 5 therein), based on the linearization of the above quadratic equation (2):

$$E_p = E^{\circ}_{>S^{\cdot+}/>S} - (3/2)D_{>S-R^+/>S^{\cdot+}+R^\cdot} + C \quad (5)$$

where

$$C = 2\left(\frac{RT}{F}\ln\left[A\left(\frac{RT}{\alpha FVD}\right)^{1/2}\right] - 0.78\frac{RT}{F}\right) - \frac{\lambda_0}{2} - T(\bar{S}_{>S-R^+} - \bar{S}_{R^\cdot} - \bar{S}_{>^{\cdot+}})$$

is about constant within a large set of compounds.[7c] The method requires the knowledge of the standard potential $E^{\circ}_{>S^{\cdot+}/>S}$. Phenyl and naphthylmethyl sulfides do not give rise to reversible oxidation waves in cyclic voltammetry at standard electrodes. They instead exhibit an irreversible wave showing the characteristics of an "EC" mechanism with a first order C step.[10b,c] Their peak potentials at 0.1 V/s are 1.41 and 1.26 V vs SCE, respectively. Using the same ultramicroelectrode technique as for the reduction of compounds **1a–c** and **3c**, we found no trace of reversibility for phenylmethyl sulfide at scan rates as high as 250 000 V/s, implying that the C step has a rate constant equal or larger than 10^7 s^{-1}. On the other hand, the value of the peak width at 0.1 V/s, 50 mV, indicates that the kinetics of the electron-transfer step just begins to interfere, besides that of the C step, in the kinetic control of the oxidation reaction. One centimeter/second is a reasonable estimate for the electron-transfer standard rate constant of a molecule of this size, thus leading to an upper limit of the rate constant of the C step of ca. 10^7 s^{-1}. Taking thus 10^7 s^{-1} as the rate constant of the C step then allows the derivation[10b,c] of the standard potential from the peak potential at 0.1 V/s (Table 2). With naphthylmethyl sulfide, no trace of chemical reversibility is observed at scan rates as high as 150 000 V/s, implying that the C step has a rate constant equal or larger than 5×10^6 s^{-1}. The kinetics of the electron-transfer step starts to interfere at 4 V/s, leading to an upper limit of the rate constant of the C step of ca. 5×10^6 s^{-1}. Taking this value, one obtains, from the peak potential at 0.1 V/s, the value of the standard potential reported in Table 2. We may then estimate the values of the bond dissociation energies in the sulfonium cations **3a**, **4a**, **3b**, and **4b** by application of eq 5, as reported in Table 2.

Passing from **3a** to **3b** (as well as from **4a** to **4b**), naphthylmethyl sulfide appears as a better leaving group in the dissociative reductive cleavage than phenylmethyl sulfide because the weakening of the bond prevails, through the 3/2 factor, over the opposite variation of the oxidation standard potential. Similar effects have already been observed when the leaving groups are halide ions.[7b,c]

As seen in Figure 9, the transfer coefficient decreases upon going to more negative potentials, as expected from the quadratic

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(12) (a) Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788. (b) Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 10595. (c) Bertran, J.; Gallardo, I.; Moreno, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 9576.

Table 2. Approximate Values of the Bond Dissociation Energies in the Sulfoniums Undergoing Concerted Reductive Cleavage

	3a	**4a**	**3b**	**4b**
$E^0_{>S\cdot+/>S}$ (V vs SCE)	1.58		1.42	
$D_{>S\cdot R^+\rightarrow >S\cdot^+ + R\cdot}$ (eV)	2.0_7	2.0_1	1.8_6	1.8_6

activation–driving force relationship above. The fact the values of the transfer coefficient are smaller with **3a** and **4a** than with **3b** and **4b** falls in line with a larger intrinsic barrier caused by a larger value of the bond dissociation energy and presumably of the solvent reorganization energy (the size of the molecule is smaller in the first cases than in the second). Using the values of the bond dissociation energy listed in Table 2, the values of the transfer coefficient predicted by the dissociative electron transfer model,

$$\alpha = 0.5\left(1 + \frac{E_p - E^{\circ}_{>S-R+/>S+R\cdot}}{4\Delta G^{\ddagger}_{0>S-R+/>S+R\cdot}}\right) \qquad (6)$$

were found to be close to 0.4, at 0.1 V/s, in satisfactory agreement with the experimental values.

The fact that sulfoniums **3a** and **3b**, as well as **4a** and **4b**, undergo a concerted reductive cleavage whereas **3c** follows a stepwise mechanism is essentially the result of a decrease of the LUMO energy upon going from phenyl to naphthyl and finally to anthracenyl, similarly to what has already been observed with benzyl halides and substituted benzyl halides[7b] as well as with aromatic *N*-halosultams.[7c] The reduction potential, as represented by the cyclic voltammetric peak potential, is indeed essentially driven by the value of $E^{\circ}_{>S-R+/>S-R\cdot}$ for the stepwise pathway, whereas for the concerted pathway, E_p is related to the bond dissociation energy $D_{>S-R^+/S\cdot^+ + R\cdot}$ and to the standard potential $E^{\circ}_{>S\cdot+/>S}$, as described by eq 5 above. From the positive shift observed from **3a** to **3b**, it is expected that the dissociative reduction potential of **3c** should continue to shift positively albeit to a smaller extent than the positive shift of $E^{\circ}_{S-R+/>S-R\cdot}$, i.e., the decrease of the LUMO energy, which parallels the positive shift of the stepwise reduction potential in the **1a**–**1b**–**1c** series.

The fact that sulfoniums **1a** and **1b** undergo a stepwise reductive cleavage whereas the reduction of **3a** and **3b** (and **4a** and **4b**) follows the concerted mechanism is essentially a consequence of the weakening of the sulfur–carbon bond upon passing from the methyl to the 4-cyanobenzyl (and phenacyl) substituent. We expect the stepwise reduction potential to shift positively from the **1** to the **3** (and **4**) series, as we have observed when comparing **1c** to **3c**. However, the positive shift of the dissociative reduction potential due to the weakening of the carbon–sulfur bond from the methyl to the 4-cyanobenzyl (and phenacyl) substituent is expected to be much larger, as discussed previously.

It has been found recently by two independent means that the strength of the carbon–halogen bond in benzyl bromides decreases upon substitution of the para position by electron-withdrawing groups.[7b,13] This effect was attributed to a destabilization of the halide rather than to a stabilization of the benzyl radical.[13] Analogously, the bond strength should be higher in the **2** series than in the **3** series and therefore be between the **1** and the **3** series. We may therefore expect with **2a** and **2b** a borderline mechanistic behavior possibly allowing the observation of a transition between mechanisms upon varying the driving force, as illustrated in Figure 1. We indeed find, with **2a** and **2b** (Figure 5), that the variations of the peak width with the scan rate are strikingly different from what we have observed with all the other sulfoniums that we have investigated. The decrease of the peak width upon raising the scan rate that is observed with **2a** at the lower edge of the scan rate range and, with **2b**, at a somewhat higher scan rate may thus be interpreted as a reflection of the passage between the concerted and the stepwise mechanism that is expected to result from an increase of the driving force in a borderline mechanistic situation. Other causes of the appearance of this particular behavior such as adsorption of reactants and/or products are unlikely to appear suddenly with these two sulfonium cations while absent with all the others. Also, the fact that the same behavior was observed (Figure 5) in the absence as well as in the presence of an acid, suppressing the formation of the ylid in the vicinity of the electrode surface, is a good indication that these variations are not related to adsorption phenomena.

Conclusions

The main conclusions to emerge from the preceding results are as follows.

1. Like the reductive cleavage of the carbon–halogen bond in benzyl halides and of the nitrogen–halogen bond in aromatic *N*-halosultams, the reductive cleavage of the carbon–sulfur bond in aryldialkyl sulfonium cations offers the example of a reaction where the concerted or stepwise nature of the electron-transfer–bond-breaking process is a function of molecular structure. In this connection, the role of the LUMO energy and of the bond strength in the starting molecule (the higher the former and the weaker the latter, the greater the tendency for the concerted mechanism to prevail over the stepwise mechanism and vice versa) is confirmed.

2. Consistently with the effect of these two mechanism-governing factors, two borderline cases were identified where the reaction passes from the concerted pathway to the stepwise pathway upon increasing the driving force by raising the scan rate and thus shifting the reduction potential toward negative values. Evidence has recently been provided that a similar phenomenon also occurs in the electrochemical reduction of 1,2-dibromo-3-(4-cyano or carbomethoxy)phenylpropanes, although the reaction is complicated by additional homogeneous chemical steps.[14]

3. After recent findings concerning the photochemically triggered reduction of benzyl and 4-cyanobenzyl bromides,[15] it is interesting to come back to the discussion of the factors that drive the reductive cleavage reactions toward the concerted or the stepwise mechanism and may make, for the same molecule, the mechanism depend upon the particular mode of electron injection, as counterintuitive as such a concept may look at first sight. As already noted, there is a striking difference between the pulse radiolytic reduction of 3-cyanobenzyl bromide in water, which was shown to follow a stepwise mechanism, even though the rate constant of the followup cleavage was too fast to be precisely measured,[16a] and the electrochemical reduction of the same compound in acetonitrile that has been shown to follow a concerted mechanism.[7c] As discussed earlier,[7] two factors are likely to govern this difference in behavior. One is that the driving force offered by the pulse radiolytic reduction is much larger than the electrochemical driving force which may result in a change of mechanism, as discussed above (Figure 1) and experimentally demonstrated with the sulfoniums **2a** and **2b**. The other is that attractive interactions between the anion radical and its environment may lower the LUMO energy and thus disfavor the concerted pathway at the expense of the stepwise pathway. In line with the importance of this factor is the observation that the cleavage of nitro-substituted benzyl halides is significantly slower in water than in acetonitrile or in *N,N'*-dimethylformamide.[7b,16b,c] In photochemically triggered reduc-

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tions, the two types of factors may also come into play. Concerning the second of these, the fact that the anion radical is formed within a tight sandwich ion pair may well induce a substantial lowering of LUMO energy, thus favoring the stepwise pathway at the expense of the concerted pathway. This would seem to be the case in experiments where the electron source for reducing benzyl bromide was excited diphenyl radicals,[15a] the reducing power of which does not appear to be sufficient per se to trigger a change of mechanism as compared to electrochemical conditions.

Experimental Section

Chemicals. Acetonitrile (Merck Uvasol) and the supporting electrolyte, n-Bu_4NBF_4 (Fluka, puriss), were used as received.

Sulfonium Salts and Sulfides.

Phenylmethyl sulfide was from commercial origin (Aldrich). 1-Naphthylmethyl sulfide, the trifluoromethanesulfonate salts of **1a**, **2b**, **3a**, **3b**, **4a**, and **4b**, and the tetrafluoroborate salts of **2a** was well as 9-anthracenylmethyl sulfide and the sulfonium trifluoromethanesulfonate salts of **1c** and **3c**[17] were prepared as previously described.[3a]

Instrumentation. Three different glassy carbon disk working electrodes were used in the standard cyclic voltammetry experiments according to the range of scan rates explored: a 3-mm-diameter disk between 0.05 and 10 V/s; a 1-mm-diameter disk between 5 and 100 V/s; and a 0.35-mm-diameter disk between 50 and 1000 V/s. The first of these was built from a 3-mm-diameter GC rod (from Tokai), the second from a 1-mm-diameter rod obtained by mechanical abrasion of the original rod, and the third by sharpening the 1-mm-diameter rod like a pencil. The GC pieces thus obtained were sealed inside a glass tube with epoxy resin. In the high scan rate experiments we used a 10-μm-diameter carbon disk (Princetown Applied Research). The electrodes were carefully polished and ultrasonically rinsed with ethanol before each run. The counter-electrode was a platinum wire, and the reference electrode an aqueous SCE electrode.

The potentiostat, equipped with a positive feedback compensation and current measurer, used at low or moderate scan rates was the same as previously described.[18a] The instrument used with ultramicroelectrodes at high scan rates has been described elsewhere.[18b]

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