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Theoretical and Electrochemical Analysis of Dissociative Electron Transfers Proceeding through Formation of Loose Radical Anion Species: Reduction of Symmetrical and Unsymmetrical Disulfides

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Abstract: The dissociative reduction of a series of symmetrical (RSSR, R = H, Me, *t*-Bu, Ph) and unsymmetrical disulfides (RSSR′, R = H, R′ = Me and R = Ph, R′ = Me, *t*-Bu) was studied theoretically, by MO ab initio calculations and, for five of them, also experimentally, by convolution voltammetry in *N,N*-dimethylformamide. The reduction is dissociative but proceeds by a stepwise mechanism entailing the formation of the radical anion species. The electrochemical data led to estimated large intrinsic barriers, in agreement with an unusually large structural modification undergone by the disulfide molecules upon electron transfer. The theoretical results refer to MP2/3-21G*//MP2/3-21G*, MP2/3-21*G*//MP2/3-21G*, CBS-4M, and G2(MP2), the latter approach being used only for the molecules of small molecular complexity. A loose radical-anion intermediate was localized and the dissociation pattern for the relevant bonds analyzed. For all compounds, the best fragmentation pathway in solution is cleavage of the S−S bond. In addition, S−S bond elongation is the major structural modification undergone by the disulfide molecule on its way to the radical anion and eventually to the fragmentation products. The calculated energy of activation for the initial electron transfer was estimated from the crossing of the energy profiles of the neutral molecule and its radical anion (in the form of Morse-like potentials) as a function of the S−S bond length coordinate. The inner intrinsic barrier obtained in this way is in good agreement with that determined by convolution voltammetry, once the solvent effect is taken into account.

Introduction

Dissociative electron transfers are processes in which electron transfer (ET) causes the cleavage of a σ bond.[1] The mechanism of these reactions depends strongly on the structure of the electron acceptor or electron donor undergoing the cleavage. Although there are systems in which ET and bond fragmentation may be concerted, such as in the dissociative reduction of most alkyl halides[2,3] and peroxides,[4−7] the majority of compounds react by a stepwise mechanism.[2b,7,8] If the electron acceptor is a neutral molecule (AB), a stepwise dissociative reduction mechanism entails the formation of an intermediate radical anion (AB$^{\bullet-}$), which only subsequently undergoes the cleavage to yield a radical (A$^{\bullet}$) and an anion (B^{-}). There are two major aspects associated with these processes. The first has been investigated by several research groups and concerns the understanding of the cleavage step and thus issues such as the rate/driving force relationship ruling the cleavage, the problem of homolytic versus heterolytic fragmentation, the solvent effect, the role of the leaving group, and the stereochemical effect on the intramolecular ET.[8−13] The second aspect, which has been much less investigated, refers to the nature of the intrinsic barrier involved in the formation of the radical anion itself. The intrinsic ET

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barrier, $\Delta G_0^{\ddagger}$, which is defined as the activation free energy ($\Delta G^{\ddagger}$) at zero reaction free energy ($\Delta G°$), is a measure of the overall ET reorganization energy and provides essential information on the intrinsic kinetic facility of the ET step. In general, the initial electron uptake is expected to cause some change of both bond lengths and angles. According to the commonly accepted ET models, these factors determine the magnitude of the inner reorganization energy ($\Delta G_{0,\mathrm{i}}^{\ddagger}$) of the reacting system. $\Delta G_0^{\ddagger}$ is obtained by summing such a reorganization term with that pertaining to the reorganization of the solvent molecules ($\Delta G_{0,\mathrm{s}}^{\ddagger}$), which accompanies the ET step.[14] Obtaining an accurate description of the ET step and thus of how the intrinsic barrier is partitioned into these two terms is important not only per se but also because it provides the basis to understand how the dynamics of the following ion-radical fragmentation develops.[7] For example, the bond dissociation energy (BDE) of the scissile bond should decrease because of the antibonding nature of the orbital that hosts the unpaired electron. In addition, knowing how the negative charge is localized or delocalized in the radical anion allows one to better understand the extent of solvent reorganization accompanying the cleavage. Both factors are responsible for the intrinsic barrier of the cleavage itself.

If the ET product is a delocalized radical anion, such as with aromatic compounds, $\Delta G_{0,\mathrm{i}}^{\ddagger}$ is rather small (because little molecular deformation occurs), usually within 1 kcal mol^{-1}. Because of this, the inner component has been regarded as being most often negligible. For these processes, the most important contribution to the intrinsic barrier is thus $\Delta G_{0,\mathrm{s}}^{\ddagger}$,[8a,15,16] the values being typically in the 2.5−3.5 kcal mol^{-1} range. On the other hand, $\Delta G_{0,\mathrm{i}}^{\ddagger}$ is expected to increase when the ET eventually provokes the cleavage of a σ bond and thus the fragmentation of the radical anion. In the limiting case of the concerted dissociative ET mechanism, in particular, $\Delta G_{0,\mathrm{i}}^{\ddagger}$ becomes as large as one-forth of the BDE of the breaking bond.[17] It is not clear, however, to which extent $\Delta G_{0,\mathrm{i}}^{\ddagger}$ affects the intrinsic barrier of those dissociative ETs involving the transient formation of a radical anion. Most often, this contribution is neglected. On the other hand, as mentioned above, it is reasonable to expect that in the formation of the radical anion the breaking bond will weaken and stretch to some extent. Although the possibility of significant internal reorganization in stepwise processes should not, as a rule, be ignored with other classes of compounds, the majority of the data supporting this expectation comes from recent studies on the cleavage of C−S or S−S bonds.[7] The first detailed studies in this field dealt with the heterogeneous and homogeneous reduction of benzyl aryl sulfides.[18−20] These studies, particularly that on the reduction of triphenylmethyl *p*-cyanophenylsulfide,[19] provided evidence that $\Delta G_{0,\mathrm{i}}^{\ddagger}$ may be even larger than $\Delta G_{0,\mathrm{s}}^{\ddagger}$. Some indication that $\Delta G_{0,\mathrm{i}}^{\ddagger}$ may be large for other molecular systems was obtained by studying the homogeneous reduction of three disulfides.[21]

A specific study of the relevance of the inner reorganization energy, however, was not available until very recently, thanks to the comparative study that we carried out on the homogeneous and heterogeneous dissociative reduction of a series of diaryl disulfides.[22] The reduction of diaryl disulfides has provided convincing examples of dissociative ETs in which significant inner reorganization is involved. However, the presence of strongly electron-withdrawing substituents capable of keeping the unpaired electron away from the breaking bond (particularly, by nitro-group substitution on the aryl ring) may decrease $\Delta G_{0,\mathrm{i}}^{\ddagger}$ substantially, pointing to the relevance of the π^* versus σ^* nature of the radical anion. The overall picture, however, is far from complete and more experimental examples and theoretical information are required to better understand stepwise dissociative electron transfers. It is particularly important to understand why there are molecular systems undergoing stepwise reduction in which the ET step is fast because little intramolecular reorganization occurs, such as ethers,[7] and others in which the ET is significantly slow, as for disulfides and sulfides.

The reduction of disulfides seemed to us a particularly convenient model to shed some light onto this general problem, also in view of the relevance of the S−S bond in biological molecules.[23] Disulfides are easily activated by reductive cleavage of the S−S bond, both chemically and electrochemically.[24] In aprotic solvents, the homogeneous or heterogeneous dissociative reduction of disulfides RSSR is irreversible and occurs by a stepwise mechanism, in which ET and S−S bond breaking occur sequentially (eqs 1 and 2).[7,21,22] Given the strength of the reductants (solution electron donors or applied electrode potential, *E*) necessary to carry out the RSSR reduction, the

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ensuing radicals are also reduced (eq 3). In fact, the standard potential of the $RS^{\bullet}/RS^{-}$ couple is generally at least 1 V more positive than the potential at which the disulfide is reduced.[7] Therefore, in the absence of side reactions, the process is an overall 2-electron reduction (eq 4).

$$\mathrm{RSSR} + \mathrm{e} \rightleftarrows \mathrm{RSSR}^{\bullet -} \tag{1}$$

$$\mathrm{RSSR}^{\bullet -} \rightarrow \mathrm{RS}^{\bullet} + \mathrm{RS}^{-} \tag{2}$$

$$\underline{\mathrm{RS}^{\bullet} + \mathrm{e} \rightarrow \mathrm{RS}^{-}\qquad\qquad} \tag{3}$$

$$\mathrm{RSSR} + 2\mathrm{e} \rightarrow 2\mathrm{RS}^{-} \tag{4}$$

There are several pieces of evidence pointing to the existence of a discrete radical anion $RSSR^{\bullet -}$. The lifetime of the $RSSR^{\bullet -}$ radical anions is usually very short, being on the microsecond time scale in water.[25] However, they have been detected and characterized by time-resolved optical methods. In one early study, γ irradiation of matrices containing alkyl and aryl disulfides provided spectroscopic evidence for the formation of the corresponding radical anions.[26] Subsequently, the formation of $RSSR^{\bullet -}$ radical anions has been well documented, particularly by EPR, flash photolysis, and pulse radiolysis. The $RSSR^{\bullet -}$ radical anions may be obtained from different approaches. One is of course by one-electron reduction of disulfides (eq 1), such as by pulse radiolysis or electrochemistry.[7,25,27,28] However, the most common approach is by association of $RS^{\bullet}$ and RS^{-} (eq 5).[28-30]

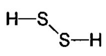
$$\mathrm{RS}^{\bullet} + \mathrm{RS}^{-} \rightleftarrows \mathrm{RS{-}SR}^{\bullet -} \tag{5}$$

The formation of $RSSR^{\bullet -}$ from $RS^{\bullet}$ and RS^{-} species is particularly relevant in the present context because it is the reverse of the electroinduced radical anion cleavage (eq 2). Equilibrium constants in the range $10^{2}-10^{4}$ M^{-1} for the association reaction (eq 5) were determined for some alkyl-type systems in water.[30,31] The rate constants for the formation of $RSSR^{\bullet -}$, determined in aqueous solution, are nearly diffusion controlled [$(3-5) \times 10^{9}$ M^{-1} s^{-1}].[31] It is thus clear that a concerted ET-bond fragmentation mechanism, leading directly to the fragmented products (eq 6), should be, as a rule, discarded.

$$\mathrm{RSSR} + \mathrm{e} \rightarrow \mathrm{RS}^{\bullet} + \mathrm{RS}^{-} \tag{6}$$

Concerning the thermodynamics of formation of $RSSR^{\bullet -}$ species in nonaqueous solvent,[32] a few estimates of the corresponding standard potential ($E^{\circ}_{RSSR/RSSR^{\bullet -}}$) could be obtained by studying the kinetics of the reduction of symmetrical diaryl disulfides as a function of the driving force.[21,22]

In this paper, we examine the dissociative reduction of a series of symmetrical and unsymmetrical disulfides **1**−**7** having the general formula RSSR′, where R and R′ are H, alkyl, or phenyl groups. The reduction was studied both experimentally, by cyclic voltammetry in *N*,*N*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium perchlorate (TBAP), and theoretically. By using the convolution analysis approach,[7,33] we could estimate the $E^{\circ}_{RSSR/RSSR^{\bullet -}}$ values of **3**−**7** and the corresponding heterogeneous standard rate constants (k_{het}°), i.e., the value of k_{het} for $E = E^{\circ}$. From the k_{het}° values, we obtained the intrinsic barrier of the heterogeneous process. The experimental outcome was then compared with the results of theoretical calculations, carried out at different levels and aimed at studying the homolytic cleavage in both the neutral molecules **1**−**7** and the corresponding radical anions **1a**−**7a**.[34] The calculations determined the relative stability of these species and also the energy changes associated with the variation of selected coordinates of the ET and the cleavage reaction. All compounds form $2\sigma/1\sigma^{*}$ radical anions undergoing endergonic cleavages. The results are rationalized by introducing a model that may be called as the "almost-dissociative" stepwise ET−bond breaking mechanism, i.e., a mechanism in which the initial electron uptake has an intrinsic barrier that is closer to that of a concerted dissociative ET than to that of the ET step of common stepwise processes.



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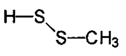

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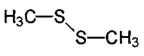

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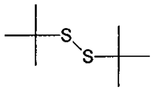

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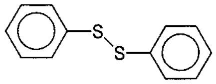

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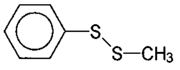

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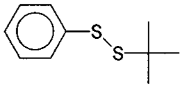

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Experimental Section

Chemicals. Dimethyl disulfide, di-*tert*-butyl disulfide, diphenyl disulfide, phenylmethyl disulfide, and *tert*-butylphenyl disulfide were commercial products (Acros or Fluka, >99%). Their purity was checked before electrochemical measurements by GC-mass spectrometry, using a Hewlett-Packard 5898A spectrometer. *N*,*N*-Dimethylformamide (Acros, 99%) and tetrabutylammonium perchlorate (Fluka, 99%) were treated as previously described.[5a]

Electrochemistry. The electrochemical experiments were carried out in DMF/0.1 M TBAP, using glassy carbon electrodes. The experimental setup and procedures were as previously described in detail.[5] Potentials were measured relative to ferrocene oxidation and are given against the KCl saturated calomel electrode (SCE); in our hands, the E° of the ferrocene/ferricenium couple is 0.464 V vs SCE. Electrochemical measurements were carried out at 25 °C, unless otherwise stated. For the temperature studies, however, the reference electrode was always kept at 25 °C, using a nonisothermal salt bridge arrangement.[35] The convolution analysis was carried out on background-subtracted cyclic voltammetry curves by using our own laboratory software. Digital simulations were carried out by using the DigiSim 3.03 software (Bioanalytical Systems Inc).

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Computational Details. Calculations were performed on compounds **1**−**7** and their radical anions **1a**−**7a** at the MO ab initio level with the GAUSSIAN-94 and GAUSSIAN-98 series of programs,[36,37] run on a Silicon Graphics 4CPU MIPS R10000 calculator and on a IBM AIX/6000 workstation. The molecules were studied at the MP2/3-21G*//MP2/3-21G* frozen core level[38,39] and the effect of diffuse augmented functions was tested at the MP2/3-21+G*//MP2/3-21G* level. Stationary points were located through full geometry relaxation. UHF wave functions were employed for the open shell systems and the spin projection operator[40] was applied to remove contamination from higher spin states. The value of $\langle s^2 \rangle$ was nevertheless greater than 0.75 for radicals and radical anions containing the phenyl ring. The CBS-4M[41] and G2(MP2)[42] methods were also employed, the latter being applied only to the molecules of smaller molecular size **1**−**3** and **1a**−**3a**, to compare the results obtained at a low level of theory with those obtained with more sophisticated methods. A further parametrization was introduced[43] in the CBS-4M method to minimize the accumulation of errors in molecules of increasing size. Thermodynamic data refer to 298.15 K. For the radical anions, real minima were located in the energy hypersurface. The solvent effect was calculated with the SM5-42R solvation model[44] and the GAMESOL program.[45]

Results and Discussion

Electrochemical Analysis. The voltammetric reduction of disulfides **3**−**7** was studied in DMF/0.1 M TBAP at the glassy carbon electrode. The reduction proceeds irreversibly, as described in eqs 1−3. Since the focus of the present investigation is on the initial ET step (eq 1), only the most relevant and pertinent features of the voltammetric pattern will be considered.[46] The irreversible reduction peak is broad and its position (peak potential, E_p) depends markedly on the R and R′ substituents (Table 1). Upon increasing the scan rate (v), E_p shifts toward more negative potentials by 91−93 mV/log v. From these values as well as from the peak width, $\Delta E_{p/2}$ ($\Delta E_{p/2}$ is the difference between the potential at mid-peak height and E_p), it is possible to calculate the transfer coefficient α. α describes the sensitivity of the activation free energy on the reaction free energy, i.e., $\alpha = \partial\Delta G^{\ddagger}/\partial\Delta G^{\circ}$. The low values of α, which are gathered in Table 1, indicate that for all compounds the initial ET controls the electrode kinetics.[47] In addition, when v increases, the peak broadens while the ratio between the peak current i_p and the square root of v (a quantity that should be independent of v according to the classical Butler−Volmer kinetic model[47]) decreases (Figure 1). This behavior indicates that the transfer coefficient α depends on the applied potential (E).[5] The kinetics of the heterogeneous ET was thus studied in detail by convolution voltammetry,[7,33] which we believe to be the most powerful electrochemical method to study the fine details of heterogeneous ET processes. The graphs corresponding to some steps of the convolution analysis are illustrated in

Table 1. Electrochemical and Kinetic Parameters for the Reduction of Disulfides in DMF/0.1 M TBAP at 25 °C

disulfide	$E_p{}^a$ (V)	α^b	$\alpha^{a,c}$	$\alpha^{d,e}$	$E^{\circ\,d,f}$ (V)	$\log k^{\circ}{}_{\mathrm{het}}{}^{d,f}$ (cm s^{-1})	$\Delta G_0^{\ddagger\,g}$ (kcal mol^{-1})
3	−2.43	0.322	0.350	0.337	−1.88	−5.45	12.6
4	−2.72	0.319	0.376	0.375	−2.34	−4.53	11.2
5	−1.65	0.325	0.432	0.430	−1.37	−4.22^h	10.7
6	−1.97	0.324	0.398	0.373	−1.62	−4.45	11.1
7	−2.19	0.324	0.366	0.359	−1.71	−5.20	12.1

[a] v = 0.2 V s^{-1}. [b] Calculated from $|\partial E_p/\partial \log v| = 1.15RT/F\alpha$.[47] [c] Calculated from the peak width $\Delta E_{p/2} = 1.857RT/F\alpha$.[47] [d] Convolution data. [e] Calculated for the mid-potential of the peak width range, i.e., for $E_p - 0.5\Delta E_{p/2}$, where $E_p = E_p(0.2\ \mathrm{V\ s^{-1}})$.[5b] [f] Within the assumptions explained in the text, the experimental uncertainty is 30−40 mV and 0.2−0.3 log units for the double-layer uncorrected E° and log k°_{het}, respectively. [g] Values obtained by using $k^\circ_{\mathrm{het}} = Z \exp[-\Delta G_0^{\ddagger}/RT]$. [h] From ref 22.

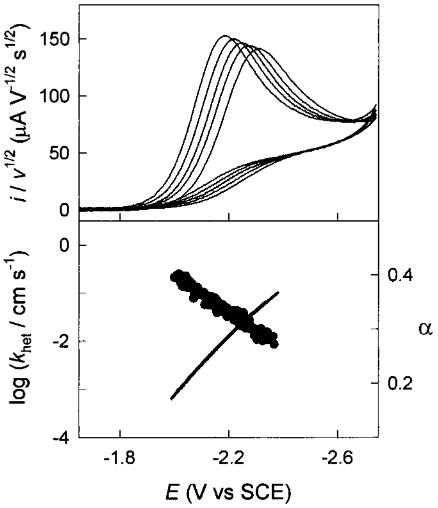

Figure 1. Reduction of **7** (2.1 mM) in DMF/0.1 M TBAP at the glassy carbon electrode. The upper graph shows a series of background-subtracted cyclic voltammograms as a function of scan rate (left to right: 0.2, 0.5, 1, 2, 5 V s^{-1}). The lower graph shows the plots of the corresponding potential dependence of log k_{het} (left scale) and transfer coefficient α (right scale).

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Table 2. Bond Dissociation Energies (BDE and $\Delta H°$, kcal mol^{-1}) from Different Theoretical Approaches for Organic Disulfides

		level of theory						
compd	bond broken	MP2/3-21G*//MP2/3-21G*	MP2/3-21+G*//MP2/3-21G*	G2(MP2) $\Delta H°$ ^{a}	CBS-4M $\Delta H°$ ^{a}	MP2/3-1G*//MP2/3-21G* ($\epsilon = 37$)^{b,c}	CBS-4M ($\epsilon = 37$)^{b,c}	exptl^{d}
1	S−S	54.07	53.50	64.72	62.20	52.53	60.66	66 ± 2^{e} 64.5
	H−S	64.74	64.68	74.64	73.82	64.80	73.88	70 ± 1.5^{f} 76.2
2	S−S	55.4	55.5	65.62	62.90	53.75	61.25	65.2
	C−S	59.5	58.3	63.46	62.25	61.13	63.88	64.1
	H−S	62.1	61.7	71.74	70.71	61.62	70.23	79.0
3	S−S	56.7	57.8	66.49	63.47	55.00	61.77	74 ± 2^{g} 65.6
	C−S	56.9	55.7	59.29	58.98	58.06	60.14	57 ± 1.5^{g} 66.6
4	S−S	61.2	62.4		65.96	59.51	64.27	67.7
	C−S	59.2	60.5		57.72	58.45	56.97	53.9
5	S−S	46.8	56.9		47.90	46.24	47.34	55.0^{h} 49.2
	C−S	77.3	69.5		79.09	76.89	78.68	75.0^{h} 71.8
6	S−S	51.6	55.5		55.48	50.46	54.34	65.0^{h} 59.6
	C(aryl)−S	74.1	78.8		76.05	73.20	75.15	69.6^{h} 82.7
	C(alkyl)−S	59.6	58.7		61.61	61.24	63.25	60.1
7	S−S	55.0	60.1		57.88	53.65	56.53	58.4
	C(aryl)−S	73.7	79.5		75.53	72.64	74.47	70.9
	C(alkyl)−S	64.7	67.4		63.18	64.14	59.92	54.7

[a] Bond dissociation enthalpy. [b] In solution. [c] Solvent effect at the HF/3-21G*//HF/3-21G* level, GAMESOL method. [d] Experimental or calculated from literature $\Delta_f H°$ data (see Supporting Information). [e] From: Benson, S. W. *Chem. Rev.* **1978**, *78*, 23. [f] Nourbakhsh, S.; Liao, C.-L.; Ng, C. Y. *J. Chem. Phys.* **1990**, *92*, 6587. [g] Reference 54. [h] From: Plaza, S.; Gruzinski, R. *Wear* **1996**, *194*, 212.

Figure 1 for compound **7**. The background-subtracted voltammograms, obtained at several scan rates in the 0.1−20 V s^{-1} range, were transformed into the corresponding convolution current (I) versus E curves. The heterogeneous rate constant k_{het} was then obtained by logarithmic analysis of the $I-E$ data as a function of E.[48,49] The apparent values of α were obtained as a function of E from the ln $k_{\text{het}} - E$ plots, being $\alpha = -(RT/F)(\text{d} \ln k_{\text{het}}/\text{d}E)$. For **3**−**7**, the ensuing α vs E plots are linear. Some representative values of α obtained by the convolution approach are reported in Table 1. The latter shows that regardless of how α is calculated, the α values are rather small, although on the average they are slightly larger than the α values corresponding to typical concerted dissociative ETs.[1,7]

Usually, provided the α vs E plot is linear within error, the standard potential $E°$ of the electrode reaction can be estimated as the E value at which $\alpha = 0.5$.[5a,7] This is because most theoretical models for outer-sphere or dissociative ETs share the result that α should be about 0.5 at zero driving force.[14a,17] Under the assumption that this may approximately hold also for the systems under investigation (we will return to that point later), the $E°$ values of disulfide reduction (eq 1) were estimated through extrapolation of the experimental α vs E plots. By using these $E°$ estimates, the apparent values of the standard rate constant, $k°_{\text{het}}$, were obtained by parabolic fit to the log $k_{\text{het}} - E$ plots. Both the $E°$ and $k°_{\text{het}}$ values are reported in Table 1. The consistency of the $E°$ and $k°_{\text{het}}$ values was finally checked by digital simulation of the cyclic voltammograms, which led to good reproduction of the experimental curves by using the convolution results.

The electrochemical results obtained with disulfides **3**−**7** are thus in agreement with the formation of discrete radical anion species at moderate overpotentials (the $E°$ values are 0.28−0.55 more positive than the corresponding E_p values at 0.2 V s^{-1}). In fact, concerted dissociative ETs take place at potentials which are normally much more negative than $E°$ (usually, by at least 0.8−1 V). The results obtained with **3**−**7** are also in line with the results previously obtained with some substituted diaryl disulfides[22] and with the evidence collected from other experimental sources for the existence of disulfide radical anions (see Introduction). A simple calculation can be carried out to verify that the concerted mechanism cannot be competitive to the stepwise one. The $E°$ corresponding to eq 6 can be expressed as $E°_{\text{RSSR/RS}^\bullet\text{,RS}^-} = E°_{\text{RS}^\bullet/\text{RS}^-} - \text{BDFE}/F$, where BDFE is the S−S bond dissociation free energy. By using the result of the calculations carried out at the MP2/3-21G*//MP2/3-21G* level (see below), the standard potentials of the PhS$^\bullet$/PhS$^-$ ($E° = 0.07$ V) couple,[50] and an entropy correction of 8.5 kcal mol^{-1} (for $T = 298.15$ K),[4b] the following $E°_{\text{RSSR'/RS'}^\bullet\text{,RS}^-}$ values can be estimated: **5**, −1.59 V; **6**, −1.80 V; **7**, −1.95 V. These values are ~0.2 V more negative than the experimental results. By

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(48) The convolution analysis allows one to obtain the convoluted current I, which is related to the actual current i through the convolution integral, $I = \pi^{-1/2} \int_0^t i(u)/[(t-u)^{1/2}]\,\text{d}u$, as a function of E. The $I-E$ plots display a plateau corresponding to diffusion-controlled conditions. The limiting value of I is $I_l = nFAD^{1/2}C^*$, where n is the overall electron consumption, A the electrode area, D the diffusion coefficient, and C^* the substrate concentration. When the back electrode reaction is absent (because the dissociative ET is concerted) or negligible (thanks to the occurrence of a fast reaction destroying the reduction product, such as in the stepwise mechanism under consideration), the heterogeneous rate constant k_{het} is related to i and I by the following equation: $\ln k_{\text{het}} = \ln D^{1/2} - \ln n\{[I_l - I(t)]/i(t)t\}$.

(49) The reduction of **4** is near the solvent-electrolyte discharge and thus, since the peak shifts toward more negative potentials by increasing v, the maximum scan rate was 10 V s^{-1}. In addition, because of the proximity of the discharge, the convolution analysis was carried out as previously described for di-*tert*-butyl peroxide[5a] or a tertiary bromide.[12]

(50) The standard potentials of the RS$^\bullet$/RS$^-$ couple was determined by studying the scan-rate dependence of the oxidation peak of the RS$^-$ anion, generated by electroreduction of the corresponding disulfide in DMF. Both cyclic voltammetry analysis and digital simulation of the experimental curves were employed, as described elsewhere.[7]

Table 3. Bond Dissociation Energies (BDE and $\Delta H°$, kcal mol^{-1}) from Different Theoretical Approaches for Radical Anions of Organic Disulfides.

		level of theory					
compd	bond-cleavage process	MP2/3-21G*// MP2/3-21G*	MP2/3-21+G*// MP2/3-21G*	G2(MP2) $\Delta H°$ [a]	CBS-4M $\Delta H°$ [a]	MP2/3-21G*// MP2/3-21G* ($\epsilon = 37$)[b,c]	CBS-4M ($\epsilon = 37$)[b,c]
1a	$\mathbf{HS^{\bullet} + {}^{-}SH}$	28.7	24.1	24.8	25.9	8.9	6.1
	$\mathbf{H^{\bullet} + {}^{-}SSH}$	41.3	42.3	44.0	47.5	35.3	41.5
2a	$\mathbf{MeS^{\bullet} + {}^{-}SH}$	23.6	19.0	19.3	20.0	4.4	0.8
	$\mathbf{MeS^{-} + {}^{\bullet}SH}$	31.7	29.1	29.4	30.3	18.6	17.2
	$\mathbf{Me^{\bullet} + {}^{-}SSH}$	29.6	28.9	26.4	29.3	25.9	25.6
	$\mathbf{MeSS^{-} + {}^{\bullet}H}$	36.0	35.5	37.8	41.0	30.6	35.6
3a	$\mathbf{MeS^{\bullet} + {}^{-}SMe}$	26.9	24.1	23.7	25.1	9.9	8.1
	$\mathbf{Me^{\bullet} + {}^{-}SSMe}$	24.1	22.1	20.0	23.5	16.5	15.9
4a	$\mathbf{\mathit{t}BuS + {}^{-}S\mathit{t}Bu}$	29.8	27.3		26.4	12.5	9.1
	$\mathbf{\mathit{t}Bu^{\bullet} + {}^{-}SS\mathit{t}Bu}$	29.1	31.1		26.7	15.9	13.5
5a	$\mathbf{PhS^{\bullet} + {}^{-}SPh}$	15.0	21.9		22.4	1.8	9.2
	$\mathbf{Ph^{\bullet} + {}^{-}SSPh}$	45.1	54.0		54.7	34.6	44.2
6a	$\mathbf{PhS^{-} + {}^{\bullet}SMe}$	19.4	19.1		16.8	7.6	5.0
	$\mathbf{PhS^{\bullet} + {}^{-}SMe}$	33.2	32.4		26.6	10.5	3.9
	$\mathbf{Ph^{\bullet} + {}^{-}SSMe}$	53.3	55.8		50.0	37.3	34.0
	$\mathbf{PhSS^{-} + {}^{\bullet}Me}$	26.7	25.9		24.1	20.2	17.6
7a	$\mathbf{PhS^{-} + {}^{\bullet}S\mathit{t}Bu}$	22.3	23.4		22.8	7.9	8.4
	$\mathbf{PhS^{\bullet} + {}^{-}S\mathit{t}Bu}$	31.3	30.6		25.5	13.9	8.1
	$\mathbf{Ph^{\bullet} + {}^{-}SS\mathit{t}Bu}$	51.2	55.7		51.8	37.2	37.8
	$\mathbf{PhSS^{-} + {}^{\bullet}\mathit{t}Bu}$	31.4	34.2		29.3	20.3	18.2

[a] Bond dissociation enthalpy. [b] In solution. [c] Solvent effect at the HF/3-21G*//HF/3-21G* level, GAMESOL method.

taking also into account that even more negative $E°_{RSSR/RS^{\bullet},RS^{-}}$ values are estimated by using experimental BDE values (Table 2), we can confidently conclude that the concerted mechanism cannot be operative.

It is worth noting that the values of the calculated heterogeneous standard rate constants are remarkably small, pointing to a large intrinsic barrier for radical anion formation. $\Delta G_0^{\ddagger}$ was calculated by using the rate constant expression $k°_{het} = Z \exp[-\Delta G_0^{\ddagger}/RT]$, with $Z = (RT/2\pi M)^{1/2}$, where M is the molar mass, assuming that the investigated processes are adiabatic. That these ETs are adiabatic was checked by carrying out a temperature study on compound **5**. The reduction was studied by convolution voltammetry at temperatures ranging from −25 to 50 °C. From the corresponding log k_{het} vs E plots, the k_{het} values measured at selected potentials were then used to calculate the Arrhenius prefactor A. The average value was found to be log $A = 3.7 \pm 0.1$, which is in agreement with an adiabatic heterogeneous outer-sphere ET (for **5**, log $Z = 3.6$).[51]

The $\Delta G_0^{\ddagger}$ values of **3**−**7** are reported in Table 1. Since the solvent contribution accompanying the heterogeneous ET, $\Delta G_{0,s}^{\ddagger}$, can be calculated for the investigated compounds to be in the range 3.8−6.3 or 2.6−4.4 kcal mol^{-1}, depending on the method adopted,[52] the inner reorganization term can be finally extracted from $\Delta G_0^{\ddagger}$. For **3**−**7**, the $\Delta G_{0,i}^{\ddagger}$ result is particularly large, its value being typically 50−64% or 65−75%, respectively, of the total. These results are in full agreement with the occurrence of major molecular reorganization during the reduction step.

Theoretical Calculations. The CBS-4M[41] and the G2(MP2)[42] methods were employed to calculate the heats of formation ($\Delta_f H°$) of molecules, radical anions, and fragments. The latter method was applied only to the molecules of smaller molecular size. The $\Delta_f H°$ values (CBS-4M) of the various species were found to be in reasonable agreement with experimental values[32a,53] also for large molecules such as **4**−**7** (see Supporting Information). The bond energy values were calculated as the difference between the total molecular energy of the neutral molecules **1**−**7** or their radical anions **1a**−**7a** and that of the fragments obtained upon homolytic fragmentation. The results are shown in Tables 2 and 3. For the neutral molecules, the BDEs obtained at the MP2/3-21G*//MP2/3-21G* level are, as a rule, slightly smaller than the corresponding experimental values (Table 2). No significant improvement was obtained by including diffuse functions. The dissociation energies of the S−S bond were found to be more underestimated than those of the C−S and H−S bonds. The systematic underestimation of the calculated BDE values of the S−S bond of disulfides and the existence of a fairly linear relationship between calculated and experimental values were previously discussed.[54] The $\Delta H°$ values calculated for **1**−**3** and their radical anions **1a**−**3a** at the G2(MP2) and CBS-4M levels, which include both electronic and vibrational energies, are in rather good agreement with experimental BDE values.

In compounds **1** and **2**, H−S is the strongest bond at all levels of theory employed. Concerning disulfides **2** and **3**, the C−S and S−S bonds have similar gas-phase bond energy values. Although the C−S bonds of **2** and **3** appear to be weaker than the S−S bond at the G2(MP2) and CBS-4M levels, the trend is inverted for **2** at a lower level of calculation. The C(alkyl)−S bond is weaker than the C(aryl)−S bond (disulfides **6** and **7**) at any level of calculation. Concerning specifically the S−S bond,

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(51) Analogous conclusion can be reached by using literature values on the homogeneous ET to disulfides **3**, **4**, and **5**[21] to estimate the homogeneous Z value, expected to be ~log $Z_{hom} = 11.5$. By using a simple quadratic activation/driving force relationship and the experimental intrinsic barriers (Table 1), log Z_{hom} can be estimated to range from 11.9 to 12.8. Lowering the intrinsic barrier by about 1 kcal mol^{-1} would lead to an even closer agreement with the above log Z_{hom}. Nonadiabaticity, i.e., much smaller apparent Z_{hom} values, would require much smaller intrinsic barriers, leading, however, to very poor agreement with the experimental results.

(52) The two sets of $\Delta G_{0,s}^{\ddagger}$ values were calculated by using the empirical equation $\lambda_S = 4\Delta G_{0,s}^{\ddagger} = 55.7/r$,[5a,15] where λ_S is given in kcal mol^{-1} and the molecular radius r is in Å, and the Marcus approach,[14a] respectively. The radii were obtained from molecular models, the experimental diffusion coefficients, and the Stokes−Einstein equation.

(53) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. *Neutral Thermochemical Data* in NIST Chemistry WebBook, NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, July 2001 (http://webbook.nist.gov).

(54) Benassi, R.; Fiandri, G. L.; Taddei, F. *J. Mol. Struct. (THEOCHEM)* **1997**, *418*, 127.

that of diphenyl disulfide **5** is, as a general rule, weaker than that of the other disulfides. The S−S bond becomes stronger as the alkyl character of the substituent increases, as can be seen along the series **1** → **4** and **6** → **7**.

The above results refer to the gas phase. The strength of the relevant bonds was examined also in solution by simulating the presence of a medium having the dielectric constant of the solvent employed for the electrochemical measurements (DMF, $\epsilon = 37$). Calculations were performed at the HF/3-21G*//HF/3-21G* level. The results are reported in Table 2. Solvent effect at this level was also employed to correct the bond dissociation enthalpies at the CBS-4M level. The results do not differ significantly from those obtained for the isolated molecules and thus the same trends described above hold.

A selection of the most relevant (i.e., weakest) bond energies of the radical anions **1a**−**7a** is reported in Table 3; full data are provided in the Supporting Information. All values are positive, pointing to homolytic fragmentation of the investigated disulfide radical anions. The bond energies calculated for the cleavage of the different bonds of **1a**−**3a** do not depend significantly on the calculation level employed.[55,56] Although different levels of theory provide different absolute values, for radical anions **1a**, **2a**, and **5a**−**7a** the common trend for the relative dissociation of the examined bonds is that S−S bond cleavage is the favored process. Only for **3a** and **4a** the gas-phase cleavage of the S−S and the C−S bonds seems to be equally favored, although it should be noted that for **2a**, **6a**, and **7a** the BDEs of the C(alkyl)−S bonds are only slightly larger than those of the S−S bond. The effect of implementing the 3-21G* basis set with diffuse functions did not lead to significant changes in the calculated BDE values of **1a**−**7a**, except for the reaction paths leading to carbanions or H$^-$. As expected, the solvent has a much larger effect on the radical anions than on the neutral molecules and, consequently, the calculated BDE and ΔH° values are generally significantly smaller in solution. Some details of the computational results are particularly worth noting. Although in the gas phase the BDEs of the S−S and C(alkyl)−S bonds may have similar or even equal values, the dissociation of the S−S bond always becomes the preferred path for the cleavage of **3a**−**7a** in solution.[56]

In Figure 2, the gas-phase energy profiles corresponding to the S−S bond and the C−S bond reaction coordinates of **3** and **3a** are compared. The energy profiles were constructed as Morse-like potential energy functions of the S−S or C−S coordinate by using the second derivative of the molecular energy with respect to the specific reaction coordinate, as previously reported.[34a] A series of calculations, however, were carried out also at different geometries along the nuclear coordinate. These values were found to be in very good agreement with the corresponding values obtained from the above Morse curves. Whereas crossing of the energy profiles of **3** and its radical anion **3a** requires ~44 kcal mol^{-1} along the C−S coordinate, the much lower value of ~19 kcal mol^{-1} is found along the S−S bond coordinate.

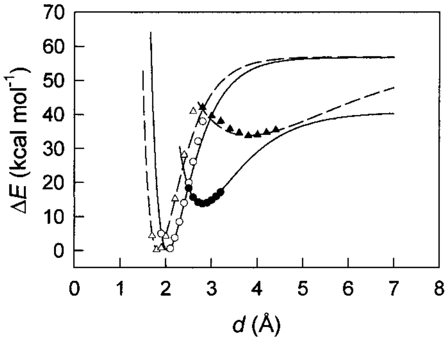

Figure 2. Energy profiles for the C−S (dashed lines) and S−S (solid lines) bond cleavage of the neutral molecule **3** and radical anion **3a** at the MP2/3-21G*//MP2/3-21G* level. The data points (S−S bond: ○, **3**; ●, **3a**; C−S bond: △, **3**; ▲, **3a**) refer to the corresponding stationary-point calculations (see text).

For the unsymmetrical radical anions **6a** and **7a**, S−S bond cleavage with formation of the PhS$^-$ anion is the favored process in the gas phase. At higher energies, there are two processes having similar energy requirements: whereas one yields the PhSS$^-$ anion and the alkyl radical, the other yields the PhS$^\bullet$ radical and the RS$^-$ anion. In solution, however, the two modes of S−S bond cleavage are the most favored processes at both levels of theory. Slightly different energy contributions, however, are required for these two reaction patterns: at the CBS-4M level, the formation of the PhS$^\bullet$ radical is the favored process, whereas the PhS$^-$ anion should form according to the lowest level of theory. Indeed, the calculated BDEs for these two patterns are rather similar. The path leading to the solvated PhS$^-$ anion, however, seems to be more realistic on the basis of the standard potentials of the *t*-BuS$^\bullet$/*t*-BuS$^-$ ($E^\circ = -0.07$ V) and PhS$^\bullet$/PhS$^-$ ($E^\circ = 0.07$ V) couples that we estimated by electrochemical methods.[50]

Kinetics of the ET Reaction. The theoretical results obtained on the ET reaction are in keeping with the outcome of the electrochemical analysis, pointing to the transient formation of radical anion species.[57] To become a radical anion, the original molecule must reach a structure that allows the ET to take place without any further structural modification, according to the Franck−Condon principle. In general terms, the energy of the system increases as a consequence of internal and solvent reorganizations. However, if we consider molecules in the gas phase, only internal rearrangements are relevant and thus only modifications of bond lengths and angles are required. On the basis of the results and evidence described in the previous section on the type of bond cleavage, we will focus on the minima having the S−S bond distance elongated with respect to the neutral molecule. In general, we found that the S−S bond increases considerably, going from 2.04−2.07 Å in the neutral

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(55) The gas-phase BDE values of **1** and **3** and their radical anions **1a** and **3a** are comparable with those obtained very recently by using different levels of calculation.[55a,b] (a) Bergès, J.; Kassab, E.; Conte, D.; Adjadj, E.; Houée-Levin, C. *J. Phys. Chem. A* **1997**, *101*, 7809. (b) Carles, S.; Lecomte, F.; Schermann, J. P.; Desfrançois, C.; Xu, S.; Nilles, J. M.; Bowen, K. H.; Bergès, J.; Houée-Levin, C. *J. Phys. Chem. A* **2001**, *105*, 5622.

(56) The energies required for fragmentation leading to carbanions or H$^-$ are significantly much lower at the G2(MP2) and CBS-4M levels of calculation. This outcome, however, is not influent in the context of the following discussion because independently of the adopted approach the dissociation modes that are more dependent on the calculation level are also those requiring the highest energy and thus are those representing the least probable reaction paths. Large negative bond energies are calculated at the CBS-4M level when the anion H$^-$ is formed due to the extremely large solvation energy calculated for this anion by the GAMESOL method. At the same level of theory, also the fragmentation paths leading to carbanions have substantially smaller energies than those calculated at the lowest level employed.

(57) It is also worth mentioning that the differences between the energies or the enthalpies of formation of the radical anion and the neutral molecule are fairly well correlated with the electrochemical E° values, particularly when the solvent effect is taken into account (see Supporting Information).

Table 4. Most Significant Structural Changes of Molecules **1**−**7** on Passing from the Neutral Species to the Radical Anion at the MP2/3-21G*//MP2/3-21G* Level[a]

compd	*d*(S–S)[b]	Δ*d*[c]	*d*(C–S)[b]	Δ*d*[c]	*d*(S–H) or *d*(C′–S)[b]	Δ*d*[c]
1	2.058	0.766			1.341	−0.001
2	2.050	0.756	1.830	0.003	1.343	−0.003
3	2.042	0.759	1.832	−0.001		
4	2.049	0.807	1.865	−0.019		
5	2.069	0.765	1.788	−0.022		
6	2.052	0.768	1.828[d]	0.004	1.793[e]	-0.043
7	2.040	0.757	1.862[d]	−0.014	1.798[e]	−0.031

[a] Bond lengths (*d*) in Å. [b] Values referring to the neutral molecule. [c] Change of bond length in the radical anion with respect to the neutral molecule: positive values indicate higher values in the radical anion. [d] S−C(alkyl) bond. [e] S−C(phenyl) bond.

molecules to 2.80−2.86 Å in the radical anions (Table 4). As a further check, the local minima corresponding to elongation of the C−S bond also were localized for **3** and its radical anion **3a** (Figure 2), using the MP2/3-21G*//MP2/3-21G* approach. We found, however, that the C−S bond length of **3a** becomes exceptionally large, ca. 3.8 Å, compared to the value in the neutral molecule, 1.83 Å, which once again points to the small relevance of this fragmentation mode.

Comparative analysis of the calculated structures of **1**−**7** and **1a**−**7a** shows that the most significant structural change brought about by the ET is, by far, stretching of the S−S bond. For example, while the S−S bond stretches, the other bonds do not change appreciably, as shown for the different C−S (or S−H) bonds in Table 4. Although the C−S−S and H−S−S bond angles do undergo some significant changes (see Supporting Information), the energy associated with these structural modifications is believed to be generally smaller than that necessary to stretch the S−S bond to reach the structure of the ET transition state. This assumption was tested in detail for compound **3**. The results showed that while decreasing the C−S−S bond angle by as much as 20° requires only 5.3 kcal mol^{-1}, more than 18 kcal mol^{-1} are required to stretch the S−S bond by 0.5 Å. The length of the cleaving S−S bond can thus be taken as the main coordinate describing the energy profile of the inner reorganization of both ET (eq 1) and bond breaking (eq 2). The values of the activation energy, $\Delta E^{\ddagger}$, and of the elongation of the bond length at the intersection of the Morse curves, $\Delta d^{\ddagger}$, are reported in Table 5 together with the Morse parameters. The $\Delta E^{\ddagger}$ values are corrected for the zero-point vibrational energy and Franck−Condon vibrational effects,[58] referred to the mode associated with the reaction coordinate, and were computed by setting the two energy minima at the same level (for the sake of comparison with the electrochemical intrinsic barriers). The calculated $\Delta E^{\ddagger}$ values, which measure the inner component of the activation energy, now can be compared with the corresponding electrochemical information, i.e., $\Delta G_{0,\mathrm{i}}^{\ddagger}$ (Table 5).[59] Despite the approximate nature of the theory employed in the calculations and the fact that $\Delta E^{\ddagger}$ is uncorrected for resonance stabilization, the trend displayed by the $\Delta E^{\ddagger}$ values is consistent with the electrochemical results, particularly those corrected for the solvent reorganization energy by using the Marcus approach.

To gain more insight into the ET step and to better compare theory and experiment, it is now useful to analyze the relationship between the Morse parameter β and the BDEs of disulfides. By carrying out an extensive analysis of the uncoupled stretching frequencies (ν) of several bonds, Zavitsas concluded that there is a linear correlation between ν and the square root of BDE.[60a] By using the equation $\beta = \nu(2\pi^2\mu/\mathrm{BDE})^{1/2}$, where μ is the reduced mass of the S−S bond, β can be related to ν and thus to BDE. The same concept was subsequently extended to other bonds, including the S−S bond.[60b] By using the same approach, we arrived at the correlation $\beta = 4.43 - 22.4/(\mathrm{BDE})^{1/2}$ (see Supporting Information), which shows that a decrease of BDE is matched by a significant decrease of β. Since it has been shown that these correlations are valid for different types of bond and bond order,[60] we may assume that disulfide radical anions obey similar rules. From a qualitative standpoint, this is in agreement with the results shown in Table 5. Conversely, it has been recently proposed that while radical anion formation entails a decrease of the BDE, $\beta_{(\bullet -)}$ may be kept equal to the Morse factor of the neutral molecule.[8c] This model has been used to describe the reactivity of some classes of compound.[2b,13b] Although acceptable for more rigid radical molecular frameworks, this seems to be too severe an assumption to describe the formation of the disulfide radical anions and, more generally, loose radical anion species. As a matter of fact, simple application of the equation that was derived for $\Delta G_{0,\mathrm{i}}^{\ddagger}$, i.e., $\Delta G_{0,\mathrm{i}}^{\ddagger} = (\mathrm{BDE}^{1/2} - \mathrm{BDE}_{(\bullet -)}{}^{1/2})^2/4$,[8c] together with the use of our theoretical BDE values of the neutral and radical anion disulfides, at the various levels employed, would lead to $\Delta G_{0,\mathrm{i}}^{\ddagger}$ values in the range 1.2−2.8 kcal mol^{-1} and thus to values that are too small compared to both the theoretical and the electrochemical evidence.

Table 5 shows that the experimental barriers are systematically smaller than suggested by the gas-phase calculations. On the other hand, although the Morse curve of the neutral disulfide is left almost unchanged by the presence of a dielectric, we have seen that the BDE of the radical anion decreases significantly, leading to a shallower potential energy curve with respect to the gas phase. The solvent effect should lead to an earlier and less energetic transition state and thus the actual $\Delta d^{\ddagger}$ and $\Delta E^{\ddagger}$ values should be smaller than those reported in Table 5. For example, by using the BDE values obtained for $\epsilon = 37$ at the lower level of calculation and the β factors of Table 5 we calculate that the "solution" $\Delta d^{\ddagger}$ and $\Delta E^{\ddagger}$ values decrease to an average of 0.23 Å and 6.9 kcal mol^{-1}. Therefore, computation of the solvent effect is indeed necessary to obtain a closer agreement between theory and experiment. It should be noted that use of the same BDE values in the equation developed for $\beta = \beta_{(\bullet -)}$ leads to average $\Delta G_{0,\mathrm{i}}^{\ddagger}$ values of 5.2 and 5.6 kcal mol^{-1} at the MP2/3-21G*//MP2/3-21G* and CBS-4M levels, respectively. These values also, although still a bit small, point to the need of including the solvent effect in any comparison between theory and experiment.

The agreement between calculations and electrochemical analysis supports the view that the ET to disulfides is associated with significant S−S bond elongation. Thus, unless very special geometrical or environmental constraints hamper S−S bond stretching, the harmonic approximation should not provide an

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(58) King, G. W. *Spectroscopy and Molecular Structure*; Holt, Rinehart and Winston, Inc.: New York, 1964.

(59) The average entropy change associated with the formation of the loose radical anions **3a**−**7a** was calculated to be $T\Delta S° = 2.5$ kcal mol^{-1} (at 298.15 K). Only a fraction of it, depending on the position of the transition state, would conceivably affect the barrier (for related arguments, see: Andrieux, C. P.; Savéant, J.-M.; Tardy, C. *J. Am. Chem. Soc.* **1998**, *120*, 4167).

(60) (a) Zavitsas, A. A. *J. Phys. Chem.* **1987**, *91*, 5573. (b) Zavitsas, A. A.; Chatgilialoglu, C *J. Am. Chem. Soc.* **1995**, *117*, 10645.

Table 5. Kinetic Parameters for the Reduction of Compounds **3**−**7** to Their Radical Anions **3a**−**7a** (Calculations Refer to the Gas Phase)

compd	$\Delta E^{\ddagger\,a}$ (kcal mol^{-1})	$\Delta d^{\ddagger\,a,b}$ (Å)	$\Delta E^{\ddagger\,c}$ (kcal mol^{-1})	$\Delta d^{\ddagger\,b,c}$ (Å)	β^{d} (Å^{-1})	$\beta_{(\bullet-)}^{e}$ (Å^{-1})	$\Delta G_{0,i}^{\ddagger\,f}$ (kcal mol^{-1})	$\Delta G_{0,i}^{\ddagger\,g}$ (kcal mol^{-1})
3	11.8	0.322	12.2	0.305	1.896	1.164	6.3	8.3
4	12.5	0.321	12.2	0.301	1.873	1.025	5.9	7.5
5	11.7	0.359	13.6	0.395	1.930	1.558	6.9	8.1
6	13.1	0.363	12.9	0.342	1.929	1.478	6.4	7.9
7	12.1	0.332	12.6	0.329	1.906	1.297	7.8	9.1

[a] From the total molecular energy (MP2/3-21G*//MP2/3-21G* level) of the neutral molecule and radical anion at the crossing point, assuming the same energy for the minima and after zero-vibrational and Franck−Condon corrections. [b] Elongation of the S−S bond distance at the crossing point. [c] From CBS-4M enthalpies, β values of columns 6 and 7 and assuming the same energy for the minima. [d] Coefficient of the Morse function (MP2/3-21G*//MP2/3-21G* energies) for the neutral molecule. [e] Coefficient of the Morse function (MP2/3-21G*//MP2/3-21G* energies) for the radical anion. [f] Calculated from the convolution analysis data, using an empirical equation (see ref 52). [g] Calculated from the convolution analysis data, using the Marcus approach (see ref 52).

accurate description of the inner reorganization energy. Again, as for concerted dissociative ETs,[17,61] Morse functions may be used to obtain a more realistic analytical description of the potential energy changes along the most important contribution to the reaction coordinate. The problem is that when the two Morse curves describing the neutral and the radical anion are different because of different β and BDE values, the ensuing rate−driving force relationship is not parabolic,[62] unless very special assumptions are explicitly made.[8c] On the other hand, our experimental $\alpha-E$ plots are pretty linear, which is in agreement with an approximately parabolic $\Delta G^{\ddagger}-\Delta G^{\circ}$ relationship. Therefore, in the absence of a general (and simple) $\Delta G^{\ddagger}-\Delta G^{\circ}$ relationship, we used our theoretical Morse curves to simulate the driving force dependence of the crossing between the reactant and product curves. Indeed, we found that for all compounds the ensuing relationship can be nicely fit by a second-order equation, leading to linear $\alpha-\Delta G^{\circ}$ plots. However, for **3**−**7** the α value corresponding to $\Delta G^{\circ} = 0$ is now smaller than 0.5, being on the average 0.41. A similar result was obtained by studying the formation of the radical anion of Cl_2.[62] As previously discussed, however, the solvent effect must be necessarily included to obtain a more realistic description of the system and thus a better comparison between experimental and theoretical data. Noteworthy, when the above analysis is carried out for **3**−**7** by taking into account the solvent effect, the average α value corresponding to $\Delta G^{\circ} = 0$ is now very close to 0.5 (0.52 ± 0.03). These differences would not affect significantly the electrochemically determined quantities (E°, log k°_{het}, $\Delta G_0^{\ddagger}$) obtained by using $\alpha = 0.5$ and thus the substance of our conclusions. In fact, the E° values would be slightly more positive, the log k°_{het} smaller by ca. 1 unit, and consequently the $\Delta G_0^{\ddagger}$ larger by ca. 1 kcal mol^{-1}. Therefore, our analysis suggests that although different Morse curves (and Morse parameters) must be used to describe the initial step of this “almost-dissociative” stepwise ET bond breaking mechanism, reasonable estimates of relevant electrochemical quantities still may be obtained along similar lines as previously applied to concerted dissociative ETs and to the ET step of “cassical” stepwise dissociative processes.

Conclusions and Final Remarks. The reductive cleavage of a series of symmetrical and unsymmetrical disulfides has been investigated by convolution analysis and carrying out specific calculations at different levels of theory. Both types of result point to a stepwise dissociative reduction involving the intermediacy of a transient radical anion followed by cleavage of the S−S bond. With respect to most compounds undergoing similar reductive cleavages, the mechanism of the stepwise dissociative ET to disulfides is peculiar in that a loose radical anion species forms. Although during the formation of the radical anion some bond angle deformation occurs, the most relevant inner reorganization has been clearly identified as the stretching of the cleaving S−S bond, which increases by as much as 0.8 Å in the radical anion. Noteworthy, this remarkably large structural reorganization is essentially independent of the R and R′ substituents in RS−SR′. The extent of this inner reorganization puts this class of dissociative ETs at the border between classical stepwise mechanisms (with little reorganization associated with the ET step) and purely dissociative reductions (where the BDE of the cleaving bond is the major parameter determining the intrinsic barrier).

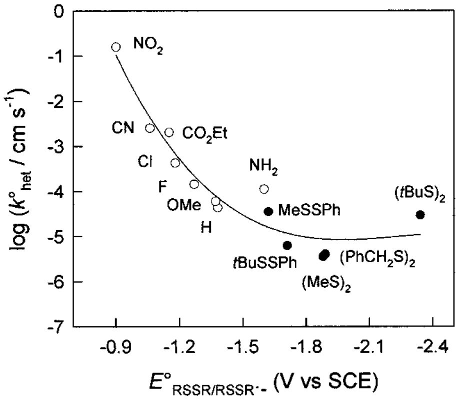

Figure 3. Comparison between the heterogeneous standard rate constants of the reduction of disulfides. The data are plotted as a function of E° and were obtained in DMF/0.1 M TBAP at 25 °C, using the glassy carbon electrode. The legends correspond to either (●) the name of the dialkyl or alkyl−aryl disulfides (this work), including dibenzyl disulfide,[63a] or (○) the para substituent of a series of disubstituted diaryl disulfides.[22] The solid line is meant to underline the experimental trend.

The large inner reorganization is responsible for the low value of the heterogeneous standard rate constant observed for the investigated compounds. This is illustrated in Figure 3 in comparison with the electrochemical results pertaining to diaryl disulfides.[23,63] The trend is that almost no differences show up for the least easily reducible compounds (which implies that the intrinsic barriers are very similar) and that only for diaryl disulfides containing good electron-withdrawing groups is the

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(61) (a) Wentworth, W. E.; Becker, R. S.; Tung, R. *J. Phys. Chem.* **1967**, *71*, 1652. (b) Wentworth, W. E.; George, R.; Keith, H. *J. Chem. Phys.* **1969**, *51*, 1791. (c) Steelhammer, J. C.; Wentworth, W. E. *J. Chem. Phys.* **1969**, *51*, 1802. (d) German, E. D.; Kuznetsov, A. M. *J. Phys. Chem.* **1994**, *98*, 6120.

(62) German, E. D.; Kuznetsov, A. M. *J. Phys. Chem. A* **1998**, *102*, 3668.

(63) The electroreduction of diaryl disulfides[22] and dibenzyl disulfide[63a] was carried out along the same lines described for **3**−**7**. (a) Antonello, S.; Maran, F. Unpublished work.

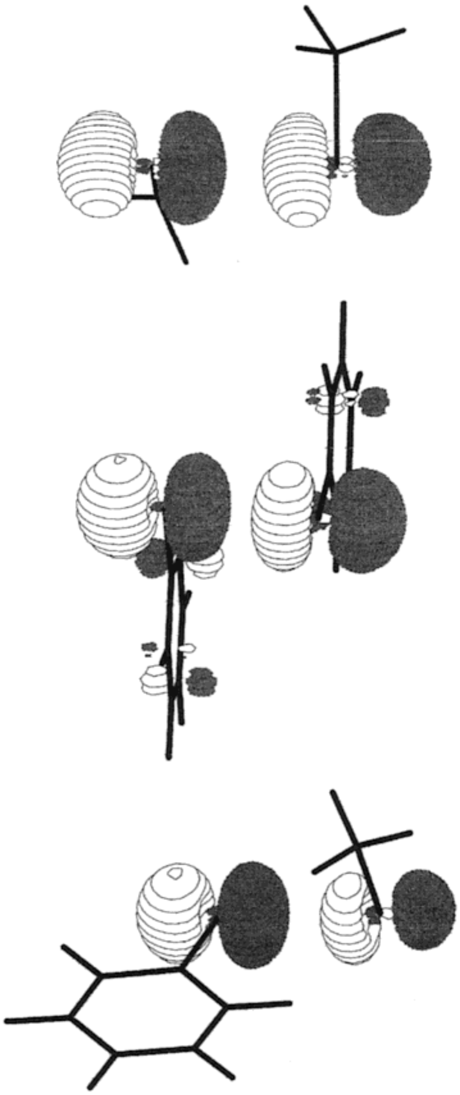

Figure 4. SOMOs of the radical anions **3a** (top), **5a** (middle), and **6a** (bottom).

π^* character of the singly occupied molecular orbital (SOMO) able to reduce the extent of the inner reorganization component. In turn, this comparison also indicates that the reduction of most nonactivated disulfides, such as the ones investigated here, does entail the formation of σ^* radical anions. In fact, when the disulfide sets up to accept the electron at the transition state, the necessary elongation of the S−S bond provokes the lowering of the energy of an antibonding orbital that, once the final radical anion equilibrium structure is reached, localizes onto the loose S−S bond.[64] In this respect, phenyl or alkyl substituents do not display significant differences. This is nicely illustrated in Figure 4 in which the SOMOs of **3a**, **5a**, and **6a** are depicted.

Because of the nature of the antibonding orbital hosting the unpaired electron, the BDE of these radical anions is much smaller than that of the neutral molecule. This is particularly true in solution because of the extensive solvation experienced by the small anionic fragments formed in the dissociation. For the neutral molecules and their radical anions, we could estimate the shape of the corresponding Morse curves, which allowed us to calculate the energy change required to reach the transition state of the ET step. Once the solvent effect is taken into account, the calculated inner barriers are in reasonable agreement with the electrochemical results. Concerning the fragmentation of the radical anions, the reaction is an endergonic, homolytic cleavage. For example, by using our experimental results, it is possible to calculate the free energy change for the fragmentation of **5a**−**7a** through the following equation:[7] $\Delta G_{\mathrm{RSSR}^{\bullet-}} = \mathrm{BDFE}_{\mathrm{RSSR}} + F(E^\circ_{\mathrm{RSSR/RSSR}^{\bullet-}} - E^\circ_{\mathrm{RS}^\bullet/\mathrm{RS}^-})$. By using the solution bond energies of Table 2 and some entropy contribution, we estimate $\Delta G_{\mathrm{RSSR}^{\bullet-}}$ to be approximately in the range 5−10 kcal mol^{-1}, pointing to radical anions having lifetimes not shorter than 1 ns.

In conclusion, the mechanism of the stepwise dissociative reduction of disulfides now seems to be reasonably well understood. We believe this result to be important in the context of future studies on these and other functional groups liable to form loose radical anion species, particularly for application in more complex molecular systems, such as in biologically relevant macromolecules.

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Supporting Information Available: Descriptions of the geometries of the stationary points and the absolute energies of each stationary point, additional tables of calculated data and illustrations of relevant orbitals, and data on the reaction energy for the formation of the radical anion (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(64) The LUMO of compounds **3** and **4** is the S−S σ^* orbital and thus essentially equal to the corresponding SOMO. On the other hand, the LUMO of **5**−**7** display a significant π^* character (examples are provided in the Supporting Information), which, however, disappears upon S−S bond elongation.