Evidence for Large Inner Reorganization Energies in the Reduction of Diaryl Disulfides: Toward a Mechanistic Link between Concerted and Stepwise Dissociative Electron Transfers?

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Bond fragmentation often accompanies electron uptake by substrates bearing suitable leaving groups.[1] Usually, bond fragmentation follows the electron transfer (ET) to the acceptor molecule (AB) (eq 1). But when the leaving group is relatively stable to oxidation and/or the bond is weak, such as with alkyl halides[1,2] or peroxides,[3] ET and bond cleavage can be concerted, and the radical A• and the anion B⁻ form in a single step (eq 2).[2]

$$A-B + e \rightleftarrows A-B^{•-} \rightarrow A^{•} + B^{-} \qquad (1)$$

$$A-B + e \rightarrow A^{•} + B^{-} \qquad (2)$$
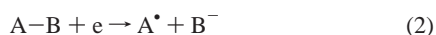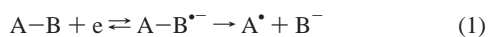
Besides the chemical difference of the ET step, an important aspect by which the two ET mechanisms differ concerns the reorganization energies. The stepwise mechanism (eq 1) is usually represented as one in which the radical anion $AB^{•-}$ forms without significant structural reorganization with respect to its precursor so that the kinetics of the injection of one electron into AB is viewed as being ruled primarily by solvent reorganization. This is not the case for a purely dissociative ET (eq 2), where $1/4$ of the bond dissociation energy (BDE) of the A−B bond contributes to the inner reorganization energy.[2] As a consequence, the intrinsic barrier, expressed as the sum of solvent and inner contributions ($\Delta G_0^{\ddagger} = \Delta G_{0,s}^{\ddagger} + \Delta G_{0,i}^{\ddagger}$), can be quite large having a significant effect on the activation free energy $\Delta G^{\ddagger}$.[4] It has already been shown that the transition between the two competitive mechanisms can be induced by changing the reducing properties of the electron donor (an electrode or a solution species).[3c,5] However, it is not so clear what happens when a stepwise ET process involves a significant inner reorganization. The problem is not trivial. In fact, an increasing contribution from inner reorganization may be viewed as a link between the above two mechanisms and thus to

a situation in which the breaking bond in $A-B^{•-}$ becomes very weak and is significantly stretched but not yet to the point of being a purely dissociative ET. We approached this problem by studying the reduction of the series of *para*-disubstituted diaryl disulfides **1a−g**, having the general formula $(X-C_6H_4S-)_2$, where $X = NH_2$ (**a**), OMe (**b**), H (**c**), F (**d**), CO₂Et (**e**), CN (**f**), or NO₂ (**g**). These substrates were chosen because of the recent findings of one of us that the homogeneous reduction of **1c** is characterized by a large reorganization energy (i.e., significantly larger than $\Delta G_{0,s}^{\ddagger}$)[6] and also because theoretical calculations point to a significant S−S bond stretching in the formation of radical anions of other disulfides.[7]

Electroreduction of **1a−g** is an irreversible process (cyclic voltammetry) leading to S−S bond cleavage and eventually to formation of two $X-C_6H_4S^{-}$ anions (controlled potential electrolysis) in an overall two-electron process.[8] The position of the voltammetric peak strongly depends on the ring substituent (Table 1) as does the oxidation of $X-C_6H_4S^{-}$, a process detectable on the backward scan. The kinetics of the heterogeneous ET was studied by convolution voltammetry, a powerful tool to observe fine details of electrode processes.[3,9] The background-subtracted voltammograms, obtained at several scan rates in the 0.1−50 V s⁻¹ range, were subjected to convolution followed by logarithmic analysis using the equation which holds for an irreversible process.[10] By this procedure, one obtains the heterogeneous rate constant (k_{het}) as a function of the potential E. These (logarithmic) plots, which have a curved shape, were then treated to obtain the corresponding derivative plots. The latter plots are linked to the apparent transfer coefficient α through the relationship $\alpha = -(RT/F)(d \ln k_{het}/dE)$[11] and, provided they are linear, can be used to estimate the value of the standard potential $E°$ of the electrode reaction, being $E = E°$ when α = 0.5. This stems from the underlying activation-driving force relationship,[4] by considering that α is actually defined as $\partial \Delta G^{\ddagger}/\partial \Delta G°$ and that $\Delta G° = -F(E° - E)$. The $E°$ values so obtained are reported in Table 1, together with representative α values. The fifth column shows the apparent values of the standard rate constant $k°_{het}$, i.e., the value of k_{het} for $E = E°$.[11] The $k°_{het}$ values were obtained by parabolic fit of the log $k_{het} - E$ plots. As a final check, digital simulation of the cyclic voltammograms was carried out, leading to a good reproduction of the experimental curves of **1a−g** in the whole scan rate range investigated.

As previously discussed on the basis of thermochemical calculations for **1c**,[6] a stepwise mechanism is favored over the concerted mechanism on thermodynamic grounds (e.g., by at least 0.3 eV for **1c**). The same holds true on kinetic grounds, because λ for a simple ET is always smaller than that of a dissociative ET.[3c,4] Furthermore, the typical values of α reported in Table 1 are too large to be in line with a concerted mechanism.[2] The focus

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(4) Both the Marcus[4a] and the dissociative ET[2] theories relate $\Delta G^{\ddagger}$ to the reaction free energy $\Delta G°$ through the simple quadratic equation $\Delta G^{\ddagger} = \Delta G_0^{\ddagger}(1 + \Delta G°/4\Delta G_0^{\ddagger})^2$. (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
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(7) Benassi, R.; Taddei, F.; Antonello, S.; Maran, F., manuscript in preparation.
(8) The electrochemical experiments were performed in DMF/0.1 M Bu₄NClO₄ (heterogeneous data) or Bu₄NBF₄ (homogeneous data) using glassy carbon electrodes. The setup and the procedures were as previously described for both direct[3b] and indirect electrochemistry and controlled potential electrolysis.[6] Potentials were measured relative to ferrocene oxidation and are given against the KCl-saturated calomel electrode (SCE). The convolution analysis was performed by using our own laboratory software. Digital simulations were performed by using the DigiSim 2.1 software (Bioanalytical Systems Inc).
(9) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1998**, *120*, 5713.
(10) $\ln k_{het} = \ln D^{1/2} - \ln[(I_l - I)/i]$, where i is the real current, I is the convoluted current, and I_l is given by $I_l = nFAD^{1/2}C^*$, where n is the number of electrons per molecule and C^* is the bulk concentration of the substrate. (Savéant, J.-M.; Tessier, D. *J. Electroanal. Chem.* **1975**, *65*, 57). Diffusion coefficients were calculated from I_l, using electrodes of known area A.
(11) The α, $E°$, and k_{het} data could not be corrected for the effect of the electric double layer because the double layer properties of glassy carbon are almost unknown. However, even apparent data should provide a reasonable estimate of the actual parameters.[3b,c]

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Table 1. Electrochemical, Kinetic and Thermodynamic Parameters for the Reduction of Disulfides **1**

1	$E_p{}^a$ (V)	$E^{\circ}{}^{b,c}$ (V)	α^d	$\log k^{\circ}_{het}$ (cm s^{-1})	$\Delta G_0^{\ddagger}$ (kcal mol^{-1})
a	−1.86	−1.60	0.384	−3.95	10.3
b	−1.71	−1.38^e	0.363	−4.36	10.8
c	−1.65	−1.37^f	0.409	−4.22	10.7
d	−1.55	−1.27	0.383	−3.84	10.1
e	−1.23	−1.15	0.457	−2.69	8.5
f	−1.15	−1.06^g	0.428	−2.60	8.4
g	−0.79	−0.90	0.674	−0.80	5.9

^{a} Peak potentials at 0.2 V s^{-1} against SCE; uncertainty is ca. 5 mV. ^{b} Against SCE and double layer uncorrected. ^{c} Although the average uncertainty on the apparent E° values is 20−30 mV, the actual error is expected to be slightly larger (see ref 11); for **1f** it becomes 80 mV because of reproducibility problems on its reduction. ^{d} Calculated from the convolution data for $E = E_p$ (0.2 V s^{-1}). ^{e} Homogeneous $E^{\circ} \approx$ −1.40 V. ^{f} Homogeneous $E^{\circ} =$ −1.40 V, from ref 6. ^{g} Homogeneous $E^{\circ} =$ −1.14 V.
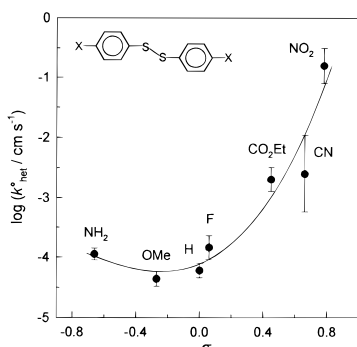

Figure 1. Hammett plot of the logarithm of the heterogeneous ET rate constant for the reduction of diaryl disulfides **1** in DMF. The solid line has only the meaning of underlining the experimental trend. The error bars are (mostly) due to the uncertainty on the E° values, which affect the $\log k^{\circ}_{het}$ calculation.

of the following discussion is thus on the formation of the radical anions of **1a−g**. Figure 1 shows the dependence of $\log k^{\circ}_{het}$ on the Hammett substituent constants σ. A very similar plot can be obtained for $\log k^{\circ}_{het}$ vs E°. In Figure 1 some interesting features are worth noting: First, the heterogeneous kinetics for reduction of substrates **1a−d** is *very sluggish*, more sluggish than for the large majority of organic radical anions.[12] Second, when the electron-withdrawing properties of the substituents are enhanced, k°_{het} *increases by as much as 3.5 orders of magnitude*.

To test the reliability of the heterogeneous data, we studied the homogeneous ET to **1b** and **1f** by using the method of redox catalysis,[13] as already described for **1c**.[6] The ET rate constants by a series of electrogenerated radical anions were then analyzed to obtain the relevant E° values, ca. −1.40 and −1.14 V respectively (see Supporting Information). These values, together with that of **1c**, −1.40 V,[6] are in very good agreement with those of Table 1. In addition, the corresponding homogeneous standard rate constant ($\log k^{\circ}_{hom}$: **1b**, 3.79; **1c**, 4.28; **1f**, 5.77)[14] is affected by the substituent in the same way as $\log k^{\circ}_{het}$. Therefore, this independent evidence ensures that the observed substituent effect on the heterogeneous ET rate is indeed real.

Analysis of the data is in agreement with a significant decrease of $\Delta G_0^{\ddagger}$ on going progressively to **1g**.[15] The $\Delta G_0^{\ddagger}$ values reported in Table 1 were obtained using the Eyring equation. $\Delta G_{0,s}^{\ddagger}$ depends only slightly on the substitution and can be evaluated for **1a−g** to be 2.5−3.1 kcal mol^{-1}.[16] This means that $\Delta G_{0,i}^{\ddagger}$ amounts to, e.g., 7.5−7.8 kcal mol^{-1} for **1a−c** (70−75% of $\Delta G_0^{\ddagger}$) and that it decreases significantly on going toward **1g**. This picture

can be ascribed to a significant elongation of the S−S bond in the ET transition state for **1a−d**. This is supported also by calculations performed on **1c**: The S−S bond stretches by 0.76 Å upon formation of the radical anion and by 0.36 Å at the transition state (for $\Delta G^{\circ} = 0$), leading to a large $\Delta G_{0,i}^{\ddagger}$.[17] Bond elongation would progressively diminish when X becomes more electron-withdrawing. On the other hand, the observed increase of k°_{het}, reaching its maximum with **1g**, points to a change in the nature of the orbital hosting the electron in the formation of the radical anion. It seems that while for **1a−d** the incoming electron goes in an antibonding π^* orbital that is partly localized on the S−S bond (resulting in a large and almost substituent-independent S−S bond elongation), in **1e**, **1f**, and, in particular, **1g,** the LUMO becomes more localized onto the aryl ring and the X substituent.[18] As a consequence, when going from **1a** to **1g**, the follow-up cleavage could be described as changing from a simple decay, where the unpaired electron is mostly located at the fragmentation site, to an intramolecular ET that now occurs from the aryl-substituent system to the S−S σ^* orbital. The observed change in the ET rate would thus monitor also a change in the overall ET-bond fragmentation mechanism.

The consistency between heterogeneous and homogeneous data together with the support provided by theoretical calculations shows (i) that there can be molecular systems in which, because of significant elongation of the breaking bond, $\Delta G_{0,i}^{\ddagger}$ can be much larger than usually assumed and (ii) that $\Delta G_{0,i}^{\ddagger}$ can be modulated by ring substitution. If we compare our experimental barriers with those expected for the corresponding concerted ET ($\Delta G_0^{\ddagger} = \Delta G_{0,s}^{\ddagger} +$ BDE/4) and for a stepwise ET in which one assumes $\Delta G_0^{\ddagger} \approx \Delta G_{0,s}^{\ddagger}$, it is found that the intrinsic barriers of most of the processes investigated here are even closer to that of the concerted path. For example, the values for **1c** are 10.7, 14.8− 16.8,[19] and 3.1 kcal mol^{-1}, respectively. Thus, the evidence presented suggests that, at least for some classes of compounds, the transition between the two (limiting) mechanisms could be much smoother than generally believed. This is expected to have implications on developments of the dissociative ET theory, an area of active testing and refinement.[1−3,5,9,20−23]

Supporting Information Available: Redox catalysis procedures and data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) A similar, though less pronounced effect, has been reported for the reduction of substituted thiocarbonates: Falsig, M.; Lund, H.; Nadjo, L.; Savéant, J.-M. *Nouv. J. Chim.* **1980**, *4*, 445.

(13) For example, see: Andrieux, C. P.; Savéant, J.-M. In *Investigation of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. 6, 4/E, Part 2, p 305.

(14) These values were obtained by regression analysis of the rate data pertaining to the activation region,[13] using the E° of Table 1. See Supporting Information for further details.

(15) The preexponential Z_{het} values were determined by equation $Z_{het} = (k_B T/2\pi M)^{1/2}$, where M is the molecular mass.

(16) Obtained by using the stokes radii of **1a−g** and the empirical equation λ_s(kcal mol^{-1}) = 55.7/r(Å), as previously discussed,[3b] where $\lambda_s = 4\Delta G_{0,s}^{\ddagger}$.

(17) Total molecular energies where obtained by MO ab initio calculations at MP2/3-21G*//MP2/3-21G* level. Morse equations for both the neutral and the radical anion were obtained with the procedure previously described (Benassi, R.; Taddei, F. *J. Phys. Chem. A* **1998**, *30*, 6173). The gas phase BDE (kcal mol^{-1}), exponential factor (Å^{-1}), and equilibrium distance (Å) for the Morse curves of **1c** and its radical anion are 46.8, 1.930, 2.069 and 15.0, 1.558, 2.831, respectively; the corresponding $\Delta G_{0,i}^{\ddagger}$ term is 11.5 kcal mol^{-1}. Calculations in solution (IPCM approach, $\epsilon \equiv \epsilon_{DMF} = 36.7$),[7] led to BDE values of 47.9 and 13.6 kcal mol^{-1}, respectively.

(18) As shown in ref 9, orbital shifts induced by substituents may affect also the rate of intramolecular ETs.

(19) This depends on the BDE value adopted.[19a−c] (a) Reference 17. (b) Benassi, R.; Fiandri, G. L., Taddei, F. *J. Mol. Struct. (THEOCHEM)* **1997**, *418*, 127. (c) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

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