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Stepwise versus Concerted Electron Transfer-Bond Fragmentation in the Reduction of Phenyl Triphenylmethyl Sulfides

Steen Jakobsen, Henrik Jensen, Steen U. Pedersen, and Kim Daasbjerg*

Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

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The link between stepwise and concerted electron transfer-bond fragmentation processes is described for the homogeneous reduction process of four para-substituted phenyl triphenylmethyl sulfides in *N*,*N*-dimethylformamide. The description is based on intrinsic barriers $\Delta G_o^\ddagger$ and standard potentials E^o determined from free energy plots. For all reactions studied $\Delta G_o^\ddagger$ is remarkable high and E^o is not far from what is expected for a concerted pathway, even if the mechanism is stepwise. This is attributed to a substantial elongation and weakening of the carbon−sulfur bond upon formation of the radical anion. At the same time, $\Delta G_o^\ddagger$ increases going from electron-withdrawing to electron-donating substituents which points to a gradual transition between the two reaction pathways within the series of compounds.

When molecules are involved in electron transfer (ET) processes their structure is often affected to such an extent that chemical follow-up reactions are induced. In particular, much attention has been addressed to the study of molecules that upon reduction are prone to undergo bond fragmentation.[1−3] The question of whether ET and bond cleavage occur in a stepwise or concerted manner is of fundamental interest if a detailed description of the processes is to be obtained.[4] The situation is exemplified by the two possible reduction routes of substituted phenyl triphenylmethyl sulfides, $\phi_3C{-}S\phi X$, shown in eqs 1 and 2.

Stepwise pathway:

$$\phi_3C{-}S\phi X + e \rightleftarrows \phi_3C{-}S\phi X^{\bullet -} \rightarrow \phi_3C^\bullet + X\phi S^- \quad (1)$$

Concerted pathway:

$$\phi_3C{-}S\phi X + e \rightarrow \phi_3C^\bullet + X\phi S^- \quad (2)$$

According to Marcus[5] and dissociative ET theory,[6] the activation free energy $\Delta G^\ddagger$ for either mechanism can be related to the reaction free energy $\Delta G°$ through eq 3,

$$\Delta G^\ddagger = \Delta G_o^\ddagger\left(1 + \frac{\Delta G°}{4\Delta G_o^\ddagger}\right)^2 \quad (3)$$

where $\Delta G_o^\ddagger$ is the intrinsic barrier and $\Delta G°$ is defined according to the mechanism in play. In the case of a concerted process the major contribution to $\Delta G_o^\ddagger$ stems from the structural (inner) reorganization energy $\Delta G_{o,i}^\ddagger$ owing to bond cleavage. For a stepwise mechanism, on the other hand, it is often assumed that $\Delta G_o^\ddagger$ primarily is made up of solvent reorganization energy. Yet, this is not always so and in a recent work concerning the reduction process of disulfides[7] $\Delta G_{o,i}^\ddagger$ was found to be remarkably high even though the stepwise mechanism was followed.

Our objective in this paper is to describe the link between the two pathways since very little quantitative information is known in this respect. In order to do so, it is essential to obtain kinetic and thermodynamic parameters such as $\Delta G_o^\ddagger$ and $\Delta G°$ for the reduction process of a series of structurally related compounds in which change-over from one mechanism to another can be observed. The compounds selected for this particular study were 4-methoxyphenyl triphenylmethyl sulfide (**1a**), phenyl triphenylmethyl sulfide (**1b**), and 4-acetylphenyl triphenylmethyl sulfide (**1c**).[8] This choice is based on literature results pertaining to the reduction process of **1b** in which even a small change in driving force was claimed to induce a mechanistic change.[4a] By including compounds with electron-donating and -withdrawing groups positioned on the phenyl ring, observation of the transition from a concerted to a stepwise process should be within reach. The fact that the carbon−sulfur bond in **1a**−**c** is relatively weak also makes it easier from an experimental point of view to extract the parameters involved in the parabolic free energy relationship (eq 3).

The three sulfide compounds were investigated by means of the homogeneous redox catalysis approach,[9] in which the substrate is reduced indirectly by a series of radical anions of aromatic and heteroaromatic compounds, $A^{\bullet -}$. The two essential reduction routes are depicted in eqs 1 and 2 (with the electron coming from $A^{\bullet -}$), while a complete reaction scheme[4a] is shown in Supporting Information together with a tabulation of all relevant rate data.

Figure 1 shows free energy plots in terms of log k_{ET} vs E_A^o for **1a**−**c**, where k_{ET} denotes the ET rate constant for the reaction between $A^{\bullet -}$ and the substrates and E_A^o the standard potential of A. Rate data available in literature for 4-cyanophenyl triphenylmethyl sulfide (**1d**)[10] are also included. Curvature is evident in all four plots; for **1a** and **1b** an activation-controlled zone (parabolic section) is observed while for **1c** and **1d**, in addition, a counter-diffusion-controlled zone (linear section of slope −1/59 mV) appears as indicated in the case of **1c** by the dashed line. The presence of such a region is attributed to a diffusion-controlled ET between the mediator A and the radical anion of the substrate, i.e., the reductions of **1c** and **1d** must

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* To whom correspondence should be addressed. Kemisk Institut, Aarhus Universitet, DK-8000 Aarhus C, Denmark. FAX: +4586196199. E-mail: kdaa@kemi.aau.dk.

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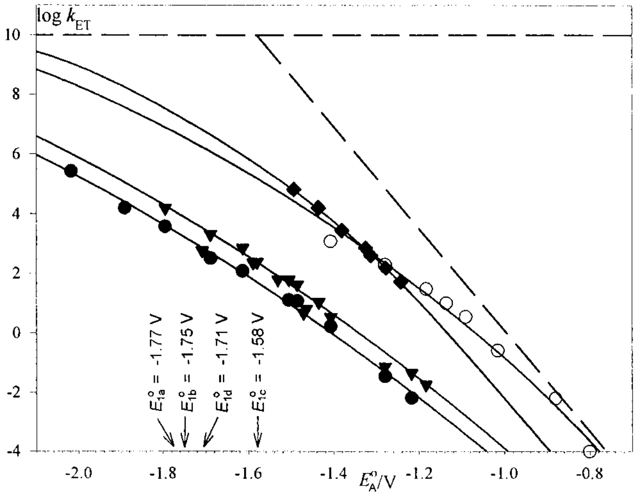

Figure 1. Plot of the logarithm of the homogeneous ET rate constant k_{ET} against E^o_A for the reduction of **1a** (●), **1b** (▼), **1c** (○), and **1d** (◆) by different aromatic radical anions in DMF/0.1 M Bu_4NBF_4 at 22 °C. The best fits are included as solid curves.

TABLE 1: Standard Potential E^o and Intrinsic Barrier $\Delta G^{\ddagger}_o$ Obtained from the Rate Data on the Homogeneous Reduction of 1a−d, the Standard Potential E^o_{con} Expected for a Concerted Mechanism and the Parameter $F\Delta E^o$ Defined as $F E^o - F E^o_{con}$

substrate	E^o (V)[a]	E^o_{con} (V)[a]	$F\Delta E^o$ (eV)	$\Delta G^{\ddagger}_o$ (eV)
1a	−1.77 ± 0.05	−1.87	0.10	0.47 ± 0.03
1b	−1.75 ± 0.03	−1.72	−0.03	0.44 ± 0.02
1c	−1.58 ± 0.02	−1.48	−0.10	0.37 ± 0.02
1d	−1.71 ± 0.01[b]	−1.45	−0.26	0.27 ± 0.01[b]

[a] Vs SCE. [b] Rate data are from ref 10.

follow a stepwise mechanism.[9] One should be aware that the lack of this region for **1a** and **1b** does not imply that the reduction processes of these compounds necessarily have to be concerted. Still, it could be stepwise reactions associated with high intrinsic barriers.

Previously, the indirect reduction of **1b** has been investigated by Severin et al.[4a] and interestingly, they observed a small shift in the log k_{ET} vs E^o_A plot for the most endergonic reactions. This was interpreted as a mechanistic shift from a stepwise to a concerted ET as the driving force was lowered. However, the extended set of data presented herein does not support this conclusion since a parabolic free energy relationship is observed throughout the driving force interval. Four of the experimental points are deviating from the general trend, but this is most likely attributed to a variation in the self-exchange reorganization energies of the mediators used. These specific results were not employed in the further analysis.

The activation-controlled ET process for either mechanism is described by the same expression, eq 3.[11] The intrinsic barrier $\Delta G^{\ddagger}_o$ and the standard potential E^o of the substrate ($=E^o_A - \Delta G^o/F$) can thus easily be obtained from fitting procedures as described in ref 12 and Supporting Information. The best fits for **1a**−**d** are included in Figure 1 as solid curves and the extracted values of $\Delta G^{\ddagger}_o$ and E^o are collected in Table 1. Also shown in Table 1 is the standard potential E^o_{con} calculated for a presumed concerted process on the basis of eq 4 as well as the parameter $F\Delta E^o$ defined in eq 5.

$$F E^o_{con} = F E^o_{x\phi s.} - BDFE(\phi_3C{-}S\phi X) \qquad (4)$$

$$F\Delta E^o \equiv F E^o - F E^o_{con} \qquad (5)$$

Expression 4 can be deduced from a thermochemical cycle, in which $E^o_{x\phi s.}$ denotes the standard potential of the substituted thiophenoxyl radical and $BDFE(\phi_3C\text{-}S\phi X)$ the bond dissociation free energy of the substrate.[13,14] One should realize that the interpretation of eq 5 depends on the mechanism in play. For a concerted process E^o equals E^o_{con}, i.e., $F\Delta E^o$ should be zero, while in the case of a stepwise mechanism $F\Delta E^o$ corresponds to the bond dissociation free energy of the substrate radical anion $BDFE(\phi_3C{-}S\phi X^{\bullet-})$.

Interestingly, $F\Delta E^o$ is slightly positive for **1a** while it becomes negative for **1b**−**d**. This might be interpreted as if **1a** and possibly **1b** are involved in concerted processes while the stepwise mechanism prevails for **1c** and **1d** with $BDFE(\phi_3C{-}S\phi X^{\bullet-})$ values of −0.10 and −0.26 eV, respectively. Such an interpretation should be viewed together with the fact that the existence of the radical anions of **1c** and **1d**[10] but not **1a** and **1b** was inferred by the redox catalysis approach. The cleavage rate constant of the radical anion of **1c** is estimated to a value of 2×10^9 s^{-1} (see Supporting Information). Still, it cannot be concluded that the radical anions of **1a** and **1b** could not have a fleeting existence, presumably then in the picosecond range, before decaying to $\phi_3C^{\bullet}$ and $X\phi S^-$. Obviously, the activation barrier associated with such a cleavage process would be extremely small. Thus, on combined kinetic and energetic grounds the radical anion and the dissociated products must be closely related in structure meaning that the carbon−sulfur bond in the radical anion is elongated almost to the point of complete bond cleavage. Consequently, for **1a** and **1b** a distinction between the two mechanistic pathways in terms of their respective free energy relationships vanishes.

A profound feature of the $\Delta G^{\ddagger}_o$ values shown in column 5 of Table 1 is their high magnitude that far exceeds the contribution from the solvent reorganization energy.[15] In fact, $\Delta G^{\ddagger}_{o,i}$ constitutes as much as 56−74% of $\Delta G^{\ddagger}_o$ going from **1d** to **1a**, i.e., from electron-withdrawing to electron-donating substituents positioned on the phenyl ring. A similar substituent effect was observed in a recent study on aromatic disulfides.[7b] This substantiates our interpretation of an appreciable bond elongation and weakening of the carbon-sulfur bond in all substrates, including **1c** and **1d**, as a result of the ET process. For **1b** and in particular **1a** the pathway followed is close to or could be the concerted ET mechanism with a complete bond fragmentation. In that instance, $\Delta G^{\ddagger}_o$ should be equal to one quarter of the sum of BDE and solvent reorganization energy according to dissociative ET theory.[6] This value (=0.65 eV)[14,15] is higher by 38% compared with the experimentally determined $\Delta G^{\ddagger}_o$, which suggests that theory overestimates somewhat the intrinsic barrier for a concerted pathway.

In conclusion, the above results point to a gradual transition between the two pathways. Within the series of compounds investigated the inner-reorganization energy associated with the stepwise reduction processes increases until the point of complete bond fragmentation is reached, i.e., the concerted process. As a consequence, the distinction between the two mechanistic pathways in terms of $\Delta G^{\ddagger}_o$ and E^o vanishes close to the borderline. Accordingly, it also seems worthwhile to reconsider ET reactions having high intrinsic barriers and believed to follow a concerted pathway.[1b,2c] In principle, these could be stepwise reactions involving substantial bond weakening in the ET step.

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

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(13) The standard potentials of the thiophenoxyl radicals were obtained as described in ref 7a from the oxidation peak of the corresponding thiophenolate ions measured at low scan rate by linear sweep voltammetry. The following values of $E^{o}_{X\phi S.}$ ensued: 0.00 V (X = OCH_3), 0.15 V (X = H),[7a] 0.39 V (X = $C(O)CH_3$), and 0.42 V vs SCE (X = CN).

(14) The bond dissociation energy, *BDE*, of **1b** in DMF (= 49.2 kcal mol^{-1}) was assumed to be the same as that in gas phase and it was calculated from the relevant enthalpies of formation ΔH_f available in *NIST Structures and Properties Database*, National Institute of Standards and Technology: Gaithersburg, 1994. For triphenylmethyl radical, however, ΔH_f (=93.7 kcal mol^{-1}) was not tabulated and instead it was obtained from the *BDE* of triphenylmethane in dimethyl sulfoxide (=80.8 kcal mol^{-1}; Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229) and the known ΔH_f values of triphenylmethane (=65.0 kcal mol^{-1}) and the hydrogen atom in gas phase (=52.1 kcal mol^{-1}). The corresponding *BDFE* of **1b** in DMF (=43.2 kcal mol^{-1}) was obtained by decreasing *BDE* by 6 kcal mol^{-1}, see ref 3b. These values of *BDE* and *BDFE* were also used for the three other sulfides since the substituent effect is expected to be relatively small.

(15) In a simple approach without taking charge localization effects into account the contribution of solvent reorganization to the intrinsic barrier is estimated to be 0.12 eV for the reactions studied.[1b,7b]