

The Role of Nonbonded Sulfur–Oxygen Interaction in the Dissociative Electron Transfer to Nitro-Substituted Arenesulfonyl Chlorides

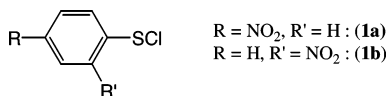
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The sulfur–oxygen nonbonded interaction in organic and bioorganic molecules has attracted considerable attention due to its role in governing important properties such as conformation,¹ spectroscopic behavior,^{1a–d} and chemical and biochemical activity.^{1e–g} Here we report the first example of how such an interaction affects the electron transfer (ET) to nitroarene sulfonyl chlorides. Cyclic voltammetry as well as convolution analysis results shows that not only the ET mechanism is affected but also its thermodynamics and kinetics. Moreover, an interesting example of an ET involving the intermediacy of a σ radical anion is encountered. Theoretical calculations help rationalize the difference in behavior between the two compounds.

In dissociative ET processes,² where a chemical bond is broken as a result of an initial ET, the initial ET and the bond breaking can be simultaneous (concerted) or a succession of two steps (stepwise). In the latter case the ET product is, most often, a delocalized π radical anion. ET processes leading to the formation of radical/anion pairs³ or σ radical anions⁴ have been reported only recently, and the dissociative ET theory² has been successfully extended to describe the dynamics of such phenomena.³



The cyclic voltammogram of 4-nitrobenzenesulfonyl chloride (**1a**) displays a first cathodic peak ($E_p = -0.04$ V vs SCE), corresponding to the irreversible reduction of **1a** (Figure 1a). Its height, measured by reference to the mono-electronic wave of ferrocene, corresponds to the consumption of one electron per molecule. The coefficient transfer values determined from both the first reduction peak width^{5a} and from the E_p -Log(ν) plot^{5b} correspond to 0.34 and 0.35 respectively, i.e., much lower than 0.5 indicating a reaction kinetically controlled by the electron-transfer step.⁴ The second irreversible peak at $E_p = -0.80$ V/SCE and the third reversible peak at $E^0 = -1.43$ V/SCE correspond respectively to the first and second reduction peaks of bis(4-nitrophenyl) disulfide (**2a**) by comparison with an authentic sample.

The cyclic voltammogram of 2-nitrobenzenesulfonyl chloride (**1b**) displays a first mono-electronic irreversible reduction peak at a potential $E_p = -0.46$ V vs SCE (Figure 1b), 420 mV more negative than **1a**. This is an unexpectedly large difference. For comparison, in the benzyl bromides the difference between the reduction potentials of the *p*- and *o*-nitro substrates is only 8 mV.⁶ The first peak width has a value of 92 mV and the slope of the E_p vs $\log(\nu)$ plot is equal to -55 mV per unit $\log(\nu)$. These peak characteristics (Table 1) correspond to a stepwise ET involving the intermediacy of a radical anion and with a mixed kinetic control by both the ET and the bond dissociation steps (Scheme 1).² The first peak is followed by a second irreversible peak ($E_p = -0.96$ V/SCE) and a third reversible peak at $E^0 = -1.74$ V/SCE

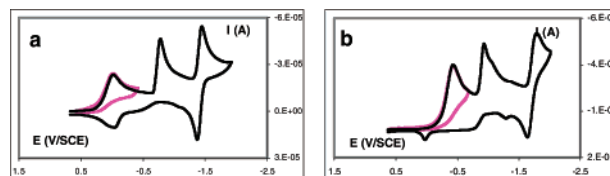
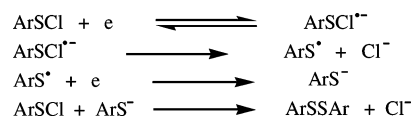


Figure 1. Cyclic Voltammetry in CH₃CN/TBAF (0.1M) at a glassy carbon electrode, $\nu = 0.2$ V/s, of (a) **1a**: 1.9 mM and (b) **1b**: 2 mM.

Table 1. Electrochemical Peak Characteristics for **1a** and **1b**

	E_p (V/SCE)	peak width (mV), α	slope $E_p - \log(\nu)$, α
1a	-0.04	138, 0.34	-84, 0.35
1b	-0.46	92, 0.51	-55, 0.53

Scheme 1



corresponding, respectively, to the first and second reduction peaks of bis(2-dinitrophenyl) disulfide (**2b**), by comparison with an authentic sample. The electrolyses of **1a** and **1b** yield the corresponding disulfides **2a** and **2b** respectively.⁷

A more negative peak potential for **1b** compared to that for **1a** does not suggest a “classical” concerted process for the latter. Further support for this idea comes from the determination of the reduction standard potential of **1a** assuming a “classical” concerted process and hence using eq 1.² The bond dissociation energy ($D_{\text{ArS-Cl}} = 47.65$ kcal/mol), and the entropy correction ($\Delta S^\circ = S_{\text{ArSCl}}^\circ - (S_{\text{ArS}^{\cdot}}^\circ + S_{\text{Cl}^-}^\circ) = -27.31$ cal/mol·K) were calculated.⁸ The standard oxidation potential of chloride ($E_{\text{Cl}^-/\text{Cl}^\cdot}^\circ = 1.86$ V/SCE) was deduced from its value in water.⁹

$$E_{\text{ArS-Cl}/\text{ArS}^{\cdot}+\text{Cl}^-}^0 = E_{\text{Cl}^\cdot/\text{Cl}^-}^0 - D_{\text{ArS-Cl}} + T\Delta S^\circ \quad (1)$$

The $E_{\text{ArCl}/\text{Ar}^{\cdot}+\text{Cl}^-}^0$ is thus estimated to be 0.148 V/SCE, a value only 188 mV more positive than the peak potential. Much larger differences are observed for “classical” concerted processes. The ET mechanism may thus involve the formation of a σ radical anion most likely through a “sticky” dissociative ET process. The following theoretical calculations support this idea.

Figure 2 shows the LUMOs of **1a** and **1b** and the SOMOs of the corresponding radical anions.¹⁰ The S–Cl group participates more in the LUMO in **1a** than in **1b**, hence increasing the probability of injecting the extra electron directly into the σ S–Cl bond, leading to its dissociation. The SOMOs clearly support this idea since the SOMO of **1b**^{•-} is delocalized over the nitro aryl moiety (π radical anion) while that of **1a**^{•-} is more localized on the S–Cl group (σ radical anion). As a result the reduction of **1b** leads to a much more stable radical anion than **1a**. This stabilization

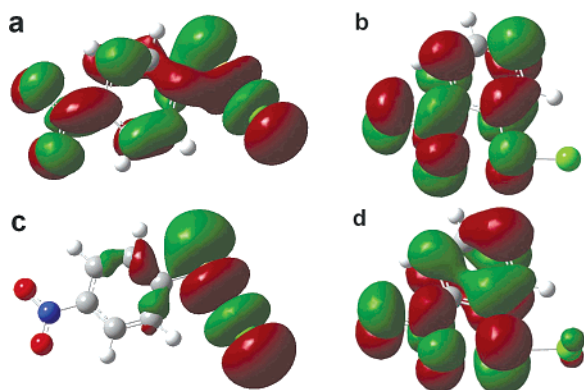


Figure 2. LUMOs of (a) **1a** and (b) **1b** and SOMOs of (c) **1a**^{•-} and (d) **1b**^{•-}.

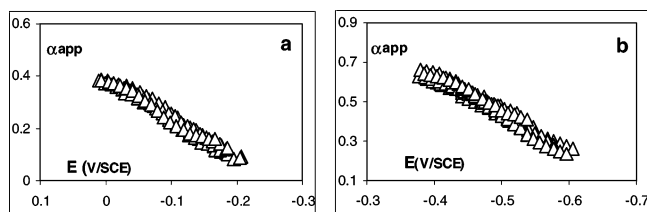


Figure 3. Variation of α_{app} with E for (a) **1a** (1.9 mM) and (b) **1b** (2 mM) at scan rate $\nu = 0.2, 0.3, 0.4, 0.6, 0.8, 1, 2, 3, 4,$ and 8 V/s.

of **1b**^{•-} is due to the through-space oxygen–sulfur interaction which exists also for **1b** but is stronger for the radical anion (**1b**^{•-}). The short S \cdots O distances have been regarded as indicative of an attractive interaction between these two atoms.¹ The distance between the oxygen and the sulfur atoms in **1b** is 2.34 Å, similar to the experimental values.^{1a} This distance decreases to 1.95 Å in **1b**^{•-} which is smaller than the sum of the van der Waals' radii of sulfur and oxygen (3.25 Å). Such a stabilizing interaction for both the neutral molecule and the corresponding radical anion is lacking for **1a**. Other important results reside in the changes of bond lengths and angles upon going from the neutral species to the corresponding radical anion. While both **1b** and **1b**^{•-} are planar, **1a** shows an important rotation (28.52°) of the C–S bond upon going from the nonplanar neutral molecule to the planar radical anion (**1a**^{•-}). The variation of the S–Cl bond length is also larger for **1a** (0.72 Å) than for **1b** (0.32 Å). These results are in agreement with large internal changes in the formation of **1a**^{•-}. The bond dissociation energies for the S–Cl bond for **1a** (47.65 kcal/mol) and **1b** (53.29 kcal/mol) are in agreement with the difference in mechanism since a stronger bond favors a stepwise ET mechanism.²

Convolution analysis,¹¹ at different scan rates, for an irreversible process, was applied to determine the heterogeneous ET rate constant (k_{het}) as a function of the potential.^{4d–f,7b,c} These plots were used to obtain the corresponding $\alpha_{\text{app}} - E$ plots using the relationship $\alpha = -(RT/F)(d \ln k_{\text{het}}/dE)$.^{4d–f,7b,c} Figure 3 shows that the $\alpha_{\text{app}} - E$ plots are linear and can be used to estimate the reduction standard potential ($E^0 = E$ at $\alpha = 0.5$) for **1a** ($E^0 = 0.074$ V/SCE) and **1b** ($E^0 = -0.476$ V/SCE). This large unexpected difference (550 mV) results from the through space S \cdots O interaction in **1b**. The apparent values of k_{het}^0 were also determined from the $\ln k_{\text{het}} - E$ plots.^{4d–f} The deduced values show that the ET is (nearly

3 times) slower for **1a** ($k_{\text{het}}^0 = 2.4 \times 10^{-4}$ cm/s) than for **1b** ($k_{\text{het}}^0 = 6.6 \times 10^{-4}$ cm/s), another consequence of the S \cdots O interaction.

In conclusion the electrochemical reduction of **1a** and **1b** provides a new example of an ET involving the formation of a σ radical anion. The elongation of the S–Cl bond and the rotation of the C–S bond are the most important geometrical changes. Large differences in the reduction standard potential and the ET rate as well as a striking change in the ET mechanism of the S–Cl bond are observed as a function of the position of the nitro group on the aryl ring. This difference in behavior is due to the nonbonded S \cdots O interaction in **1b**. A more expanded series is being synthesized. Quantitative analyses concerning their ET mechanisms, kinetics, and thermodynamics will be reported.

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Supporting Information Available: Electrochemical data and theoretical calculations for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) The BDEs have been calculated as the difference between the total molecular energy of the neutral molecules and that of the radical fragments obtained by homolytic dissociation.
- (9) (a) The $E_{\text{Cl}^+/\text{Cl}^-}^0$ was calculated from the equation $E_{\text{Cl}^+/\text{Cl}^-}^0 = E_{\text{Cl}^+/\text{Cl}^-}^0 - \Delta G_{\text{Cl}^+/\text{H}_2\text{O}-\text{CH}_3\text{CN}}^0$.^{9b} (b) Marcus, Y. *Pure Appl. Chem.* **1985**, *57*, 1103.
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