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Evidence for Orbital Symmetry Restrictions in Intramolecular Dissociative Electron Transfer

William Adcock,[*,†] Claude P. Andrieux,[‡]
Christopher I. Clark,[†] Andreas Neudeck,[‡]
Jean-Michel Savéant,[*,‡] and Caroline Tardy[‡]

Department of Chemistry
The Flinders University of South Australia
Adelaide, Australia 5001
Laboratoire d'Electrochimie Moléculaire de l'Université
Denis Diderot (Paris 7), Unité Associée au CNRS No. 438
2 place Jussieu, 75251 Paris Cedex 05, France

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Besides nuclear reorganization,[1] the influence of orbital overlap factors on the dynamics of outer-sphere electron transfer reactions, including long-range electron transfers, has been actively investigated theoretically and experimentally.[2] This is not the case for dissociative electron transfer whereby a bond is cleaved concertedly with electron transfer. For these reactions, attention has so far been focused on nuclear reorganization factors, particularly on the contribution of the bond dissociation energy to the activation barrier.[3−5] Cleavage of a nucleofugal anion in anion radicals may be viewed as an intramolecular dissociative electron transfer process.[3b,e,f,6] The contribution of nuclear reorganization to their dynamics has therefore been modeled by an extension of the dissociative electron transfer theory.[7] Relationships between reactivity and molecular structure have been rationalized on these bases for anion radical cleavage as well as for the reverse reaction, i.e., coupling of radicals with nucleophiles. These two reactions are the key steps of electron transfer triggered aromatic nucleophilic substitutions ("$S_{RN}1$").[8] For both reactions, the question of symmetry restrictions arises since an electron is transferred from the π^* orbital of the aryl moiety to the σ^* orbital of the breaking bond or vice versa. Such restrictions do not seem to operate since these reactions are fast and their kinetics can be rationalized on the basis of quite large exponential factors.[8] These observations are usually explained by assuming that bending vibrations of the breaking bond would lift the orbital symmetry restriction.[7,8] Thus, so far, no example of orbital symmetry restrictions has been given for dissociative electron transfer reactions.

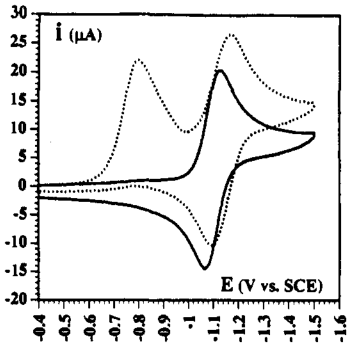
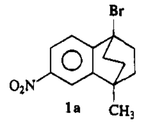
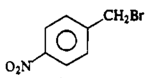


Figure 1. Cyclic voltammetry of 1 mM **1a** (solid line) and of 1 mM **2a** (dotted line) in DMF + 0.1 M n-Bu_4NBF_4 at a 3 mm diameter glassy carbon electrode. Scan rate: 0.1 V/s. Temperature: 20 °C.

We have addressed this question by comparing the cleavage kinetics of the anion radicals of compounds **1a**[9] and **2a**. In the former, the rigid bicyclooctane structure indeed precludes overlap between the π^* orbital where the unpaired electron initially sits and the σ^* orbital of the C−Br bond where it should be transferred concertedly with bond dissociation when Br^- is expelled.



1a



2a

From the cyclic voltammograms of **1a** and **2a** in *N,N'*-dimethylformamide (DMF) at a low scan rate (Figure 1), we observed a considerable decrease of the cleavage rate from **2a** to **1a**.

With **2a**, the first wave is irreversible owing to the rapid decay of the anion radical leading to the 4-nitrobenzyl radical, which immediately undergoes a $e^- + H^+$ reduction to 4-nitrotoluene. The latter species gives rise to a reversible wave at a more

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[†] The Flinders University of South Australia.

[‡] Laboratoire d'Electrochimie Moléculaire de l'Université Denis Diderot.

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(9) (a) Compound **1b**[9b] was obtained from 4-methyl-1,4-ethano-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid[9b] by use of the same methodology as recently described for the preparation of 1-bromo-3-chloroadamantane.[9c] **1b** was nitrated to afford a mixture of the 6- and 7-nitro derivatives. The isomeric mixture was separated by flash column chromatography. 1-Bromo-4-methyl-6-nitro-1,4-ethano-1,2,3,4-tetrahydronaphthalene (**1a**): mp 99−101 °C; ^{13}C NMR ($CDCl_3$) δ 22.61, 34.95, 35.60, 38.88, 63.57, 116.01, 121.81, 125.92, 146.06, 147.33, 148.85. 1-Bromo-4-methyl-7-nitro-1,4-ethano-1,2,3,4-tetrahydronaphthalene: mp 88−90 °C; ^{13}C NMR ($CDCl_3$) δ 22.55, 35.00, 35.47, 38.67, 63.19, 120.05, 121.74, 122.61, 143.37, 146.68, 151.86. The assigned structures were clearly in accord with the ^{13}C NMR spectral data[9b,d] as well as the mass spectral information. (b) Adcock, W.; Abeywickrema, A. N. *J. Org. Chem.* **1982**, *47*, 779. (c) Adcock, W.; Clark, C. I. *J. Org. Chem.* **1993**, *58*, 7341. (d) Adcock, W.; Abeywickrema, A. N. *Aust. J. Chem.* **1981**, *34*, 1253.

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negative potential.[4c] With **1a**, the first wave is perfectly reversible, even at a scan rate as low as 0.1 V/s, and no wave corresponding to a cleavage product is seen at more negative potentials.

As discussed earlier,[4c] the rate of cleavage of **2a** anion radical, $RX^{\bullet-} \rightarrow R^{\bullet} + X^-$, is too high to be measured even using micrometric electrodes and scan rates as high as 100 000 V/s, indicating that its value is larger than $4 \times 10^7\ s^{-1}$.[10] In contrast, the cleavage rate constant of **1a**$^{\bullet-}$ is too low to be measured by cyclic voltammetry, indicating that its value is smaller than 0.1 s^{-1}.[7] In order to get a more precise estimate of the cleavage rate of **1a**$^{\bullet-}$ we resorted to spectroelectrochemistry. **1a**$^{\bullet-}$ was generated electrochemically in a spectrophotometric capillary slit cell at a honeycombed microstructured gold-LIGA plate electrode in which complete electrolysis could be achieved in less than 2 s.[8] From the observed first-order homogeneous decay a rate constant of $k_{\mathbf{1a}^{\bullet-}}^{\text{cleavage}} = 9.3 \times 10^{-3}\ s^{-1}$ was obtained. To estimate the cleavage rate of **2a**$^{\bullet-}$, we may combine two previous observations.[4c] One is that the characteristics of low scan rate cyclic voltammetry of **2a** indicate that its reduction at $v = 0.1$ V/s takes place at a peak potential of -0.79_2 V vs SCE, under mixed kinetic control by the initial electron transfer step generating the anion radical and the following cleavage step. The other is that cyclic voltammetry at a micrometric electrode has allowed the determination of the standard potential of the $RX/RX^{\bullet-}$ couple as -1.14_0 V vs SCE (and a cleavage rate constant of $4 \times 10^6\ s^{-1}$) for 4-nitrobenzyl chloride. From the application of the equation,

$$E_p = E^{\circ}_{RX/RX^{\bullet-}} - 0.78\frac{RT}{F} + \frac{RT}{2F}\ln\left(\frac{RT\,k^{\text{cleavage}}_{RX^{\bullet-}}}{V}\right)$$

that relates the peak potential to the follow-up rate constant in the case of a fast initial electron transfer step,[12] we can estimate that $k_{\mathbf{2a}^{\bullet-}}^{\text{cleavage}} \geq 7.9 \times 10^8\ s^{-1}$. There are two reasons to believe that this value can be regarded as a lower limit. One is that the standard potential of the **2a/2a**$^{\bullet-}$ couple should be, in terms of an inductive effect, somewhat more negative than that of 4-nitrobenzyl chloride. The other is that the positive shift of the peak potential of **2a** is somewhat less than predicted by the above equation owing to the interference of the electron transfer kinetics in the kinetic control of the overall process. On total we can conclude that $\log (k_{\mathbf{2a}^{\bullet-}}^{\text{cleavage}}/k_{\mathbf{1a}^{\bullet-}}^{\text{cleavage}}) \geq 12$.

What is the cause (or what are the causes) of this huge difference in reactivity? A large part of it pertains to nuclear reorganization insofar as the bridgehead unconjugated sp^3 radical formed upon cleavage of **1a**$^{\bullet-}$ is certainly less stable than the conjugated 4-nitrobenzyl radical. The same factor has been shown to be responsible for the fact that bridgehead halides in the adamantane, bicyclooctane, and bicyclopentane series have reduction potentials significantly more negative than analogous halides giving rise to sp^2 radicals in dissociative electron transfer reactions where the activation energy is mostly governed by the magnitude of the homolytic bond dissociation energy.[4f] In more quantitative terms, the activation free energy for anion radical cleavage may be obtained through the following equations:[4]

$$\Delta G^{\ddagger}_{RX^{\bullet-}\rightarrow R^{\bullet}+X^-} = \Delta G^{\ddagger\circ}_{RX^{\bullet-}\rightarrow R^{\bullet}+X^-}\left(1 + \frac{\Delta G^{\circ}_{RX^{\bullet-}\rightarrow R^{\bullet}+X^-}}{4\Delta G^{\ddagger\circ}_{RX^{\bullet-}\rightarrow R^{\bullet}+X^-}}\right)^2 \approx \Delta G^{\ddagger\circ}_{RX^{\bullet-}\rightarrow R^{\bullet}+X^-} + \frac{\Delta G^{\circ}_{RX^{\bullet-}\rightarrow R^{\bullet}+X^-}}{2} \quad (1)$$

where the standard free energy of the reaction, $\Delta G^{\circ}_{RX-R^{\bullet}+X^-}$, is expressed as

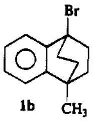
$$\Delta G^{\circ}_{RX^{\bullet-}\rightarrow R^{\bullet}+X^-} = D_{RX\rightarrow R^{\bullet}+X^{\bullet}} + E^{\circ}_{RX/RX^{\bullet-}} - T\Delta S \quad (2)$$

(D is the homolytic dissociation energy of the R−X bond, the E°s are the standard potentials of the subscript couples, and TΔS is an entropic term) and the intrinsic barrier free energy can be expressed as

$$\Delta G^{\ddagger\circ}_{RX^{\bullet-}\rightarrow R^{\bullet}+X^-} = \frac{D_{RX\rightarrow R^{\bullet}+X^{\bullet}} + E^{\circ}_{RX/R^{\bullet-}} - E^{\circ}_{R^{\bullet}/(R^{\bullet})^{\bullet-}} - T\Delta S^{\ddagger}}{4} \quad (3)$$

(where $(R^{\bullet})^{\bullet-}$ derives from $R^{\bullet}$ by injection of one electron into its π^* orbital).

An estimation of the difference in bond dissociation energy between **1a** and **2a** can be obtained from the difference in peak potential for the reduction of **1b**[9] and **2b**, −2.60 and −1.71 V vs SCE at 0.1 V/s, respectively. In the electrochemical reduction of these two compounds, electron transfer and bond breaking are concerted and therefore[3e,f,4d] the difference between their bond dissociation energies can be obtained from $\Delta\Delta D_{RX^{\bullet-}\rightarrow R^{\bullet}+X^-} = 2/3\Delta\Delta E_p$ at the same scan rate. Thus, $D_{\mathbf{1a}} - D_{\mathbf{2a}} \approx D_{\mathbf{1b}} - D_{\mathbf{2b}} = 0.59_3$ eV. Taking also into account the slight difference in the values of $E^{\circ}_{RX/RX^{\bullet-}}$ (−1.023 and −1.140 V vs SCE for **1a** and **2a**, respectively), the difference in the reaction free energies is $\Delta G^{\circ}_{\mathbf{1a}} - \Delta G^{\circ}_{\mathbf{2a}} = 0.71_0$ eV (2). As to the difference in intrinsic barrier free energies (3), the potential $E^{\circ}_{R^{\bullet}/(R^{\bullet})^{\bullet-}}$ is expected to be more positive for **1a** than for **2a** because the unconjugated radical deriving from the cleavage of **1a**$^{\bullet-}$ is less stable than the conjugated 4-nitrobenzyl radical deriving from **2a**$^{\bullet-}$. The variation of this term should overcompensate the variation of $E^{\circ}_{RX/RX^{\bullet-}}$. A lower limit of the difference in intrinsic barrier free energies is therefore obtained if we only take the variation in bond dissociation energy into account: $\Delta G^{\ddagger\circ}_{\mathbf{1a}} - \Delta G^{\ddagger\circ}_{\mathbf{2a}} \leq (D_{\mathbf{1a}} - D_{\mathbf{2a}})/4 = 0.148$ eV. Using eq 1 we can conclude that the contribution of the activation free energies alone to the variation in cleavage rate constants ($\Delta G^{\ddagger}_{\mathbf{1a}} - \Delta G^{\ddagger}_{\mathbf{2a}} \leq 0.503$ eV) would imply that $\log (k_{\mathbf{2a}^{\bullet-}}^{\text{cleavage}}/k_{\mathbf{1a}^{\bullet-}}^{\text{cleavage}}) \leq 8.6$, to be compared with an experimental variation larger than 12.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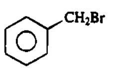
2b

This difference in reactivity is already a consequence of orbital symmetry restrictions since a substantial part of it arises from the lack of exchange between the π orbital in the benzene ring and the sp^3 orbital containing the unpaired electron in the cleaved radical. There is, however, an additional effect of orbital symmetry restriction present in the electronic factor of the reaction. The difference between the above estimation and the experimental data can indeed be ascribed to the lack of exchange between the benzene ring π^* orbital, where the unpaired electron is initially located, and the σ^* orbital of the C−Br bond where it is transferred upon cleavage. This effect would thus be responsible for at least 3$^1/_2$ orders of magnitude in the decrease of the cleavage rate constant. It involves a change both in the pre-exponential factor and in the resonance energy at the transition state.[13]

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(13) If Δ log $k = 3.5$, it can be estimated[2a−d] that the former and the latter factors participate equally to a resonance energy of 5 kcal/mol **2a**$^{\bullet-}$, while with 1 kcal/mol, the former factor is predominant.