

Can Single-Electron Transfer Break an Aromatic Carbon–Heteroatom Bond in One Step? A Novel Example of Transition between Stepwise and Concerted Mechanisms in the Reduction of Aromatic Iodides

Laurence Pause, Marc Robert, and Jean-Michel Savéant*

Laboratoire d'Electrochimie Moléculaire
Unité Mixte de Recherche Université - CNRS No 7591
Université de Paris 7 - Denis Diderot
2 Place Jussieu, 75251 Paris Cedex 05, France

Received April 27, 1999

Single-electron transfer is often accompanied by bond cleavage or bond formation reactions converting initially formed ion radicals into radicals. Electron transfer and bond breaking may involve a transient ion radical intermediate or occur in a concerted manner, as sketched in Figure 1.¹

The question of the distinction between these two mechanisms and of the nature of the molecular factors that favor one mechanism over the other arises for thermal (electrochemical, homogeneous)² as well as for photoinduced^{3,4} reactions.⁵ With aliphatic molecules, injection of an electron leads to a purely dissociative state, and accordingly, reductive cleavage follows a concerted mechanism. With molecules containing low lying orbitals, such as π^* orbitals, able to host temporarily the incoming electron, reductive cleavage may follow one or the other of the two mechanisms. When the cleavage of the anion radical is fast, the rate-determining step of the stepwise pathway is the initial electron transfer. Under these conditions, the thermodynamic factor governing the competition between the two mechanisms is the standard free energy of anion radical cleavage, ΔG_C^0 (eq 1)

$$\Delta G_C^0 = \text{BDFE} + E^0_{\text{RX/RX}^-} - E^0_{\text{X}^{\cdot-}/\text{X}^-} \quad (1)$$

(BDFE: R–X bond dissociation free energy, E^0 s: standard potentials of the subscript couples). The influence of these three parameters on the mechanism has been illustrated by several experimental examples.^{1d,2,6}

There are also a few borderline cases where, as shown in Figure 1, for the same cleaving acceptor molecule, a transition between concerted and stepwise mechanisms has been observed upon

(1) (a) Andrieux, C. P.; Savéant, J.-M. *J. Electroanal. Chem.* **1986**, *205*, 43. (b) Andrieux, C. P.; Gallardo, I.; Savéant, J.-M. *J. Electroanal. Chem.* **1986**, *205*, 43. (c) Severin, M. G.; Farnia, G.; Vianello, E.; Arévalo, M. C. *J. Electroanal. Chem.* **1988**, *251*, 369. (d) Savéant, J.-M. Single Electron Transfer and S_N2 Substitution. In *Advances in Physical Organic Chemistry*; Bethel, D., Ed.; Academic Press: London, 1990; Vol. 26, pp 1–130.

(2) (a) Savéant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455. (b) Savéant, J.-M. Dissociative Electron Transfer in *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: New York, 1994; Vol. 4, pp 53–116.

(3) (a) Saeva, F. D. *Top. Curr. Chem.* **1990**, *156*, 61. (b) Saeva, F. D. Intramolecular Photochemical Electron Transfer (PET)-Induced Bond Cleavage Reactions in some Sulfonium Salts Derivatives. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: New York, 1994; Vol. 4, pp 1–25. (c) Gaillard, E. R.; Whitten, D. G. *Acc. Chem. Res.* **1996**, *29*, 292.

(4) (a) Arnold, B. R.; Scaiano, J. C.; McGimpsey, W. G. *J. Am. Chem. Soc.* **1992**, *114*, 9978. (b) Chen, L.; Farahat, M. S.; Gaillard, E. R.; Gan, H.; Farid, S.; Whitten, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 6398. (c) Chen, L.; Farahat, M. S.; Gaillard, E. R.; Farid, S.; Whitten, D. G. *J. Photochem. Photobiol. A: Chem.* **1996**, *95*, 21. (d) Wang, X.; Saeva, F. D.; Kampmeier, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 4364. (e) Robert, M.; Savéant, J.-M., submitted for publication.

(5) (a) The question of concerted vs stepwise mechanisms is an important problem in the theory of chemical reactivity in general.^{5b} Electron-transfer/bond-breaking reactions offer a unique opportunity of investigating the subtleties in details. (b) Williams, A. *Chem. Soc. Rev.* **1994**, *23*, 93.

(6) (a) Andrieux, C. P.; Le Gorande, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892. (b) Andrieux, C. P.; Differding, E.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1993**, *115*, 6592. (c) Andrieux, C. P.; Robert, M.; Saeva, F. D.; Savéant, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 7864. (d) Andrieux, C. P.; Tallec, A.; Tardivel, R.; Savéant, J.-M.; Tardy, C. *J. Am. Chem. Soc.* **1997**, *119*, 2420.

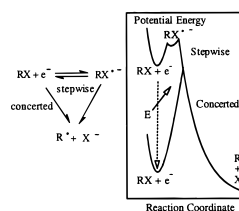


Figure 1. Stepwise and concerted reductive cleavage mechanisms. Transition as a function of the driving force provided by the electrode potential or by the standard potential of an homogeneous donor.

increasing the driving force of the reaction by decreasing the electrode potential or the standard potential of the donor in electrochemical^{6c,7} and homogeneous examples,^{1c,8} respectively. The observation of such mechanism transitions demonstrates that the occurrence of a concerted mechanism is related not merely to the fact that the intermediate does not exist, but rather to the energetic advantage of one pathway over the other. It also allows a clear-cut experimental distinction between the two mechanisms in situations where the kinetics of the stepwise process is controlled by the initial electron-transfer pathway and is therefore not easy to distinguish from the concerted mechanism. In cyclic voltammetry,⁹ when the wave remains irreversible whatever the scan rate, mechanism diagnosis is based on the value of an apparent transfer coefficient, α that may be derived from the variation of the peak potential, E_p , with the scan rate, ν , or from the value of the peak width, $E_{p/2} - E_p$,

$$\alpha = -(RT/2F)/(\partial E_p/\partial \ln \nu) = (1.86RT/F)/(E_{p/2} - E_p)$$

When the value of α reaches 0.5 or less, the rate-determining step is an electron-transfer step and α is then a true transfer coefficient (symmetry factor). The rate-determining electron-transfer step may then be either the initial electron transfer of the stepwise pathway or the dissociative electron transfer of the concerted pathway. In both cases, the activation free energy is expected to be a quadratic function of the standard free energy of the reaction and thus α varies linearly with the latter parameter.¹⁰

$$\Delta G^\ddagger = \Delta G_0^\ddagger \left(1 + \frac{\Delta G^0}{4\Delta G_0^\ddagger} \right)^2, \quad \alpha = \frac{1}{2} \left(1 + \frac{\Delta G^0}{4\Delta G_0^\ddagger} \right)$$

with $\Delta G^0 = E - E^0$ (E : electrode potential, E^0 : standard potential of the outersphere and dissociative electron transfers respectively) and $4\Delta G_0^\ddagger = \lambda_0 + \lambda_i$ or $\lambda_0 + D$, respectively (λ_0 : solvent reorganization energy, λ_i : intramolecular reorganization energy, D : R–X bond dissociation energy). D is usually larger than λ_i , resulting in a smaller value of α in the concerted case, but ambiguous situations may nevertheless be met. In such cases, the observation of a transition between stepwise and concerted pathways as the reductive cleavage driving force increases allows an unambiguous distinction between the two.

(7) (a) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1997**, *119*, 12595. (b) Andrieux, C. P.; Savéant, J.-M.; Tardy, C. *J. Am. Chem. Soc.* **1997**, *119*, 11546.

(8) Costentin, C.; Hapiot, P.; Médebielle, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1999**, *121*, 4451.

(9) (a) Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1973**, *48*, 113. (b) Andrieux, C. P.; Savéant, J.-M. In *Electrochemical Reactions in Investigation of Rates and Mechanisms of Reactions, Techniques of Chemistry*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. VI/4E, Part 2, pp 305–390. (c) Andrieux, C. P.; Hapiot, P.; Savéant, J.-M. *Chem. Rev.* **1990**, *90*, 723.

(10) (a) For outersphere electron transfers, see refs 10b and c and for dissociative electron transfers, refs 10d–f. (b) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 4966. (c) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 962. (d) Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788. (e) Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 10595. (f) Andrieux, C. P.; Savéant, J.-M.; Tardy, C.; Savéant, J.-M. *J. Am. Chem. Soc.* **1998**, *120*, 4167.

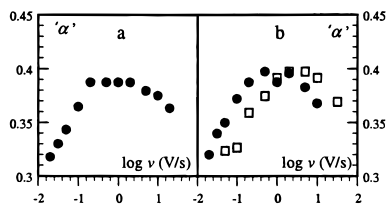


Figure 2. Cyclic voltammetry of iodobenzene (1.35 mM) in acetonitrile (a) and DMF (b) + 0.1 M *n*-Bu₄BF₄. Variation of the apparent transfer coefficient, with the scan rate. Temperature: 294 (●) and 329 (□) K.

Reductive cleavage of bonds involving an aromatic carbon are usually considered to follow a stepwise mechanism (see eq 1) owing to relatively large bond dissociation energies and to the presence of a π^* orbital able to accommodate the incoming electron ($E_{\text{RX/RX}^-}^0$ is not very negative). A large number of aromatic chlorides and bromides, including chloro and bromobenzene, have indeed been shown to follow a stepwise reductive cleavage in electrochemical and homogeneous reactions, and no examples have been provided so far of a one-step reductive cleavage of bonds involving an aromatic carbon.¹¹ We have found that the reductive cleavage of aromatic iodides may follow such a concerted mechanism at low driving forces.

The cyclic voltammetry of iodobenzene exhibits a wave that remains irreversible in the scan rate domain we have explored both in acetonitrile and in *N,N*-dimethylformamide (DMF).¹² In both solvents, at 21 °C, the apparent transfer coefficient, α , derived from the peak-width (Figure 2), begins to increase with the scan rate and passes through a maximum before decreasing in the rest of the range of explored scan rates. These variations are typical of the passage from a concerted mechanism, at the lower end of the scan rate domain, to a stepwise mechanism, at its upper end, upon increasing the driving force as schematically depicted in Figure 1 (see similar behaviors in refs 6c and 7a). Over this range of scan rates, the variation of the driving force, measured by the location of the peak potential, is ca. 200 mV on total.¹³

At a higher temperature, 56 °C, the same type of variation of α are observed (Figure 2b), confirming the existence of a transition between the two mechanisms. We also note that the increase of temperature shifts the $\alpha - \log \nu$ profile toward higher scan rates, thus giving more room to the concerted mechanism. This effect of temperature provides a further confirmation of the existence of a transition between the two mechanisms, since, as

(11) (a) For reviews, see refs 1d, 2. For the specific case of chloro and bromobenzene see ref 11b. (b) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; M'Halla, F.; Savéant, J.-M. *J. Am. Chem. Soc.* **1980**, *102*, 3806.

(12) (a) Two glassy carbon disks were used as working electrodes, one with a 3-mm diameter and the other with a 1-mm diameter from 0.02 to 1 V/s and from 1 to 50 V/s, respectively. They were carefully polished (1-mm diamond paste) and ultrasonically rinsed in pure ethanol after each cyclic voltammetric run. The instrument was a home-built potentiostat equipped with a positive feedback compensation.^{12b} Each peak width determination was repeated 3 to 6 times. The error on the averaged value is $\pm 2-3$ mV. (b) Garreau, D.; Savéant, J.-M. *J. Electroanal. Chem.* **1972**, *35*, 309. (c) The electron stoichiometry is 2 as found by comparison of the peak with the reversible peak of anthracene and expected from the fact that the phenyl radical is quite easy to reduce, easier than iodobenzene.

(13) In both the outersphere and the dissociative cases, increasing the scan rate shifts the potential toward more negative values, thus offering a larger driving force to the reductive cleavage reaction.

(14) (a) Subtracting $T\Delta S \approx 0.3$ eV from the BDE.^{14c} (b) The $E_{\text{RX/RX}^-}^0$ s for Br and Cl are from ref 11b. The difference between the effects of Br and I is likely to be smaller than the difference between the effects of Cl and Br. A 200 mV shift instead of 300 mV seems a reasonable approximation. The $E_{\text{X}^{\cdot-}/\text{X}^-}$ s are from ref 14d and references therein. (c) *Handbook of Chemistry and Physics*, 72nd ed.; CRC: Cleveland, OH, 1991-1992; p 9-121. (d) Savéant, J.-M. *J. Phys. Chem.* **1994**, *98*, 3716.

(15) With a preexponential factor of 4×10^3 cm² s⁻¹ and a diffusion coefficient of 10^{-5} cm² s⁻¹ $\Delta G^\ddagger = 0.433$ eV.^{7b,10d,f} Application of eq 4 with $4\Delta G_{\text{C}}^\ddagger = \lambda_0 + D$ leads to $E^\ddagger = -0.541$ V vs SCE, $D + \lambda_0 = 4.22$ eV and therefore to $\lambda_0 = 1.4$ eV, i.e., an equivalent reactant radius for solvent reorganization of 2.2 Å, a quite reasonable value since it is practically equal to the ionic radius of I⁻.^{15b} (b) *Handbook of Chemistry and Physics*, 72nd ed.; CRC: Cleveland, OH, 1991-1992; p 12-8.

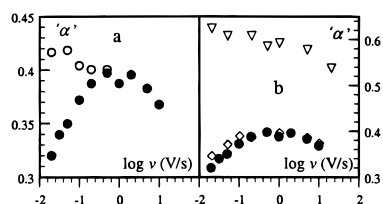


Figure 3. Cyclic voltammetry of 1.35 mM iodo-benzene (●), 1 mM bromobenzene (○), 3-methyl-iodobenzene (◇), 1-iodonaphthalene (▽) in DMF + 0.1 M *n*-Bu₄BF₄. Variation of the apparent transfer coefficient, with the scan rate. Temperature: 294 K.

Table 1.

X	BDFE ^a	$E_{\text{RX/RX}^-}^0$ ^b	$E_{\text{X}^{\cdot-}/\text{X}^-}$ ^b	ΔG_{C}^0 ^a
I	2.52	-2.24	0.99	-0.71
Br	3.21	-2.44	1.48	-0.71
Cl	3.86	-2.78	1.85	-0.77

^a In eV. ^b In V vs SCE.

detailed elsewhere,^{7b} an increase in temperature is equivalent to a decrease of the scan rate and hence of the driving force, thus favoring the concerted pathway over the stepwise pathway.

Comparing iodobenzene with bromobenzene (Figure 3a) clearly shows that the later undergoes a stepwise reductive cleavage with, unlike the former, no trace of mechanism transition at the lower end of the scan rate domain, in line with the mechanism previously found for its homogeneous reductive cleavage by a series of aromatic anion radicals.^{11b}

Why is the concerted mechanism more favorable with iodobenzene than with bromo and chlorobenzene? Using eq 1, we can see from the following approximate figures¹⁴ that, because of mutual compensation of the three terms, thermodynamics does not favor clearly the possibility of a concerted mechanism in the case of iodobenzene (Table 1). However, in terms of intrinsic barrier, the concerted cleavage is favored for iodobenzene as compared to bromobenzene by ca. 0.17 eV ($\Delta D/4$), i.e., a factor of 10^3 in terms of rate constants, whereas the rate of the outersphere initial electron transfer of the stepwise pathway is not expected to vary much from I to Br.

As seen in Figure 3b, the reductive cleavage of another aromatic iodide, namely 3-methyl-iodobenzene, also shows a transition between stepwise and concerted mechanisms at scan rates closely similar to values observed with iodobenzene. In contrast, 1-iodonaphthalene undergoes a stepwise reductive cleavage, with mixed kinetic control by electron transfer and follow-up bond breaking, whatever the scan rate. The later observation may be explained as follows. While the BDFE is about the same in both cases, the energy of the π^* orbital is expected to be lower in the first case than in the second in line with the difference of peak potentials, -2.08 vs. -2.30 (V vs SCE), at a scan rate, 10V/s, where both molecules undergo a stepwise reductive cleavage.

As seen earlier, at 56 °C and at a scan rate of 0.1 V/s the reductive cleavage of PhI follows a concerted mechanism. The values of the peak potential, -2.14 V vs SCE, and $\alpha = 0.32$ are in good agreement with the predictions of the dissociative electron transfer theory.^{10d,f,15}

In conclusion, the reductive cleavage of iodobenzene and 3-methyl iodobenzene provides two novel examples of a transition between concerted and stepwise mechanisms upon increasing the driving force of the reaction. Evidence is thus provided that bonds involving an aromatic carbon may be cleaved in one step by single-electron transfer at low enough driving forces. Other examples, not necessarily restricted to electrochemical reactions, that may appear in the future concern other leaving groups with weak cleaving bonds (e.g., oniums) or cleavages assisted by strong ion-pairing of the leaving anions.