

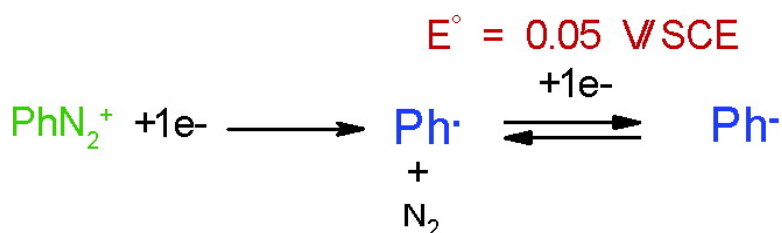
Article

The Standard Redox Potential of the Phenyl Radical/Anion Couple

Claude P. Andrieux, and Jean Pinson

J. Am. Chem. Soc., **2003**, 125 (48), 14801-14806 • DOI: 10.1021/ja0374574 • Publication Date (Web): 11 November 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 14 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

The Standard Redox Potential of the Phenyl Radical/Anion Couple

Claude P. Andrieux* and Jean Pinson*

Contribution from the Laboratoire d'Electrochimie Moléculaire, Université Paris 7-Denis Diderot, Unité Mixte Université Paris 7-CNRS 7591, 2 Place Jussieu, 75251, Paris Cedex 05, France

Received July 22, 2003; E-mail: andrieux@paris7.jussieu.fr; jean.pinson@laposte.net

Abstract: The voltammogram of aryl diazonium tetrafluoroborates in acetonitrile (ACN), at low concentration, shows a first one-electron wave followed at a more negative potential by a small second wave; this last one corresponds to the reduction of the radical formed at the level of the first wave. Simulation of the voltammogram permits one to determine the standard redox potential of the radical/anion couple $E^\circ(\text{Ph}^\bullet/\text{Ph}^-) = 0.05 \text{ V/SCE}$ and the reduction mechanism of the diazonium cation. An electron transfer concerted with the cleavage of the C–N bond furnishes the aryl radical; this radical undergoes two competitive reactions: reduction at the electrode and H-atom transfer.

Introduction

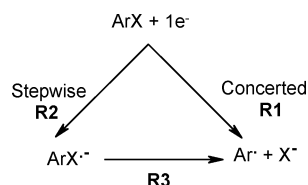
An ever increasing number of reactions involve radicals as intermediates. This development of radical chemistry has included the synthetic aspects of organic chemistry,¹ the polymerization reactions,² and also a new reaction: the modification of conductive surfaces through the electrografting of organic groups.^{4,5} It is therefore of importance to be able to characterize the physicochemical properties of these species. Among the many types of radicals which have been produced, investigated, and reacted, aryl radicals are interesting intermediates. They can be used in $\text{S}_{\text{RN}}1$ aromatic nucleophilic substitution by reaction with a nucleophile,^{6–8} they can add to double bonds,⁹ giving rise to intramolecular cyclization reactions and^{10–13} leading to the elegant synthesis of natural compounds such as

cephalotoxinone¹⁴ and aspidospermidine,¹⁵ and they also lead to the modification of conductive surfaces: carbon,¹⁶ metals,¹⁷ or semiconductors.¹⁸ Aryl radicals can be prepared through different means: (i) chemical reduction of an aryl halide with NaBH_4 ,¹⁹ with alkali metals in liquid ammonia,⁶ with Fe^{2+} , SmI_2 , or sodium amalgam,⁶ but also through the radical-polar crossover reaction²⁰ which involves a one-electron reduction of diazonium salt by an easily oxidized sulfide such as tetrathiafulvalene; (ii) photochemistry;²¹ and (iii) electrochem-

- (1) *Radicals in Organic Synthesis*; Renaud, P., Sibi, M., Eds.; Wiley-VCH: Weinheim, 2001.
- (2) Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *2*, 208.
- (3) Georges, M. Living-Radical Polymerization, an Overview. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M., Eds.; Wiley-VCH: Weinheim, 2001.
- (4) Downard, A. J.; Roddick, A. D. *Electroanalysis* **1995**, *7*, 376.
- (5) Maeda, H.; Yamauchi, Y.; Ohmori, H. *Curr. Top. Anal. Chem.* **2001**, *2*, 121.
- (6) (a) Rossi, R. A.; Pierini, A. B.; Peñenory, A. B. *Chem. Rev.* **2003**, *103*, 71. (b) Santiago, A. N.; Martin, S. E.; Rossi, R. A. *Trends Org. Chem.* **2001**, *9*, 1.
- (7) Simonet, J.; Pilard, J.-F. Electrogenenerated Reagents. In *Organic Electrochemistry*; Lund, H., Hammerich, O., Eds.; Marcel Dekker: New York, 2003; p 1163.
- (8) Costentin, C.; Hapiot, P.; Médebielle, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 5623 and references therein.
- (9) Chami, Z.; Gareil, M.; Pinson, J.; Savéant, J.-M.; Thiébaud, A. *J. Org. Chem.* **1991**, *56*, 586.
- (10) *Radicals in Organic Synthesis*; Renaud, P., Sibi, M., Eds.; Wiley-VCH: Weinheim, 2001; p 151.
- (11) Bowman, W. R.; Fletcher, A. J.; Potts, G. B. S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2747.
- (12) (a) Elofson, R. M.; Eldsberg, R. L.; Mecherly, P. A. *J. Electrochem. Soc.* **1950**, *97*, 166. (b) Elofson, R. M.; Gadallah, F. F. *J. Org. Chem.* **1969**, *34*, 854. (c) Gadallah, F. F.; Elofson, R. M. *J. Org. Chem.* **1969**, *34*, 333. (d) Elofson, R. M.; Gadallah, F. F.; Schulz, K. F. *J. Org. Chem.* **1971**, *36*, 152. (e) Elofson, R. M.; Gadallah, F. F. *J. Org. Chem.* **1971**, *36*, 1769. (f) Elofson, R. M.; Cantu, A. A.; Gadallah, F. F. *J. Org. Chem.* **1973**, *38*, 2386.

- (13) (a) Dias, M.; Gibson, M.; Grimshaw, J.; Hill, I.; Trocha-Grimshaw, J.; Hammerich, O. *Acta Chem. Scand.* **1998**, *52*, 549. (b) Donnelly, S.; Grimshaw, J.; Trocha-Grimshaw, J. *Electrochim. Acta* **1996**, *41*, 489. (c) Donnelly, S.; Grimshaw, J.; Trocha-Grimshaw, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2171.
- (14) (a) Semmelhack, M. F.; Chong, B. P.; Stauffer, R. D.; Rogerson, T. D.; Chong, A.; Jones, L. D. *J. Am. Chem. Soc.* **1975**, *97*, 2507. (b) Semmelhack, M. F.; Bargar, T. M.; Spencer, T. O. *J. Org. Chem.* **1977**, *42*, 1481.
- (15) (a) Callaghan, O.; Lampard, C.; Kennedy, A. R.; Murphy, J. A. *Tetrahedron Lett.* **1999**, *40*, 164. (b) Callaghan, O.; Lampard, C.; Kennedy, A. R.; Murphy, J. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 995.
- (16) (a) Delamar, M.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 5883. (b) Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1997**, *119*, 201. (c) Bourdillon, C.; Delamar, M.; Demaille, C.; Hitmi, R.; Moiroux, J.; Pinson, J. *J. Electroanal. Chem.* **1992**, *336*, 113. (d) Delamar, M.; Désarmot, G.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *Carbon* **1997**, *35*, 801. (e) Coulon, E.; Pinson, J.; Bourzat, J.-D.; Commerçon, A.; Pulicani, J.-P. *Langmuir* **2001**, *17*, 7102. (f) Coulon, E.; Pinson, J.; Bourzat, J.-D.; Commerçon, A.; Pulicani, J. P. *J. Org. Chem.* **2002**, *67*, 8513. (g) Boukerma, K.; Chehimi, M. M.; Pinson, J.; Blomfield, C. *Langmuir* **2003**, *19*, 6333.
- (17) (a) Adenier, A.; Bernard, M. C.; Chehimi, M. M.; Deliry, E.; Desbat, B.; Fagebaume, O.; Pinson, J.; Podvorica, F. *J. Am. Chem. Soc.* **2001**, *123*, 4541. (b) Chaussé, A.; Chehimi, M. M.; Karsi, N.; Pinson, J.; Podvorica, F.; Vautrin-UI, C. *Chem. Mater.* **2002**, *14*, 392. (c) Adenier, A.; Cabet-Deliry, E.; Lalot, T.; Pinson, J.; Podvorica, F. *Chem. Mater.* **2002**, *14*, 4576.
- (18) (a) Henry de Villeneuve, C.; Pinson, J.; Bernard, M. C.; Allongue, P. *J. Phys. Chem. B* **1997**, *101*, 2415. (b) Allongue, P.; Henry de Villeneuve, C.; Pinson, J.; Chazalviel, J. N.; Wallart, X. *Electrochim. Acta* **1998**, *43*, 5791. (c) Allongue, P.; Henry de Villeneuve, C.; Pinson, J. *Electrochim. Acta* **2000**, *45*, 3241.
- (19) Lesage, M.; Chatgililoglu, N.; Griller, D. *Tetrahedron Lett.* **1989**, *30*, 2733.
- (20) Murphy, J. A. The Radical-Polar Crossover Reaction. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M., Eds.; Wiley-VCH: Weinheim, 2001.
- (21) (a) Albini, A.; Sulpizio, A. Aromatics. In *Photoinduced Electron Transfer*; Fox, M. A.; Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Vol. C, p 88. (b) Albini, A.; Fasani, E.; Mella, M. *Top. Curr. Chem.* **1993**, *168*, 143.

Scheme 1



istry,²² a very convenient mean of generating aryl radicals through a one-electron reduction of an aryl derivative (halide, sulfide, ether, etc.), as shown in Scheme 1.

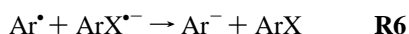
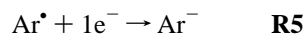
The electron transfer can be concerted (reaction **R1**), in which case the radical is obtained directly²³ or stepwise (reaction **R2** + **R3**); that is, the reaction path goes through the cleavage of a radical anion. With aryl halides, sulfides, and ethers, the electrochemical cleavage is most often stepwise, but iodobenzene cleaves concertedly at low scan rates, that is, at a small driving force, to a phenyl radical and iodine ion.²⁴ The radical anions of aromatic derivatives are usually very unstable (with some exceptions, for example, in the benzophenone and nitrobenzene series where the radical anions are stable for fractions of seconds). For some of them, the rate of cleavage can be observed by cyclic voltammetry at high scan rates ($k = 1.7 \times 10^4 \text{ s}^{-1}$ for 2-chloroquinoline²⁵). When the cleavage is too fast to permit the observation of the radical anion by cyclic voltammetry, it is still possible to measure their lifetimes through redox catalysis²⁶ ($k = 5 \times 10^8 \text{ s}^{-1}$ for 4-chlorobenzonitrile) or through competition with other reactions such as a nucleophilic attack²⁷ ($k = 2 \times 10^7 \text{ s}^{-1}$ for 2-bromoquinoline to $2.5 \times 10^{10} \text{ s}^{-1}$ for iodobenzonitrile).

Therefore, aryl radicals are formed through fast reactions, but they are also consumed through fast reactions. With no purposely added reagent in the electrochemical cell where they are produced, these radicals can react with the solvent (SH) to abstract a hydrogen atom.



The rate of abstraction of a hydrogen atom from acetonitrile (ACN), a usual electrochemical solvent, by the 4-cyanophenyl radical has been measured²⁸ to be $k_{\text{H}} = 4 \times 10^7 \text{ s}^{-1}$, and the rate of abstraction by the phenyl radical can be obtained from literature data:^{29,30} $k_{\text{H}} = 6.7 \times 10^6 \text{ s}^{-1}$.

Another reaction often undergone by these radicals (mostly when they are produced by electrochemistry) is a further reduction either at the electrode (this occurs in the case of fast cleaving radical anions or in the case of a concerted mechanism) or in solution (this occurs for slower cleaving radical anions)²⁵ by the parent radical anion.



The further reduction of the radical is clearly evidenced in liquid ammonia, a solvent where there is no hydrogen abstraction. For example, the first wave of 4-bromobenzophenone in liquid ammonia is bielectronic.³¹ This is possible because the radical is more easily reduced than the starting compound. The formation and further reduction of the radical occurs through reactions **R2** + **R3** + **R6** (overall consumption of 2e^{-}).

Under these conditions, it is not possible to measure the redox potential of this radical. To achieve such a measurement, one should look for very easily reduced aromatic derivatives in the hope that they be more easily reduced than the follow-up radical. Diazonium salts should fulfill these conditions; for example, benzenediazonium tetrafluoroborate is reduced at $E_{\text{p}} = -0.16_{\text{V}}/\text{SCE}$ (Table 1). However, with these derivatives, a new reaction occurs:^{16–18} the radical attacks the surface of the electrode (carbon, C; metal, M; or semiconductor, SC) to establish a covalent carbon or metal–aryl bond as shown in reaction **R7**.



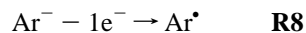
The same occurrence of this reaction is a good indication that the radical is not reduced at the potential of the diazonium salt; however, this reaction results in a major drawback: as the reduction proceeds, a blocking of the electrode occurs. As a consequence, in cyclic voltammetry, on the second scan, the reduction wave of the diazonium decreases or even disappears. If one could find conditions under which this blocking of the electrode is minimized, it should be possible to observe a voltammogram where a first one-electron wave of the diazonium salt is followed by the wave of the more difficultly reduced aryl radical. In this case, the system would resemble that of alkyl halides^{32a,b} where the reduction leads to an alkyl radical which can be reduced or not depending on the potential at which it is formed. The reduction wave of *tert*-butyl bromide which is reduced at -2.5 V/SCE is bielectronic, while that of the *tert*-butyl iodide – reduced at more positive potential ($E_{\text{p}} = -1.91 \text{ V/SCE}$) – is mono-electronic and is followed by the reduction wave of the *t*-Bu radical. In the same way,^{32c} the reduction of the α -hydroxybenzyl radical could be observed during the reduction of benzaldehyde in an ethanolic buffer at a potential negative to that of benzaldehyde itself. Analysis of the voltammogram, taking into account the different thermodynamic (standard redox potentials) and kinetic (rate constant of the electron transfer, follow-up chemical reaction, and diffusion of the species in solution) parameters, should permit one to determine the standard redox potential of aryl radicals as done before for alkyl radicals and the α -hydroxybenzyl radical.³² This is the main goal of this investigation. Indeed, any reaction involving an aryl radical produced by electrochemical reduction

- (22) Schäfer, H. J. *Electrochemical Generation of Radicals*. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M., Eds.; Wiley-VCH: Weinheim, 2001.
- (23) Savéant, J.-M. *Adv. Phys. Org. Chem.* **2000**, *35*, 117.
- (24) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 9829.
- (25) Amatore, C.; Chaussard, J.; Pinson, J.; Savéant, J.-M.; Thiébaud, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012.
- (26) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; M'Halla, F.; Savéant, J.-M. *J. Am. Chem. Soc.* **1980**, *102*, 3806.

- (27) Amatore, C.; Oturan, M. A.; Pinson, J.; Savéant, J.-M.; Thiébaud, A. *J. Am. Chem. Soc.* **1985**, *107*, 6012.
- (28) M'Halla, F.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1980**, *102*, 4120.
- (29) Bridger, R. F.; Russell, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754.
- (30) Kryger, R. G.; Lorand, J. P.; Neal, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589.
- (31) Savéant, J.-M.; Thiébaud, A. *J. Electroanal. Chem.* **1978**, *89*, 335.
- (32) (a) Andrieux, C. P.; Gallardo, I.; Savéant, J.-M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638. (b) Andrieux, C. P.; Gallardo, I.; Savéant, J.-M. *J. Am. Chem. Soc.* **1989**, *111*, 1620. (c) Andrieux, C. P.; Greszczuk, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1991**, *113*, 8811.

will potentially be in competition with the further reduction of the radical, and the knowledge of the redox potential should permit one to define conditions which maximize the yield of the reaction at the expense of a competitive ionic reaction.

Although a number of reduction potentials are known for a variety of radicals,³³ aryl radicals have resisted such measurements. The available data concern the reverse reaction³⁴



or, in a more chemically realistic fashion, the reaction:



By oxidation of phenyllithium in tetrahydrofuran/hexamethylphosphoramide (30%) at -65°C , it was possible to observe a broad cyclic voltammetric wave with a peak potential at ca. -0.340 V/SCE . It is interesting to note that successive scans yielded rapidly diminishing peak currents which could be restored only by polishing the electrode, a phenomenon exactly parallel to the fouling of the electrode observed during the reduction of the diazonium salts (reaction **R7**). Although (i) the above peak potential concerns phenyllithium and not the phenyl anion and (ii) the above potential is not a standard redox potential as the wave is irreversible, the above value gives a rough estimate of the range of potential where the E° of the phenyl radical should be located. Photoelectron injection^{35a,b} permits one to measure redox potentials. When a laser beam is shined onto the electrode, an electron is injected into the solution; it can then reduce a dissolved species, and the resulting product, in this case a radical, can in turn be reduced at the electrode depending on its potential. This method has been used successfully for the measurement of standard redox potentials^{35b,c} of benzyl and arylmethyl radicals. However, phenyl radicals should be reduced at relatively low potentials. When such potentials are applied to the illuminated electrode, the photo-injection yield (to produce the radical) is too low to record any useful photopolarogram. Konovalov and al.³⁶ could estimate the reduction potential of 3-chlorophenyl radical (-1.06 V/SCE) produced by reduction of 3-chlorophenyl trimethylammonium in water. This is not a standard redox potential but only a composite reduction potential including, in addition to the thermodynamic E° , kinetic parameters: rates of electron transfer and associated reactions. Although the standard redox potential of the phenyl radical has never been measured, other characteristics such as its Raman and electronic spectra have been characterized in low-temperature argon matrixes.^{37,38}

A second objective of this paper is to determine the reduction mechanism of diazonium salts. In view of further applications of reaction **R7**,^{39–42} it is important to know whether the diazenyl radical is an intermediate on the reaction path or not; that is, is

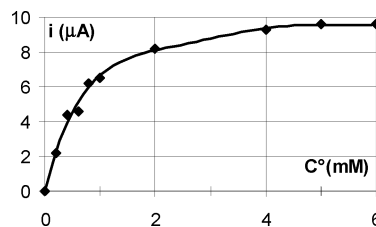
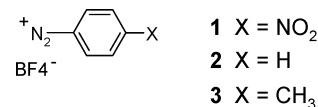


Figure 1. Height of the wave of 4-nitrobenzenediazonium tetrafluoroborate **1** as a function of the concentration. GC electrode. Scan rate $\nu = 0.2\text{ V s}^{-1}$. Reference SCE. $T = 20^\circ\text{C}$.

Scheme 2



the reaction going through reaction **R1** or through reactions **R2** + **R3**? If a stepwise mechanism is taking place, one could expect that the organic layer bonded to the electrode surface should in part be the result of a reaction of the diazenyl radical either on the radical itself or on the first grafted aryl groups. Conversely, if the aryl radical is formed directly, this very reactive radical should be the only species responsible for the growth of the layer.¹⁷

Results

As stated in the Introduction, one should try to minimize the electrografting reaction on the glassy carbon (GC) electrode. Figure 1 presents the height of the cyclic voltammetric wave of 4-nitrobenzenediazonium tetrafluoroborate **1** (Scheme 2) as a function of concentration.

At high concentration, the height of the wave becomes constant, reflecting the formation of the organic layer on the surface and the progressive blocking of the electrode. However, at concentrations lower than 1 mM, the curve can be approximated by a straight line as it should be for a diffusion-controlled mass transport, indicating that, at these low concentrations, fouling of the electrode is not too important. We therefore examined the voltammogram of carefully purified benzenediazonium tetrafluoroborate. The voltammogram at 1 V s^{-1} is shown in Figure 2. It presents a first broad irreversible one-electron wave (by comparison of $ip/C\nu^{0.5}$ with the reversible one-electron wave of ferrocene); the peak potential is $E_p^1 = -0.17\text{ V/SCE}$. This wave is clearly followed by a smaller wave at more negative potentials $E_p^2 = -0.64\text{ V/SCE}$. On the second scan, the first wave shifts to more negative potentials due to the progressive modification of the electrode but does not disappear as occurs at higher concentrations, indicating that the electrode is still active after one scan. A similar voltammogram is observed in DMSO. The second wave can also be observed under the same conditions starting from 4-methylbenzene diazonium **3** (Figure 3) or 4-nitrobenzene diazonium **1**; however, in the last case, this second wave is so small that comparison of experimental and simulated curves would not be significant. When the solvent is changed for dimethylformamide, the second wave became indistinguishable from the decay of the first one.

(33) (a) The different methods available for the measurements of redox potentials of radicals as well as the resulting values have been discussed in ref 33b. (b) Daasbjerg, K.; Pedersen, S. U.; Lund, H. Measurement and Estimation of Redox potential of Organic Radicals. In *General Aspects of the Chemistry of Radicals*; Alfassi, Z. B., Ed.; J. Wiley: Chichester, 1999; p 385.

(34) Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741.

(35) (a) Benderskii, V. A.; Krivenkov, A. G. *Russ. Chem. Rev. (Engl. Transl.)* **1990**, *59*, 1. (b) Gonzalez, J.; Hapiot, P.; Konovalov, V.; Savéant, J.-M. *J. Electroanal. Chem.* **1999**, *463*, 157. (c) Gonzalez, J.; Hapiot, P.; Konovalov, V.; Savéant, J.-M. *J. Am. Chem. Soc.* **1998**, *120*, 10171.

(36) Konovalov, V. V.; Bilkis, I. I.; Selinanov, B. A.; Shteingarts, V. D.; Tsetkov, Y. D. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1707.

(37) Lapinski, A.; Spanget-Larsen, J.; Langgard, M.; Waluk, J.; Radziszewski, J. G. *J. Phys. Chem. A* **2001**, *105*, 10520.

(38) Radziszewski, J. G. *Chem. Phys. Lett.* **1999**, *301*, 565.

(39) Bureau, C.; Levy, E.; Viel, P. *PCT Int. Appl.* **2003**, WO 0318212.

(40) Hartig, P.; Dittrich, T.; Rappich, J. *J. Eur. Pat. Appl.* **2003**, EP 1271633.

(41) Bureau, C.; Palacin, S.; Bourgoin, J.-P.; Ameer, S.; Charlier, J. *PCT Int. Appl.* **2002**, WO 0270148.

(42) Levesque, L.; Lawrence, M. F.; Bourguignon, B.; Leclerc, G. *PCT Int. Appl.* **2002**, WO 0266092.

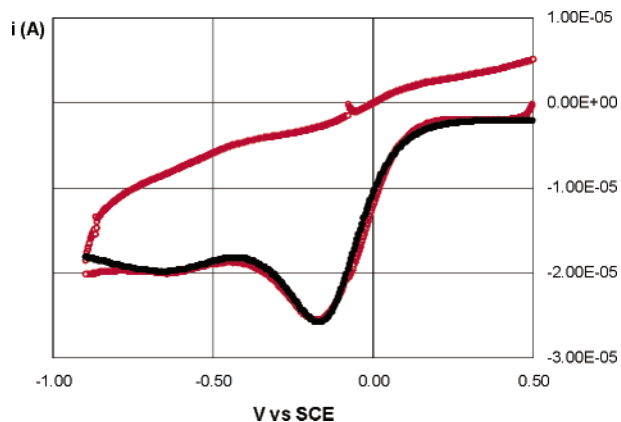


Figure 2. Cyclic voltammetry of benzenediazonium tetrafluoroborate **2**, $C = 0.60$ mM in ACN + 0.1 M NBu_4BF_4 . GC electrode. Scan rate $\nu = 1$ V s^{-1} . Reference SCE. $T = 25$ °C. Red points, experimental; black points, simulated curve.

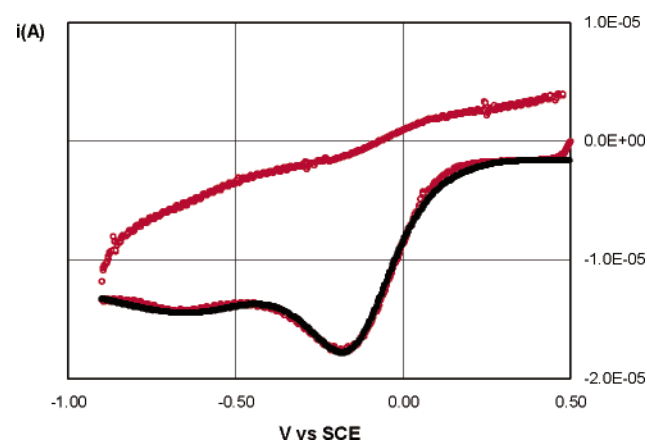


Figure 3. Cyclic voltammetry of 4-methylbenzenediazonium tetrafluoroborate **3**. $C = 0.45$ mM in ACN + 0.1 M NBu_4BF_4 . GC electrode. Scan rate $\nu = 1$ V s^{-1} . Reference SCE. $T = 25$ °C. Red points, experimental; black points, simulated curve.

Simulations of this second wave are performed to show that a small second wave should be observed corresponding to the reduction of an intermediate radical, this radical also undergoing a chemical reaction before its reduction. A similar voltammogram was obtained^{32b} with alkylidides where the chemical reaction of the radical is a dimerization. The small current obtained at the level of the second wave is explained by the fact that the radical produced at the potential of the first wave is consumed by the chemical reaction and only the species reaching the electrode at the potential of the second wave can be reduced by an overall two-electron transfer. Another effect of this reaction, acting as a preceding chemical reaction to the reduction of the radical, is the negative shift of the reduction potential of the radical.

A complete simulation of the experimental voltammograms must take into account several parameters. (i) As the first wave appears as a broad peak (the difference between the peak potential and the half peak potential is on the order of 150–220 mV), it is necessary to introduce a kinetic law for the first electron transfer leading to the aryl radical after cleavage of the carbon–nitrogen bond in one or two steps; a Butler–Volmer law was used with an apparent transfer coefficient α_1 . (ii) The chemical reaction involving the aryl radical was shown to be a

Table 1. Thermodynamic and Kinetic Parameters for the Reduction of the Aryldiazonium Cations and the Aryl Radicals^a

	2 in ACN	3 in ACN
E_p^1 (V/SCE)	−0.16 ₆	−0.18 ₂
α_1	0.34	0.30
k_1^f (cm s^{-1})	0.0026	0.003
E_p^2 (V/SCE)	−0.64	−0.69 ₅
α_2	0.28 ^(a)	0.275 ^(b)
k_2^f (cm s^{-1})	0.03	0.03
$\Delta G_{0,2}^\ddagger$ (eV)	0.40	0.38
E_2^0 (V/SCE)	+0.05 ^(c)	−0.02 ^(d)

^a By comparison between experimental and simulated curves, the extreme values are: (a) 0.26 and 0.30 V/SCE, (b) 0.25 and 0.30 V/SCE, (c) −0.10 and +0.26 V/SCE, and (d) −0.20 and +0.25 V/SCE.

hydrogen atom transfer from the ACN to the radical^{28–30} with a first-order reaction with $k_H = 6.7 \times 10^6$ s^{-1} . The same value is used for **2** and **3**. (iii) For the reduction of the radical, we used another Butler–Volmer law with an apparent transfer coefficient α_2 . As in the example of the reduction of aliphatic radicals,^{32b} this procedure is possible even when a small value of α_2 results from a large activation energy leading to a Marcus law for this electron transfer. As an approximation, in the small potential range of the second wave, a constant value of α_2 is taken into account.

The two Butler–Volmer laws are written as:

$$\frac{i_{1,2}}{FS} = k_{1,2}^f \exp\left(-\frac{\alpha_{1,2}FE}{RT}\right) C_{1,2}$$

i_1 and i_2 are the contributions of the reduction of the diazonium salt i_1 and of the radical i_2 to the total current, k_1^f and k_2^f are the respective forward reaction rate constants of electron transfer referred to the reference electrode potential, and C_1 and C_2 are the concentrations of diazonium and aryl radical at the electrode surface.

Simulated curves in ACN are presented in Figures 2 and 3. The parameters corresponding to the best fit between experimental and simulated curves are listed in Table 1. The procedure used for the determination of the standard potential of reduction E_2^0 of the aryl radical is similar to that used for alkyl radicals,^{32b} as the reduction of the radical involves a slow electron transfer, the possible reactions of the anion obtained after the second transfer are without effect on this determination. We use a quadratic activation–driving force free energy relationship

$$\Delta G^\ddagger = \Delta G_{0,2}^\ddagger \left(1 + \frac{E - E_2^0}{4\Delta G_{0,2}^\ddagger}\right)^2$$

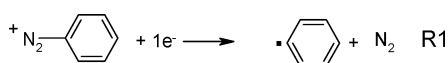
and the value

$$\alpha_2 = \frac{1}{2} \left(1 + \frac{E - E_2^0}{4\Delta G_{0,2}^\ddagger}\right)$$

and the definition of k_2^f :

$$k_2^f = Z^{\alpha_2} \exp\left(-\frac{RT\Delta G_{0,2}^\ddagger}{F}\right)$$

Scheme 3



leading at the peak potential E_2^p to:

$$\Delta G^\ddagger = 4\alpha_2^2(\Delta G_{0,2}^\ddagger) = \frac{RT}{F} \ln \frac{Z^{\text{el}}}{k_2^f} + \alpha_2 E_2^p$$

and

$$E_2^0 = E_2^p + 4\Delta G_{0,2}^\ddagger(1 - 2\alpha_2)$$

With $Z^{\text{el}} = 4.6 \times 10^3 \text{ cm s}^{-1}$, the values of E_2^0 in ACN are listed in Table 1.

The very positive value E_2^0 obtained for the standard redox potential of the radicals is in agreement with the two-electron reductions observed for arylhalides. The electrografting reactions with aryldiazonium salts are due to the fact that the radical is not reduced at its standard redox potential but at more negative potentials for kinetic reasons (see Figure 2). Electrografting does not occur with arylhalides as they are reduced at much more negative potentials where the aryl radical is reduced to the anion.

As indicated in the Introduction, a second outcome of this investigation is to demonstrate that during the reduction of the diazonium salt the transfer of the electron is concerted with the cleavage of the dinitrogen molecule as shown in Scheme 3.

As indicated in Table 1, the value of the transfer coefficient α_1 for the first wave is far from 0.5, pointing to a very slow electron transfer. As discussed elsewhere²³ for aromatic compounds, when an outersphere electron transfer involves only a modification of the charge between reagent and product, the reduction potential of the reagent is expected to be not very far from the standard potential even with a very fast follow-up chemical reaction. In the reduction of the aryldiazonium cations, the values of α_1 are on the order of 0.3, showing that the reduction peak potential is far from the standard reduction potential and that the activation free energy is large. This is in line with a large reorganization energy and with an electron transfer concerted with the cleavage of the dinitrogen molecule as shown in Scheme 3 (R1). Therefore, under the conditions of electrochemical reduction, the diazenyl radical is not an intermediate, and the analysis of the grafted layer should not reveal any feature which could derive from this radical. We can examine if this is indeed the case through the various investigations performed on the formation of covalently bonded organic layers (excluding nitrobenzene diazonium where the nitro groups could yield azo compounds upon reduction). Raman⁴⁴ and IR^{45–47} spectra of carbon surfaces (glassy carbon or highly oriented pyrolytic graphite (HOPG)) modified by reduction of diazonium salts have been published, and the authors never mention the presence of the $-\text{N}=\text{N}-$ group. This azo group should have been detected through Raman absorptions at 1412, 1449, 1470, and 1492 cm^{-1} as in nitroazobenzene.⁴⁴ However, XPS signals were observed at 400 eV, but they were

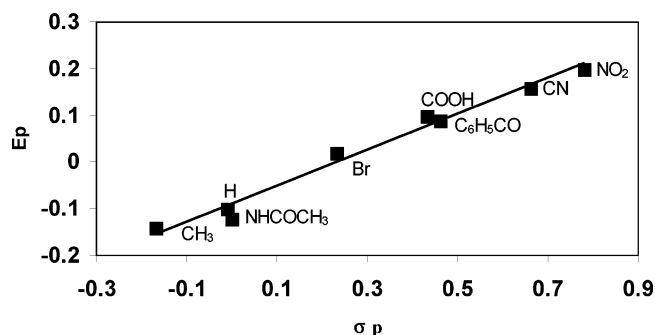


Figure 4. Peak potential of aryldiazonium salts (in ACN at 0.2 V s^{-1} , $C = 0.1 \text{ mM}$) as a function of Hammett substituent constant σ_p . Data are from ref 16b and from this paper.

assigned to the reaction of the diazonium with surface phenolic groups.⁴⁸ Altogether, these results are in agreement with a concerted electrochemical cleavage of the diazonium cation.

The primary events related to the reduction of diazonium salts have also been examined by pulse radiolysis in water.⁴⁹ In strongly acidic medium (1 M HClO_4), an H adduct (ArN_2H^+) is formed initially, and therefore this radiolytic reaction cannot be compared to our electrochemical experiments. In neutral medium, the first event is the reduction of the diazonium cation by a solvated electron to give a diazenyl radical ($\text{C}_6\text{H}_5\text{N}_2^\bullet$) which cleaves reversibly with a rate constant of $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ($K = 160$). Thus, under these conditions, the reduction is stepwise (reaction R2 + R3) at the difference of what we observe by electrochemistry. This can be easily rationalized on the basis of the driving force of the reaction. It has been demonstrated²³ that the cleavage passes from concerted to stepwise as the driving force becomes larger and larger. Under our electrochemical conditions, at the peak potential, the driving force is $\sim 0.07 \text{ eV}$, while it is on the order of 3.20 eV when solvated electrons are the reducing species (oxidation potential -3.10 V/SCE); this large difference is therefore responsible for the difference in the observed mechanisms.

Another question related to this mechanism is whether it is general for a variety of substituents or limited to the compounds examined in this paper. The straight line of Figure 4, which represents the peak potential of different diazonium cations as a function of Hammett substituent constant σ , clearly indicates that there is no change of mechanism between the different substituents and that in all cases the diazenyl radical is not an intermediate on the way from the diazonium cation to the aryl radical.

Conclusion

The electrochemical reduction of the benzenediazonium cation and its 4-nitro and 4-methyl derivatives permits one to observe two successive waves. The first one corresponds to the transfer of $1e^-$; it is followed by a small second wave at more negative potentials. Simulation of the voltammograms allows one to determine the standard redox potential of the phenyl radical $E^\circ(\text{Ph}^\bullet/\text{Ph}^-) = +0.05 \text{ V/SCE}$. It also permits one to establish the reduction mechanism: the electron transfer to the diazonium cation is concerted with the cleavage of dinitrogen; it leads to the phenyl radical and a dinitrogen molecule. This

(43) Liu, Y.-C.; McCreery, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 11254.

(44) Itoh, T.; McCreery, R. L. *J. Am. Chem. Soc.* **2002**, *124*, 10894.

(45) Kariuki, J. M.; McDermott, M. T. *Langmuir* **2001**, *17*, 5947.

(46) Coulon, E.; Pinson, J.; Bourzat, J.-D.; Commerçon, A.; Pulicani, J.-P. *Langmuir* **2001**, *17*, 7102.

(47) Coulon, E.; Pinson, J.; Bourzat, J.-D.; Commerçon, A.; Pulicani, J.-P. *J. Org. Chem.* **2002**, *67*, 8513.

(48) Saby, C.; Ortiz, B.; Champagne, G. Y.; Bélanger, D. *Langmuir* **1997**, *13*, 6805.

(49) (a) Daasbjerg, K.; Sehested, K. *J. Phys. Chem. A* **2002**, *106*, 11098. (b) Daasbjerg, K.; Sehested, K. *J. Phys. Chem. A* **2003**, *107*, 4462.

radical can competitively abstract a hydrogen atom from the solvent or be reduced at the electrode to a carbanion.

Experimental Section

Glassy carbon electrodes (Tokai, Japan) were carefully polished with diamond paste down to 1 μm and cleaned in acetone under sonication.

4-Nitrobenzediazonium tetrafluoroborate **1** is a commercial compound (Aldrich). Benzene diazonium tetrafluoroborate **2** and 4-methyl benzenediazonium tetrafluoroborate were prepared as previously

described^{16a} from freshly distilled aniline or recrystallized toluidine, reprecipitated twice from reagent grade acetonitrile and ethyl ether, and dried under vacuum.

The equipment for cyclic voltammetry has been described previously.^{16a} Simulations were performed with the help of Digisim.⁵⁰

JA0374574

(50) Rudolf, M.; Feldberg, S. W. *Digisim 3.03*; Bioanalytical Systems Inc.: West Lafayette, IN, 1996.