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PHOTOCHEMICAL VS. ELECTROCHEMICAL ELECTRON-TRANSFER REACTIONS. ONE-ELECTRON REDUCTION OF ARYL HALIDES BY PHOTOEXCITED ANION RADICALS

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Abstract. *Electrochemical reduction of aryl halides generally leads to expulsion of halide ion. The product aryl radical is unavoidably further reduced. In contrast, reduction of aryl halides by photoexcited anion radicals may be stopped at the aryl radical stage owing to the bimolecular nature of electron-transfer reactions. We have tested this hypothesis by photoinducing electron-transfer from anthraquinone anion radical to several aryl halides. For each halide it was possible to trap the corresponding radical by anthracene forming substituted 9-phenylanthracenes.*

The pioneering work on electron-transfer fluorescence quenching by Weller[1] and the exploitation of these reactions in organic synthesis by Arnold[2] have stimulated much research in photochemical electron-transfer within the last decade[3]. We have recently studied the electron-transfer fluorescence quenching of radical cations and anions[4] and had previously shown that photoexcited anion radicals and dianions were able to transfer electrons to certain aryl halides whereas the ground state of the same ions were not[5].

Mechanistic and preparative exploitation of such electron-transfer from photoexcited anion radicals is of interest since an electronically excited anion radical is a very strong reductant[6]. Hence, it is possible to create a very strong reductant in a medium only slightly reducing. In contrast to the permanent electrode in an electrochemical reduction, the photoexcitation of an anion radical creates a short-lived local electrode in solution.

In the electrochemical reduction of an aryl halide (AX) further reduction at the electrode or by electron-transfer in solution after the first electron uptake usually cannot be avoided since the produced radical ($A^{\bullet}$) is more easily reduced than AX (Scheme 1). In the bimolecular photochemical reduction of AX by a photoexcited anion radical $(D^{\overline{\bullet}})^*$, further reduction of $A^{\bullet}$ is unlikely due to the very low concentration of $(D^{\overline{\bullet}})^*$. Instead, $A^{\bullet}$ may undergo chemical reaction or be trapped (Scheme 1). Thus, the low concentrations of electron donors in the photochemical reduction favours formation of product 2 (Scheme 1).

Scheme 1

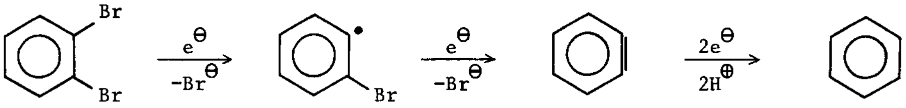
Electrochemical Reduction:

$$AX \xrightarrow{e^{\ominus}} AX^{\dot{-}} \xrightarrow{-X^{\ominus}} A^{\bullet} \xrightarrow{e^{\ominus}} A^{\ominus} \longrightarrow \qquad \text{Product 1}$$

Photochemical Reduction:

$$D^{\dot{-}} \xrightarrow{h\nu} (D^{\dot{-}})^{*} \xrightarrow[-D]{AX} AX^{\dot{-}} \xrightarrow{-X^{\ominus}} A^{\bullet} \longrightarrow \qquad \text{Product 2}$$

This proposal has been tested in a system originally examined by Wawzonek and Wagenknecht[7]. They found that electrochemical reduction of 1,2-dibromobenzene (1) gave benzene via the bromobenzene radical and benzyne:



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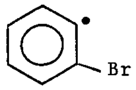
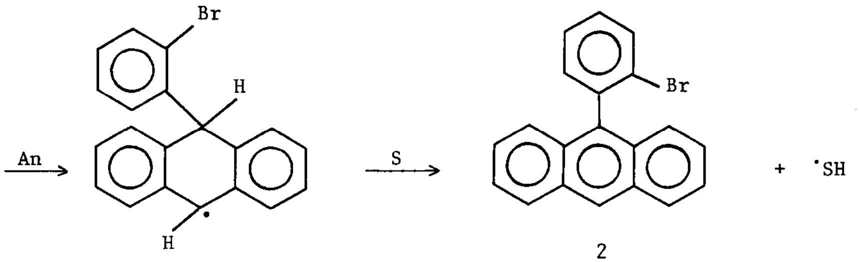
Reduction of the bromobenzene by a second electron uptake could not be avoided.

We have now examined the bimolecular reduction of 1 by photoexcited anthraquinone anion radical $(Aq^{\dot{-}})^{*}$ in the presence of anthracene (An)[8]. The main product isolated was 9-(2-bromophenyl)anthracene (2) in addition to small amounts of 9,10-bis(2-bromophenyl)anthracene. The products were identified from their spectral properties[9]. We suggest the following mechanism involving initial electron-transfer from excited $Aq^{\dot{-}}$ to 1 followed by expulsion of bromide. The resulting bromobenzene radical is trapped by An to give 2:

Scheme 2

$$Aq^{\dot{-}} \xrightarrow{h\nu} (Aq^{\dot{-}})^{*} \xrightarrow[-Aq]{\underline{1}} \underline{1}^{\dot{-}} \xrightarrow{-Br^{\ominus}}$$





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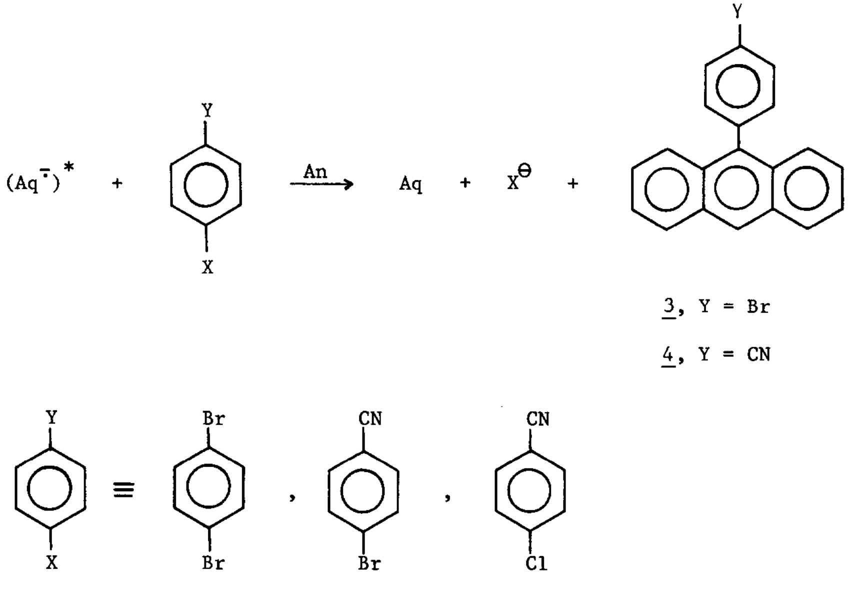
S may be the solvent or $Aq^{\overline{\cdot}}$. The mechanism is supported by the following observations: a) reaction of electrogenerated $An^{\overline{\cdot}}$ with 1 gave no bromine-containing coupling products; b) photoexcited An did not react with 1; and c) $Aq^{\overline{\cdot}}$ in the ground state did not react with 1.

The reaction was performed with other aryl halides as electron acceptors. Scheme 3 summarizes the results.

Scheme 3



3, Y = Br

4, Y = CN

5 6 7

Electron-transfer to 5 gave 3, while 6 and 7 both led to 4 supporting the mechanism outlined in Scheme 2. Product identifications were again based on spectral data[10]. The reaction is presumably quite general. $Aq^{\overline{\cdot}}$ may be replaced by other anion radicals (e.g. 9,10-dicyanoanthracene anion radical) and An may be replaced by other radical trapping compounds such as quinoxaline.

In summary we have shown that one-electron reductions of aryl halides may be carried out by means of photoexcited anion radicals. Very recently, Fox has shown that titanium dioxide microparticulate electrodes under low light flux may induce single electron-transfer; thus, a vicinal diacid was oxidatively decarboxylated to the monoacid in contrast to the conventional electrochemical two-electron oxidation to an alkene[11]. Likewise, transfer of electrons from 1,1-diphenyl ethylenes to photoexcited cation radicals has been demonstrated and it was found that the ratio was dependent on the redox potential of the cation radical[12].

References and Notes

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2. A.J. Maroulis, Y. Shigemitsu, and D.R. Arnold, *J. Am. Chem. Soc.*, 100 535 (1978), and references cited therein.
3. For a review, see L. Eberson, *Adv. Phys. Org. Chem.*, 18 79-185 (1982).
4. J. Eriksen, K.A. Jørgensen, J. Linderberg, and H. Lund, *J. Am. Chem. Soc.*, 106 5083 (1984); J. Eriksen, H. Lund, and A.I. Nyvad, *Acta Chem. Scand.*, Ser. B., B37 359 (1983).
5. H. Lund and H.S. Carlsson, *Acta Chem. Scand.*, Ser. B., B32 505 (1978); B34 409 (1980).
6. By the same token, photoexcited radical cations are strong oxidants and may be produced in a medium slightly oxidizing.
7. S. Wawzonek and J.H. Wagenknecht, *J. Electrochem. Soc.*, 110 420 (1963).
8. $\mathrm{Aq}^{\overline{\cdot}}$ was generated electrochemically in oxygen-free acetonitrile or dimethylformamide. The solution with added 1 and An was circulated through a photochemical reaction well and irradiated with a Philips 6070C/05 250W projector lamp.
9. Spectral data on 2: ^{1}H-NMR $\delta(CDCl_3)$: 7.32 - 7.60(m, 9H), 7.83(m, 1H), 7.95 - 8.14(m, 2H) 8.53(s,H); ^{13}C-NMR $\delta(CDCl_3)$: 125.2, 125.5, 125.8, 126.2, 127.2, 127.5, 128.5, 129.4, 129.8, 131.3, 132.9, 133.0, 135.5, 139.7; IR ν_{KBr}: 3075, 1630, 1480, 1440(S), 1360(S), 1050, 1040, 940, 900, 850, 795, 755, 740 cm^{-1}; MS m/e: 332 + 334 (1:1, M$^+$), 252, 250, 126.5, 126, 125.
10. a) Spectral data on 3: ^{1}H-NMR $\delta(CDCl_3)$: 7.31 - 7.67(m,8H), 7.87 - 8.07(m, 4H), 8.39 (S, 1H); IR-ν_{KBr} - 3030, 1680, 1490, 1470, 1240, 1220, 1020, 940, 820, 780, 755, 700 cm^{-1}, MS m/e: 332 + 334 (1:1, M$^+$), 253, 252, 250, 126.5, 126, 125.
    b) Spectral data on 4: ^{1}H-NMR $\delta(CDCl_3)$: 7.32 - 7.60(m, 8H) 7.78 - 8.11(m, 4H), 8.51(S, 1H) ^{13}C-NMR $\delta(CDCl_3)$: 111.6, 118.9, 125.3, 125.9, 126.1, 127.6, 128.6, 129.7, 131.2, 132.24, 134.4, 144.2; IR ν_{KBr}: 3060, 2240(S), 1600, 1440, 1410, 1360, 1185, 1020, 940, 880, 850, 820, 790, 610 cm^{-1}; MS m/e 280, 279(M$^+$), 278, 277, 139.5, 139.
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