Photoelectrochemistry with Quinone Radical Anions—Photoassisted Reduction of Halobenzenes and Carbonyl Compounds

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Photoexcited electrochemically generated quinone radical anions reduced 1,2-dibromobenzene to bromobenzene, 1,4-dibromobenzene to bromobenzene and 4-chlorobenzonitrile to benzonitrile. In the presence of anthracene, 2-bromophenyl-, 4-bromophenyl- and 4-cyanophenyl-anthracenes were formed. With acetaldehyde, acetone, acetophenone, benzaldehyde and benzophenone, the major products were the corresponding pinacols, with small amounts of the two-electron secondary alcohols. In acetonitrile as solvent, cinnamonitriles, hydrocinnamonitriles and phenylglutaronitriles were formed in addition to the alcohols. Glyoxylic acid was reduced to tartaric, glycolic and malic acids. The reduction of CO_2 was unsuccessful.

Energy to activate chemical reactions can be provided by heat, light or electricity. An interesting variation is to use a combination of light and electricity—photoelectrochemistry.[1] A great deal of work in this area has been carried out using semiconductor electrodes in which a light is shone on the electrode surface during the process.[2] A similar effect can be obtained by irradiating semiconductor particles directly without any formal electrode.[3] A number of workers have used different electron donors or electron acceptors as electron transfer intermediates.[4]

Most of the work in this area has been fluorescence quenching[5] and other kinetic studies,[6] such as that by Lund *et al.*,[7] using photoexcited anthraquinone, anthracene and dicyanoanthracene radical anions with 12 different substrates. Only a few preparative studies have been carried out.[7] An example of a preparative reduction is that between photoexcited anthraquinone radical anions and 1,2-dibromobenzene[7] (see Results and Discussion).

Moutet and Reverdy[8] have used photoexcited cation radicals in a similar way for oxidations, such as the oxidation of benzyl alcohol to benzaldehyde using the cation radical of 2,2′,4,4′,6,6′-hexamethoxydiphenylamine (HMDPA).[9]

$$\mathrm{HMDPA} - \mathrm{e}^- \longrightarrow \mathrm{HMDPA}^{+-} \xrightarrow{+h\nu} \mathrm{HMDPA}^{+-*}$$

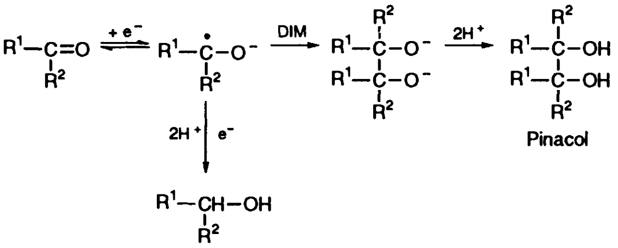
$$2\mathrm{HMDPA}^{+-*} + \mathrm{PhCH_2OH} \longrightarrow 2\mathrm{HMDPA{\cdot}H}^+ + \mathrm{PhCHO}$$

We have been studying the use of quinone radical anions as photoelectron transfer intermediates.[10,11] We have demonstrated the photoelectrochemical effect visually using photoexcited quinone radical anions with methyl viologen,[11] giving a purple colour, and with neutral red which goes from red to yellow.

In another set of experiments, kinetic data were obtained from cyclic voltammetry experiments in which the electrode was irradiated with light.[11] We have also calculated quenching rate constants from cyclic voltammetry and fluorescence spectral data, and have fitted these data to a Rehm–Weller curve.[10]

In this work we present the results of photoelectrochemical reduction reactions using three different quinones and ten different substrates including three halobenzenes and six carbonyl compounds.

Carbonyl compounds can be reduced electrochemically in aqueous[12] and in aprotic[13] solvents at fairly negative potentials (*ca.* −2.0 V). The highest yields for single electron reaction products (pinacols) have been obtained in basic aqueous media.[13] However, reduction of acetophenone, benzaldehyde and acetone in aprotic media have also been reported.[13–15] The reduction is shown in Scheme 1. In more acidic media the two electron reduction to secondary alcohols is observed.



Scheme 1

Experimental

Materials.—Anthraquinone (AQ) (BDH) was recrystallised from acetonitrile, m.p. 289.4 °C; naphthoquinone (NQ) (BDH) was recrystallised from ethanol, m.p. 120.2 °C; 2,6-di-*tert*-butylbenzoquinone (DTBQ) (Aldrich) was used as supplied; benzoquinone (Aldrich) was recrystallised from water and then twice from ethanol, m.p. 112.3 °C; tetrachlorobenzoquinone (chloranil) (BDH) was recrystallised twice from acetone, m.p. 287.6 °C; tetrafluorobenzoquinone (fluoranil) (BDH) was recrystallised from acetone, m.p. 187.8 °C.

Acetonitrile (BDH Spectrasol) was dried over molecular sieves (BDH Linde 4A) and then fractionally distilled over P_2O_5. Tetramethylammonium perchlorate (TEAP) (Fluka) was recrystallised from water, m.p. 348 °C. Argon (BOC) was used as supplied. Oxygen-free nitrogen was purified through a vanadium(II) solution, then through water and finally through the solvent to be used over molecular sieves (BDH Linde 4A). Dimethylformamide (DMF) and dimethylacetamide (DMA) (Aldrich, spectrosol) were both dried over anhydrous copper sulfate and then distilled at reduced pressure (12 mmHg).

1,2-Dibromobenzene, 1,4-dibromobenzene and 1,4-dibromobenzonitrile (Aldrich) were all used as received. Acetone (BDH) was dried over molecular sieves (BDH Linde 4A) and then fractionally distilled twice; acetaldehyde (BDH) was dried over molecular sieves (BDH Linde 4A); acetophenone (Aldrich) was fractionally distilled twice, finally collecting the fraction boiling between 199 °C and 203 °C; benzaldehyde (BDH Analar) was washed with 10% aq. sodium carbonate, separated, dried (magnesium sulfate) and then distilled; benzophenone (Aldrich) was recrystallised from ethanol to give white prism-shaped crystals, m.p. 48 °C.

Photoelectrochemistry.—Controlled potential electrolysis was carried out with an EG & G PAR 173 potentiostat or a Chemical Electronics 703A potentiostat in a two or three compartment cell with the compartments separated by a fine porosity frit.

For each of the reductions the quinone radical anion was generated electrochemically in argon- (or nitrogen-) saturated acetonitrile containing 0.1 mol dm^{-3} TEAP for 20 min at the appropriate potential.[11] The substrate was added and the cell was then photolysed with a Wotan 150 W tungsten halogen lamp fitted with a sodium nitrite filter to give light of >410 nm, for 18–24 h, while maintaining the electrolysis potential. Samples were withdrawn for analysis by GLC or HPLC. Blanks were run, one without electrolysis and one without light.

Analysis.—All samples were treated with analytical grade cation exchange resin (BDH, Amberlite IR120) to remove the tetraalkylammonium salts.

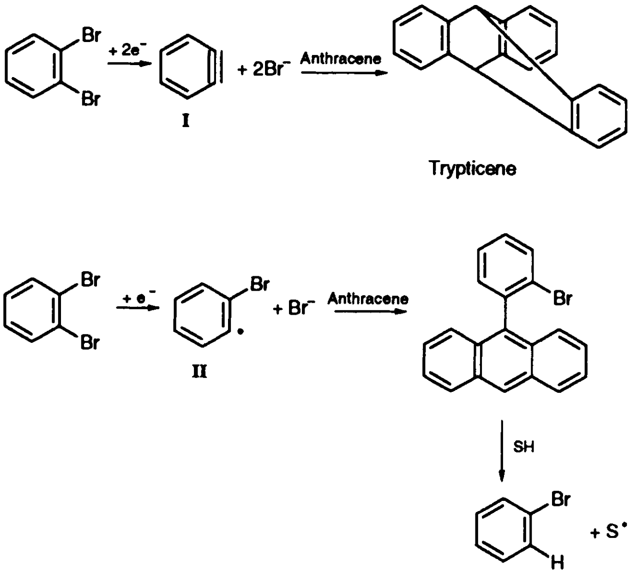
The aryl halides were analysed on a Perkin-Elmer Sigma 10 GC with both flame ionisation and electron capture detectors. The column was a 25 m cyanopropylphenylsilicone capillary column with a temperature program from 60 to 250 °C. The aliphatic aldehydes and ketones were analysed on a Hewlett Packard HP5890 GC with a 50 m methylsilicone column with a temperature program from 60 to 200 °C using a flame ionisation detector. Internal standards of benzophenone and quinoline were used.

GC–MS was used to aid the analysis of carbonyl compounds and halobenzenes and the products of their reduction. The Hewlett Packard HP5890 GC was connected to a Hewlett Packard 5970 MS feeding a Hewlett Packard 200 data station. The ion patterns corresponding to peaks in the chromatograms were compared with a library of standards.

HPLC was used to analyse the reduction products from the aromatic aldehyde and ketones and glyoxylic acid. It consisted of an Altex 110A pump with a Phillips PU4026 variable wavelength detector and a Shimadzu CR3A integrator. For the analysis of the aromatic aldehydes and ketones a Waters RCM reversed phase ODS cartridge column was used with a mobile phase of 75% acetonitrile–water mixture and the detector set at 254 nm. For glyoxylic acid products an Aminex HPX87H ion exclusion column (Biorad) was used with 1.6×10^{-3} mol dm^{-3} sulfuric acid as the mobile phase. The detector was set at 210 nm. Anisole and benzophenone were used as internal standards for the aromatic compounds.

Results and Discussion

Aryl Halides.—1,2-Dibromobenzene can be electrochemically reduced in one two-electron step to yield benzyne (**I**) (Scheme 2), which can be trapped with anthracene to form the trypticene adduct.[16] However, a single electron transfer reaction will produce a bromophenyl radical (**II**) which can be protonated to form bromobenzene or trapped with anthracene to form a bromophenyl anthracene.[7] Lund *et al.*[7] carried out this reaction with photoexcited anthraquinone radical anions generated electrochemically in DMF. They claimed the structure of the product (bromophenyl)anthracene on the basis of ^{13}C and ^{1}H NMR evidence; the yields are not quoted and not many details of the NMR spectra are given.



Scheme 2

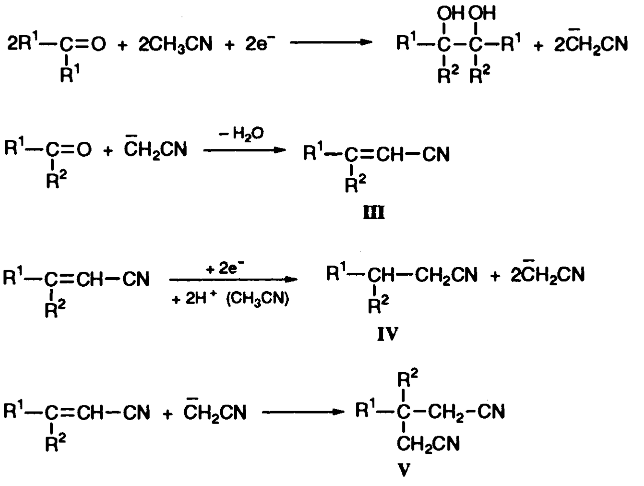
We have repeated this experiment, also using photoexcited, electrochemically generated anthraquinone radical anions in AN in the absence of anthracene under argon. We obtained bromobenzene (5%), detected by GC–MS. No bromobenzene was detected in blank experiments, carried out on the solution with electrolysis only or with photolysis only.

A similar experiment was done including anthracene. This time a (bromophenyl)anthracene (4%) was detected by GC–MS together with bromobenzene (0.1%). No trypticene was found in the GC–MS analysis. Our ^{1}H NMR spectra of products did not show much detail, as is to be expected with the low yields, but were consistent with the data given by Lund *et al.*[7] We also reduced 1,4-dibromobenzene to bromobenzene (1.0%). The lower yield may have been due to the large difference in reduction potentials between the prouct and the substrate. 4-Chlorobenzonitrile was similarly reduced, in the presence of anthracene, to 9-(4-cyanophenyl)anthracene (3.8%) and benzonitrile (0.2%).

We could not get the reactions to work in DMF because of hydrogen abstraction reactions between the quinone and the solvent.[17,18] We conclude that the single electron transfer mechanism is operative in these reactions. The reduction of 1,2-dibromobenzene to bromobenzene shows the increased selectivity of this system compared with the direct electrolysis. Only anthraquinone and naphthoquinone were successful electron transfer mediators.

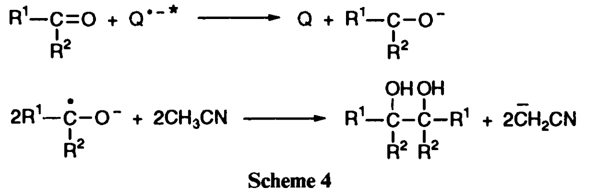
Aldehydes and Ketones.—The single electron transfer reduction reaction was tried with acetaldehyde, acetone, benzaldehyde, acetophenone and benzophenone using six quinones as mediators. In each case the quinone radical anion was generated electrochemically as before in argon-saturated acetonitrile using a two compartment cell. This was then irradiated with a tungsten lamp for 18–24 h. Samples were removed for analysis by GC or HPLC. Blanks were run on solutions with electrolysis only and photolysis only.

The electrochemical reduction of benzaldehyde to hydrobenzoin has been reported in both aqueous and non-aqueous solutions[13,14] but at much more negative potentials. In our system, hydrobenzoin (18%) was produced by photolytic single electron transfer, together with a small amount of the two-electron product, benzyl alcohol (0.25%). However, some nitrile compounds were also produced which were not reported during



Scheme 3

indirect electrochemical reactions. Bellamy *et al.*,[19] in studies of the electrochemical reaction of aromatic aldehydes and ketones in acetonitrile found that the major products were nitrile compounds, with very little of the diol or alcohol. He found cinnamonitrile (R^1 = Ph, R^2 = H) (**III**), hydrocinnamonitrile (**IV**) and phenylglutaronitrile (R^1 = Ph, R^2 = H) (**V**) and proposed the reaction Scheme 3. Bellamy[19] observed that at −3.0 V the acetonitrile was deprotonated, probably by the dimerised radical anions of the carbonyl compound. This produced a hydroxycinnamonitrile which dehydrated to form cinnamonitrile (**III**). This was reduced in a two-electron step to form hydrocinnamonitrile (**IV**). This step produced more acetonitrile anions. A Michael addition of the acetonitrile anion to cinnamonitrile gave glutaronitrile (**V**).



Scheme 4

Similar products were obtained in our system, but at much lower potentials (Scheme 4). In our reaction mixture from benzaldehyde, we found hydrocinnamonitrile (9.2%), (*E*)-cinnamonitrile (16%), (*Z*)-cinnamonitrile (3.5%) and phenylglutaronitrile (10.1%) as well as the expected hydrobenzoin (18.1%) and benzyl alcohol (0.25%).

The primary difference between our system and that of Bellamy[19] was that he used a potential more than 2 V more negative than ours and that we used a photochemical mediator.

The reduction of cinnamonitrile[20] with the photoexcited anthraquinone anion radical was investigated in acetonitrile under conditions identical with those of the benzaldehyde reaction. After 15 h GC–MS showed that most of the cinnamonitrile had been reduced to hydrocinnamonitrile (57.4%) and phenylglutaronitrile (19.3%).

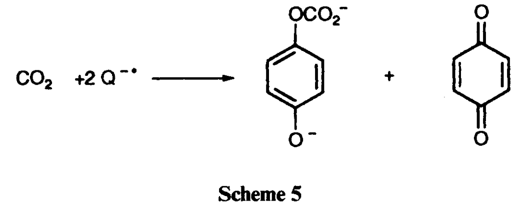
Acetophenone was similarly reduced to 2,3-diphenylbutane-2,3-diol (12.9%) and 2-phenylethanol (0.3%) together with (*E*)-3-methylcinnamonitrile (11.8%), (*Z*)-3-methylcinnamonitrile (2.0%), 3-methylhydrocinnamonitrile (8.7%) and 3-phenyl-3-methylglutaronitrile (1.0%). The lower yield of this latter product was also observed by Bellamy.[19]

Benzophenone was reduced similarly to the 1,1,2,2-tetraphenylethane-1,2-diol (18.7%), 3-phenylcinnamonitrile (22.5%) and diphenylmethanol (0.27%). In accordance with Bellamy's results,[19,20] no 3,3-diphenylglutaronitrile was found. Acetone was reduced to 2,3-dimethylbutane-2,3-diol (pinacol) (6.5%), 3-methylbutanenitrile (8.0%) and 3-methylbut-3-enenitrile (4.4%). Propan-2-ol was not resolvable from acetone under our analytical conditions. Acetaldehyde was reduced to butane-2,3-diol (2.5%) and butanenitrile (7.3%).

Similar results for the carbonyl compounds were also obtained with naphthoquinone and DTBQ, but not with benzoquinone, chloranil or fluoranil, even after 72 h photolysis. With naphthoquinone and DTBQ lower yields were found as these two had lower reduction potentials. The reason the reductions were not possible with chloranil, fluoranil or benzoquinone radical anions is probably because of the order of potential difference between the anion radicals and the substrate, with the rate of electron transfer being too slow to build up any appreciable yield of products.[21] The deactivation of the excited state *via* a process other than electron transfer may be another reason why these quinones were unable to reduce the substrates.[4,22] Reactions were also attempted in DMF and DMA solutions. No alcohol, diol or nitrile compounds were formed.

The yields of diol from the various carbonyl compounds roughly follow the order of the quenching rate constants calculated from the Rehm–Weller equation[11,23] and also the rate constants determined by cyclic voltammetry at illuminated electrodes,[10] as shown in Table 1, with benzaldehyde > benzophenone > acetophenone > acetone > acetaldehyde. It may be noted that the order of the peak reduction potentials is the same.

Carbon Dioxide.—Considerable interest has been shown in recent years in the fixation of carbon dioxide[24] as a result of the energy crisis and the greenhouse effect. This has been particularly directed towards the electrochemical fixation of carbon dioxide.[25,26] Another approach has been photoelectrochemical reduction using semiconductor powders, such as CdS[27,28] and ZnS.[29] In this work we attempted to apply the excited quinone radical anion system to the reduction of carbon dioxide. However this was not successful. During 48 h photolysis of carbon dioxide with electrochemically generated anthraquinone radical anions, none of the expected reduction products such as formic acid, formaldehyde, glyoxylic acid or oxalic acid were detected by HPLC. We did not test for carbon monoxide. It is likely that the carbon dioxide coupled with the quinone radical anions, as shown by Wrighton[30] and by Dubois *et al.*[31] (Scheme 5).



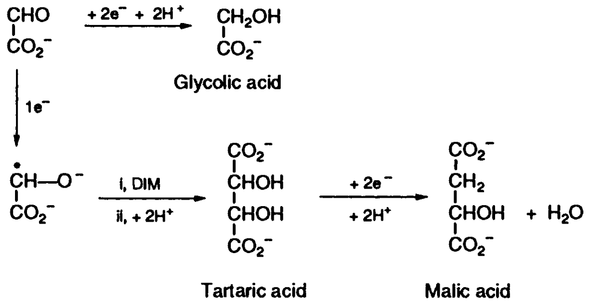
Scheme 5

Glyoxylic Acid.—Glyoxylic acid is an important product from the electrochemical reduction of carbon dioxide.[26] It is also formed by the photolysis of carbon dioxide on semiconductor powders and colloids such as CdS[27] and ZnS.[29] It is reduced electrochemically in aqueous solutions to yield glycolic acid by a two-electron step or to tartaric acid by a single-electron step.[32] We found that it may be reduced at −2.1 V in acetonitrile. Because of this interest we subjected glyoxylic acid to photoelectrochemical reduction using the anthraquinone radical anion as mediator in acetonitrile. Tetramethylammonium hydroxide was added to deprotonate the acid group. Small yields of tartaric acid (1.76%), glycolic acid (0.89%) and malic acid (0.21%) were detected by HPLC. Malic acid could be formed by further reduction of tartaric acid (Scheme 6).

Table 1 Quenching rate constants[11] and yields of diols compared with reduction potentials (E_p) for carbonyl compounds photolysed with different quinone radical anions

		AQ[a]		NQ[b]		DTBQ[c]	
Compound	E_p/V	k_q[d]	Yield[e]	k_q	Yield	k_q	Yield
Benzophenone	−1.85	11.1	18.7	—	—	—	—
Benzaldehyde	−1.80	12.3	17.9	9.0	12.7	14.1	9.0
Acetophenone	−2.02	6.8	12.9	3.1	8.7	9.8	3.2
Acetone	−2.40	0.29	6.5	0.063	2.5	0.81	2.3
Acetaldehyde	−2.55	0.049	2.5	0.0085	1.5	0.16	0.9

[a] E_p = −0.98 V. [b] E_p = −0.68 V. [c] E_p = −0.65 V. [d] $k_q/10^9$ dm^3 mol^{-1} s^{-1}. [e] Yield (%).



Scheme 6

The formation of malic acid was reported by Bewick and Greener[33] and by Wolf and Rollin[34] in the electrochemical reduction of carbon dioxide, and also by ourselves in the electrochemical reduction of oxalic acid on mercury at −1.4 V.[35]

Conclusions

We have confirmed and extended the evidence for the formation of single electron reduction products by the reaction of photoexcited quinone radical anions with halobenzenes. These high potential reducing agents have been applied to the reduction of a range of carbonyl compounds to produce largely dimeric products consistent with a radical reduction mechanism followed by dimerisation to pinacol-type products. An unexpected complication was the formation of nitriles which confirmed the work of Bellamy,[19,20] but at much lower potentials, confirming the high potential reducing power added by the photoexcitation. The attempted reduction of carbon dioxide was not successful, probably due to coupling between CO_2 and the quinone radical anion. Reduction of glyoxylic acid was successful, giving the expected tartaric and glycolic acids together with some malic acid. However, the yields of these products were small.

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