# Free Radical Intermediates in the Photoreduction of *p*-Benzoquinone in Ethanol Solution

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To gain deeper insight into the mechanism of photoreduction of *p*-benzoquinone in ethanol, free radicals from solvent ethanol have been studied by means of e.s.r. using phenyl-*N*-t-butyl nitrone as a spin trap, and compared with supplementary results for semiquinone intermediates and the final photoreduction products. Ethoxyl radical and *p*-benzosemiquinone anion have been detected as primary intermediates. The efficiency of their formation can be correlated with the absorption spectrum of the quinone. These results support an ' anionic mechanism ' for the photoreduction of the quinone to the hydroquinone. The photo-induced one-electron transfer results in the formation of the ethanol positive ion and the semiquinone anion, the former is transformed into the ethoxyl radical by rapid proton transfer, the latter into a dinegative ion by a disproportionation reaction, and this is protonated to give the final product, hydroquinone.

ALTHOUGH the photoreduction of quinones has been long studied,[1] there is still controversy about whether the primary chemical reaction of photolytically generated quinone triplets is an electron or a hydrogen transfer. The flash photolysis–optical absorption technique has provided results favouring the latter [2-6] by detecting semiquinone radicals as the primary intermediates from quinone triplets in hydrogen-donating solvents such as alcohols or in the presence of hydrogen donors. The formation of the semiquinone radicals has also been indicated by e.s.r. studies under steady-state [7-9] or flash (or intermittent) photolysis [10-15] of several quinones in alcoholic solutions. However, our steady-state photolysis–e.s.r. studies on *p*-benzoquinone (BQ) in ethanol [16,17] suggested that the photoexcitation of the quinone caused a one-electron transfer from ethanol resulting in the formation of *p*-benzosemiquinone anion ($BQ^-$), and that the *p*-benzosemiquinone radical ($BQH^\cdot$) resulted from reaction between the quinone and hydroquinone ($BQH_2$). Based on the observed kinetic behaviour of $BQ^-$, we proposed an anionic mechanism for the photoreduction of BQ [reactions (1)—(3)]. A one-electron transfer such as reaction (1) has also been demonstrated by Scheerer and Grätzel [18] for duroquinone in water–ethanol solution. Laser photolysis combined with fast conductance measurements showed the quantitative conversion of triplet duroquinone into semiquinone anion with ethanol acting as an electron donor.

$$^3BQ^* + CH_3CH_2OH \longrightarrow BQ^- + CH_3CH_2OH^+ \quad (1)$$

$$2\,BQ^- \longrightarrow BQ + BQ^{2-} \quad (2)$$

$$BQ^{2-} + 2H^+ \longrightarrow BQH_2 \quad (3)$$

The study of free radicals from solvent alcohols may provide a clue for the elucidation of the primary reaction, because the formation of hydroxyalkyl radical is expected from the widely accepted radical mechanism (hydrogen transfer), whereas the alcohol positive ion generated by the anionic mechanism will be transformed into an alkoxyl radical. Although no e.s.r. study has succeeded in detecting either of these radicals directly, McLauchlan and Sealy [19] have briefly communicated a spin trap–e.s.r. study for several combinations of quinones and solvent alcohols. They have detected alkoxyl radicals, whose formation is difficult to interpret on the basis of a radical mechanism.

The present investigation is aimed at providing evidence for the anionic mechanism for quinone photoreduction by extending the spin trap–e.s.r. study for a particular system, BQ in ethanol, though the photoreduction mechanism may perhaps depend on the choice of quinones and alcohols. To provide supplementary data, the semiquinone intermediates and final photoreduction products for the present system will be studied by the flow–e.s.r. during photolysis and the optical absorption photometric methods, respectively, and then compared with the spin trap–e.s.r. results.

## EXPERIMENTAL

*Chemicals*.—BQ and $BQH_2$ were purified as described elsewhere.[17] Ethanol of claimed purity 99.5% was further purified by distilling it after reflux with sodium hydroxide and zinc powder to remove acetaldehyde, except for the flow–e.s.r. experiments where the ethanol was used as received. Phenyl-*N*-butyl nitrone (PBN) was synthesized by refluxing, in dry acetonitrile, 2-t-butyl-3-phenyloxaziridine obtained by *m*-chloroperbenzoic acid oxidation of *N*-t-butylbenzaldimine,[20,21] and used as a spin trap.

*Spin Trap–E.s.r. Experiments*.—The BQ solutions in ethanol containing a small amount of PBN were degassed, sealed in Pyrex e.s.r. sample tubes (0.2 cm i.d.), and photolysed with light of 440 ± 35 nm from a 500 W xenon lamp through filters (Toshiba VY–42 and VV–42). To study the wavelength dependence, light from the xenon lamp was successively cut off with a long-wave pass filter for which 50% transmission wavelengths were 303, 355, 421, 448, 517, and 577 nm. The solutions were subjected to e.s.r. measurements immediately after photolysis. All photolyses and measurements were carried out at ambient temperature (20 ± 2 °C).

*Flow–E.s.r. Experiments during Photolysis*.—The transient semiquinone intermediates were studied by e.s.r. during continuous photolysis of flowing BQ solutions in ethanol, as described in detail elsewhere.[16,17] Photolysis was carried out with light from a super-high pressure mercury lamp (Philips SP–500) passed through a long-wave pass filter, for which 50% transmission was at 316, 346, 390, 441, 485, or 520 nm.

*Optical Absorption Measurements.*—The decay of BQ and the formation of BQH$_2$ were followed by observing their absorption spectra using a recording spectrophotometer (Shimadzu MPS–5000) after photolysis for a given period of a BQ solution in ethanol sealed in a rectangular quartz cell under a pressure of $10^{-5}$ Torr. Photolyses were carried out with either of two monochromatic light sources, a sharp resonance line at 254 nm from a low-pressure mercury lamp (Toshiba GL–15) through a glass filter (Toshiba UVD33S) and an aqueous solution of NiSO$_4$,H$_2$O (500 g dm$^{-3}$) of 1 cm path length, or a 436 nm resonance line from a high pressure mercury lamp (Toshiba SHL–100UV) through glass filters (Toshiba L–42 and V–42).

*Photometry.*—The spectra of all the light sources used were measured by means of a recording monochromator (Nikon G–250) and a photomultiplier (Hamamatsu 1P28) and corrected by means of the diffraction efficiency–wavelength curve of the monochromator and the sensitivity–wavelength curve of the photomultiplier provided by the manufacturers. The light intensity incident on the sample solutions was, when needed, corrected by actinometry with potassium ferrioxalate.[22]

## RESULTS AND DISCUSSION

*Optical Absorption Spectra.*—The optical absorption spectrum of BQ in ethanol is shown in Figure 1A. It consisted of an intense π–π* band with a maximum at 245 nm (ε 22 800 mol$^{-1}$ dm$^3$ cm$^{-1}$) and a shoulder at *ca.* 295 nm (ε 577 mol$^{-1}$ dm$^3$ cm$^{-1}$) and a weak *n*–π* band with a maximum at 435 nm. The molar absorption coefficient of the *n*–π* band is observed to be 18 mol$^{-1}$ dm$^3$ cm$^{-1}$, though this value is not very certain because of a weak background absorption due to unidentified species. These absorption coefficients are in agreement with those reported previously.[23] The absorption spectrum of BQH$_2$ in ethanol is also shown in Figure 1A. The light of 440 ± 35, 436, or 254 nm can excite BQ without interference due to the absorption of the photoproduct BQH$_2$.

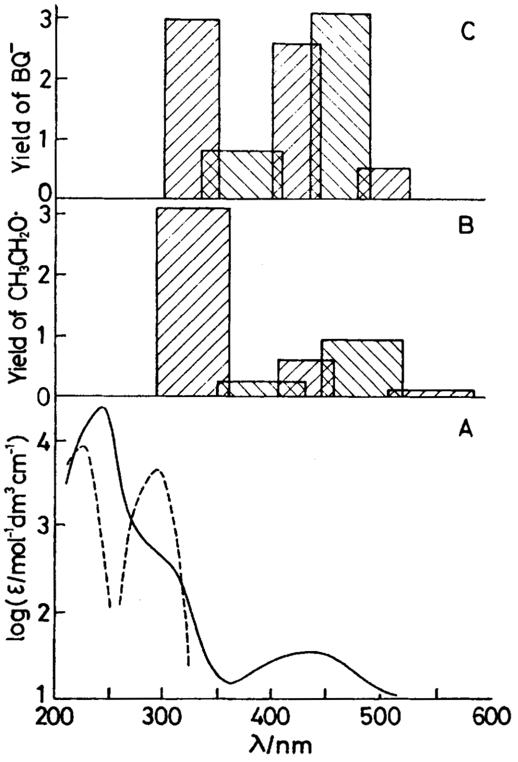

FIGURE 1 A, Optical absorption spectra of (——) *p*-benzoquinone and (– – –) hydroquinone in ethanol solution. B, Dependence of the efficiency of ethoxyl radical formation on the wavelength of light determined by spin trap–e.s.r. measurements for a solution of *p*-benzoquinone (10mM) in ethanol. C, Dependence of the efficiency of the *p*-benzosemiquinone anion formation on the wavelength of light determined by e.s.r. measurements during photolysis of flowing solution of *p*-benzoquinone (1mM) in ethanol. The width of the bars in B and C indicates the effective range of the wavelength of the photolysing light

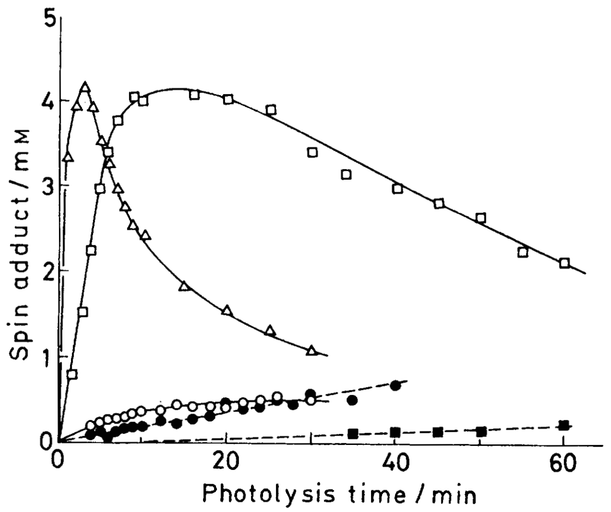

FIGURE 2 Dependence of spin adduct yields on photolysis time for a solution of *p*-benzoquinone and spin trap (10mM) in ethanol. The yields of ethoxyl radical adduct are shown by solid curves for (○) 1, (□) 10, and (△) 100mM-*p*-benzoquinone and the yields of hydroxyethyl radical spin adduct are shown by dashed curves for (●) 1 and (■) 10mM-*p*-benzoquinone. For 100mM-*p*-benzoquinone, no hydroxyethyl radical adduct is observed

*Spin-trapping of Free Radicals from Solvent Ethanol.*—E.s.r. signals observed from BQ solution in ethanol in the presence of the spin trap were generally the superposition of two components. The main component shows a hyperfine splitting constant of 1.46 mT due to a nitrogen nucleus and 0.26 mT due to a proton, and is attributed to the spin adduct generated by the spin trapping reaction between PBN and ethoxyl radical.[24,25] The minor component is assigned from its hyperfine splitting constants (1.53 mT due to nitrogen and 0.37 mT due to a proton) to the spin adduct of hydroxyethyl radical.[24,25]

The dependence of the yield of spin adduct on the photolysis time has been studied for a fixed PBN concentration (10mM) and different BQ concentrations. The results shown in Figure 2 indicate that the ethoxyl radical adduct increases in yield with the length of photolysis. The initial slope is ten times larger for a BQ concentration of 10mM than for 1mM. This proportionality implies that the rate of ethoxyl radical formation is proportional to the rate of photoreduction of BQ. The decay of the ethoxyl radical adduct towards the end of photolysis is a general phenomenon for spin trapping kinetics: spin adducts disappear by reacting with free radicals formed in the reaction.[26,27] In the present system, a slow reaction with the photoproduct $BQH_2$ is also responsible for decay of the ethoxyl radical adduct.

If the BQ concentration is comparatively low, the spin adduct of the hydroxyethyl radical is generated at prolonged photolysis times. This radical can be effectively spin-trapped only when BQ becomes depleted. Reaction (4) is likely to compete preferentially with the

$$BQ + CH_3\dot{C}HOH \xrightarrow{k_4} BQ^- + H^+ + CH_3CHO \qquad (4)$$

spin trapping of the hydroxyethyl radical at high BQ concentration. By adopting the reported value, $4.5 \times 10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$, for $k_4$,[28] a rate constant in the order of magnitude of $10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$ can be estimated for spin trapping of the hydroxyethyl radical from the observation that competition becomes apparent at a BQ concentration of $10^{-3}$—$10^{-2}$M.

The initial slope of ethoxyl radical adduct formation has been studied for a fixed BQ concentration, 10mM, and different PBN concentrations. The rate of adduct formation increases by only ten times, even if the PBN concentration is increased by two orders of magnitude, from 1 to 100mM. Thus, spin trapping of the ethoxyl radical competes with its transformation into the hydroxyethyl radical [reaction (5)]. By utilizing the rate con-

$$CH_3CH_2O\cdot + CH_3CH_2OH \xrightarrow{k_5} CH_3CH_2OH + CH_3\dot{C}HOH \qquad (5)$$

stant for a similar transformation reaction for methanol at 25 °C,[29] the rate constant for spin trapping of the ethoxyl radical can be estimated, by standard competition kinetics, as *ca.* $4 \times 10^8$ mol$^{-1}$ dm$^3$ s$^{-1}$.

These kinetic studies show that PBN is an efficient spin trap for hydroxyalkyl and alkoxyl radicals, though it is inefficient in trapping alkyl radicals.[26,30] McLauchlan and Sealy[19] did not detect hydroxyalkyl radicals but did detect alkoxyl radicals in their spin trapping experiments for several quinones in alcohols, and they have asserted that reaction (4) preferentially competes with the spin trapping reaction. The present results give, on a semiquantitative basis, support for their assertion. It is also probable that, in the photoreduction of BQ in ethanol, ethoxyl radical is the primary radical intermediate generated from the solvent.

The dependence of ethoxyl radical formation on the wavelength of the incident light was determined from the initial slope of the adduct yield–photolysis time curves for a BQ concentration of 10mM and a PBN concentration of 100mM. The rate of adduct formation decreases when photolysing light is successively cut out with the long-wave pass filters. The decrease in the formation rate divided by the difference spectrum from two adjacent filters is shown in Figure 1B as a measure of the wavelength-dependent efficiency. It shows a maximum at *ca.* 450 nm and probably increases with decreasing wavelength below 350 nm, parallel with the absorption spectrum of BQ. This indicates that the ethoxyl radical formation is closely related to the photoexcitation of BQ.

*Formation of Semiquinone Anion and Hydroquinone.*—The wavelength-dependent formation of semiquinone intermediates has been studied by means of e.s.r. during continuous photolysis of a solution of 1mM-BQ flowing rapidly (residence time of the solution within the cell was 75 ms). $BQ^-$ is the only detectable intermediate under these conditions for unfiltered light.[17] The $BQ^-$ spectrum is decreased by cutting out the light successively with the long-wave pass filters. The dependence of the efficiency of formation on the wavelength has been determined in the same way as for ethoxyl radical formation, and is shown in Figure 1C. It does not correspond directly to the spectrum for $BQ^-$ formation, because the observed $BQ^-$ yield depends on the lifetime and hence the concentration of $BQ^-$, the flow rate of $BQ^-$ out of the cell, the change in the optical absorption of the solution during the photolysis, *etc.* However, an efficiency peak at *ca.* 450 nm indicates that $BQ^-$ is generated by $n$–$\pi^*$ excitation of BQ. The increase in efficiency with decreasing wavelength below 350 nm strongly suggests that $\pi$–$\pi^*$ excitation also results in $BQ^-$ formation.

The photolysis of BQ in a dilute ethanol solution (0.5mM) at its $n$–$\pi^*$ band with light of 436 nm results in the decay of the absorption bands of BQ and the growth of $BQH_2$ bands. Isosbestic points observed at 218 and 270 nm indicate a simple transformation of BQ into $BQH_2$. The transformation proceeds almost linearly with the number of absorbed photons. The quantum yields are 0.24 and 0.22 for BQ decay and $BQH_2$ formation, respectively. The results are similar for the photolysis at the $\pi$–$\pi^*$ band of BQ with light of 254 nm; the quantum yields are 0.36 and 0.30 for BQ decay and $BQH_2$ formation.

There is effectively no $BQH_2$ present in the solution at the very beginning of the photolysis. The curves for the formation of $BQH_2$ can be linearly extrapolated to zero. This indicates no change in the reaction mechanism for the photoreduction of BQ to $BQH_2$ in dilute BQ solution regardless of the absence or presence of $BQH_2$, insofar as the photolysing light excites BQ exclusively. Nafisi-Movaghar and Wilkinson[31] have studied the photoreduction of duroquinone in propan-2-ol, and have found a quantum yield of $0.39 \pm 0.02$ for the formation of durohydroquinone; this decreases with the time of photolysis. This decrease has been attributed to quenching of the triplet duroquinone by the photoproduct durohydroquinone. In contrast, the quantum yields are almost unchanged for BQ photoreduction. This difference can be interpreted in terms of the shorter lifetime of the BQ triplet state.[5]

*Reaction Mechanism for the Photoreduction of Benzoquinone.*—The present observations as a whole show that the photoexcitation of BQ results in the formation of the ethoxyl radical from solvent ethanol and simultaneously the formation of $BQ^-$ from BQ. Reactions generating these intermediates lead to the formation of

$BQH_2$ as the main final product of BQ photoreduction. The detection of the ethoxyl radical gives strong support to the anionic mechanism for the BQ photoreduction previously proposed [17] solely on the kinetic behaviour of $BQ^-$ observed by the flow–e.s.r. technique. The only possible source of the ethoxyl radical is reaction (1) followed by the rapid proton transfer reaction (6).

$$CH_3CH_2OH^+ + CH_3CH_2OH \longrightarrow CH_3CH_2O\cdot + CH_3CH_2OH_2^+ \qquad (6)$$

Although no experimental evidence has been obtained for the formation of the dinegative ion, $BQ^{2-}$, reactions (2) and (3) lead to the formation of $BQH_2$ under conditions where $BQH\cdot$ is not observed. The anionic mechanism is also consistent with the second-order decay of $BQ^-$ reported by Harbour and Tollin.[32]

According to the generally postulated radical mechanism, $BQH\cdot$ and hydroxyethyl radical should have been generated as primary intermediates. However, the present results do not accord with this mechanism. Although the formation of the hydroxyethyl radical has been detected in the spin trapping experiments, it is only for such low BQ concentrations that $BQH\cdot$ is undetectable and $BQ^-$ is preferentially observed in the flow–e.s.r. experiment.[17] Therefore, the generation of the hydroxyethyl radical is ascribed to reaction (5) and it is the secondary intermediate.

A crucial argument has recently been put forward by Wong,[15] based on his CIDEP study on naphthosemiquinone intermediates in butan-2-ol, that the weaker signal (or the absence of a signal) for $BQH\cdot$ in our study [17] might be due to the 'accidental' cancellation of the initial emission signal due to the triplet mechanism of CIDEP and the relaxed absorption signal of the residue. Although our previous steady-state e.s.r. study [17] and the present results do not give a definite answer, the observed results are likely to contradict the above view. For instance, the $BQH\cdot$ signal has not been detected at all (either in emission or in absorption) in the present investigation, though the light intensity is reduced by the long-wave pass filters. The reduction of the light intensity results in a decrease in the steady-state concentration of $BQH\cdot$ and an increase in its effective lifetime determined by bimolecular decay. Accordingly, filtering the light should remove the accidental cancellation of the signals for unfiltered light, if any, so that the absorption signal of $BQH\cdot$ should appear for filtered light. The absence of the $BQH\cdot$ signal throughout the present flow–e.s.r. study is very probably not due to a CIDEP effect but to the absence of $BQH\cdot$ formation. Further study is desirable to see to what extent the anionic mechanism valid for the BQ–ethanol system can be generalized to combinations of other quinones and other alcohols.

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