Time-domain electron-spin-resonance studies on hydrogen atom transfer to photoexcited quinones

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Abstract. Time-domain electron-spin-resonance studies on *p*-benzoquinone using ethanol and isopropanol as solvents show emissively polarized ESR spectra of semiquinone and hydroxyalkyl radicals within $0.5\,\mu s$ after the laser pulse at 248 nm. The hydrogen abstraction from the alcohols by the triplet excited quinone is concluded to be the primary photochemical step.

Keywords. Time domain ESR; electron spin polarization; CIDEP; benzoquinone; hydroxy-alkyl radical; semiquinone radical.

1. Introduction

It has been well established during the past decade that time-domain electron-spin-resonance (TDESR) studies provide considerable insight into the dynamics of the elementary steps of photochemical reactions involving free radicals (Muus *et al* 1977; Kevan and Schwartz 1979; Hoff 1989; Kevan and Bowman 1990). In this brief report, we present our recent investigations on the transfer of hydrogen atoms from alcoholic solvents to photoexcited *p*-benzoquinone (PBQ). Kemp and Porter (1971) and later Amouyal and Bensasson (1976) have established the formation of the neutral duro-semiquinone, DQH˙, by the reaction of the triplet of duroquinone (DQ) with solvents such as ethanol and cyclohexane. However, Kemp and Porter (1971) reported their inability to identify the triplet state of *p*-benzoquinone in ethanol, benzene and water. Whether the singlet or the triplet excited state of *p*-benzoquinone was quenched by the solvents could not be ascertained through their flash photolysis experiments with a time resolution of 10 ns. Using a low-frequency modulated light source in time-resolved ESR experiments, Pedersen *et al* (1975) have established that in photolytically produced *p*-benzosemiquinone radical (PBQH˙) in ethylene glycol, the chemically induced dynamic electron polarization (CIDEP) is mainly due to the triplet mechanism (TM). They observed very little CIDEP in the semiquinone spectrum in isopropanol and none in ethanol and methanol. Further, the ESR spectrum of the semiquinone anion radical (PBQ⁻˙) was also observed in ethylene glycol and it also exhibited negligible CIDEP. They postulated that the anion radical was formed by the scheme,

$$PBQH^{\cdot} \rightarrow PBQ^{-\cdot} + H^{+}.$$

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A time-domain ESR study with sub-microsecond time resolution (Trifunac *et al* 1978) of the photolysis of duroquinone in isopropanol has established that at short times after the laser pulse one observes emissive (E) ESR spectrum of the durosemiquinone radical due to TM polarization (all hyperfine lines are in emission) and this gradually changes with the passage of time into an E/A pattern (low field lines in emission/high field lines in absorption) due to the radical pair mechanism (RPM). The radical from the solvent isopropanol was not observed. With *p*-benzoquinone in isopropanol, the ESR spectra of *p*-benzosemiquinone radical alone was observed in emission. However, with benzophenone and isopropanol, the ESR spectrum of the benzophenone ketyl radical and the hydroxy–isopropyl radical, $(CH_3)_2\dot{C}OH$, were observed with E/A polarization showing the dominance of RPM. We have undertaken TDESR studies to delineate the mechanism of hydrogen atom transfer to the quinones in solvents such as ethanol and isopropanol.

Radical formation from alcohols in the presence of duroquinone has been inferred from spin-trapping techniques. In such traps, however, only alkoxy radicals of the type $R_2CH\dot{O}$ have been identified while the hydroxy alkyl radical of type $R_2\dot{C}OH$ have eluded trapping (McLauchlan and Sealy 1976). Chemically induced nuclear polarization studies on the products of the disproportionation of the radical pair have confirmed that the photoreduction of the quinone proceeds through its triplet state (Kuznets *et al* 1977, 1978).

2. Experimental

The time-domain ESR spectrometer described elsewhere (Das *et al* 1986) has been modified to improve its sensitivity by incorporating the following changes: (1) a GaAsFET microwave amplifier (California Amplifier model C53112-5M; gain: 30 dB, noise figure: 2·5 dB) has been incorporated before the mixer detector; (2) the mixer detector has been replaced by a double-balanced mixer (Triangle microwave model FP-1421). For TDESR-flash photolysis studies, the various microwave switches were kept in the appropriate configuration. The photolysis was carried out with an excimer laser (Questek model 2240) with a KrF fill ($\lambda = 248$ nm). The output power was maintained at a constant level during the course of recording a spectrum by the Powerlok feature of the laser. Laser energy of 50–70 mJ per pulse was used. About half of this energy fell on the sample for photolysis. The laser beam was focussed just a short distance away from the sample inside the microwave cavity.

The sample was made to continuously flow through a flat quartz rectangular ESR sample cell at a rate of about 3 ml/min. Pure and dry nitrogen gas, obtained by evaporation of liquid nitrogen, was bubbled through the solution to remove any oxygen. The laser was externally triggered at about 60 Hz. The transient ESR signal from the preamplifier was fed to a pair of boxcar integrators (PARC model 165). One of the integrators, named B, was triggered at a certain time τ_B *before* the laser flash, whereas the other integrator, named A, was triggered at a time τ_A *after* the laser emission. The integrated signal was processed in the difference (A–B) mode by the averager (PARC model 162) and was plotted by an X-Y recorder while scanning the magnetic field linearly by a computer. While the Y-axis of the recorder plots the output of the boxcar, the X-axis is driven by the same linearly changing voltage as the magnetic field scanning voltage provided by the computer. The advantage of

recording the A — B signal with the above setting of τ_A and τ_B is that while it improves the signal-to-noise ratio by subtracting low frequency noises, it also removes the ESR signal of radicals which survive longer than the time interval between two laser flashes (about 17 ms for 60 Hz operation). Thus the recorded signal represents the true ESR intensity of the radical after the laser pulse.

p-Benzoquinone was prepared by oxidation of hydroquinone and purified by recrystallization from benzene followed by sublimation (Gilman 1941).

3. Results and discussion

At 248 nm only the quinone absorbs strongly. The concentration of quinone was adjusted such that 90% of the incident laser energy was absorbed by the sample in a path length of 0·5 mm. Figure 1a is the TDESR spectrum of p-benzoquinone (5 mM concentration) in isopropanol at 1.5 μs after the laser flash. The spectra of both the semiquinone and hydroxy-isopropyl radicals are totally in emission showing the dominance of TM in causing the spin polarization. There is merely a 20% contribution from the RPM mechanism which has an E/A pattern. The overall intensities, though totally emissive, are such that the high-field lines are less intense than the corresponding low-field lines. As expected, the RPM effects are greater on the lines farther from the centre, while the semiquinone spectrum shows very little effect due to RPM. These observations unequivocally show that the hydrogen atom abstraction from alcohol to the photoexcited quinone occurs by the reaction of the triplet state of the quinone. Further, the reaction time is less than the spin-lattice relaxation time of the triplet so that the spin polarization established during the intersystem crossing is passed on to the doublet radicals. The intersystem crossing leaves the $|T_+\rangle$ state of p-benzoquinone preferentially populated. The hydrogen abstraction in the $|T_+\rangle$ state generates both the semiquinone and the hydroxyalkyl radicals in the $|\alpha\rangle$ spin state and thus gives rise to their emissively polarized ESR spectra. The spin-lattice relaxation time of the duroquinone triplet has been reported to be 9·7 ns (Atkins et al 1974). The p-benzoquinone molecule, being smaller that duroquinone, should have a triplet spin-lattice relaxation time of 10 ns or less. Thus the hydrogen abstraction reaction from the alcohol to benzoquinone is essentially complete within this time. This explains why earlier photolysis studies were unable to observe triplets of quinones in alcohols (Kemp and Porter 1971).

As is usual (Verma and Fessenden 1973; Hore et al 1981), the early spectra after the laser flash are broader and, hence, one has to wait about 3 μs to resolve all the hyperfine lines of the semiquinone (figure 1b). At higher concentrations of quinone, which implies that the light is absorbed in the layers close to the laser entry port, the local concentration of radicals is higher. With the benzoquinone concentration just 20 mM, the ESR spectra of both the radicals become broader. When the concentration of benzoquinone was increased to 100 mM we failed to see the radical from the isopropanol though a broad semiquinone spectrum could be seen. The earlier failure to observe the TDESR signals from the alcohol radicals may be attributed to the use of very high concentrations of quinone. Trifunac et al (1978), for example, used 100 mM of benzoquinone in isopropanol. With the local concentrations being high, radical termination reaction could be dominant. Further, concentration broadening of the ESR lines is also quite likely.
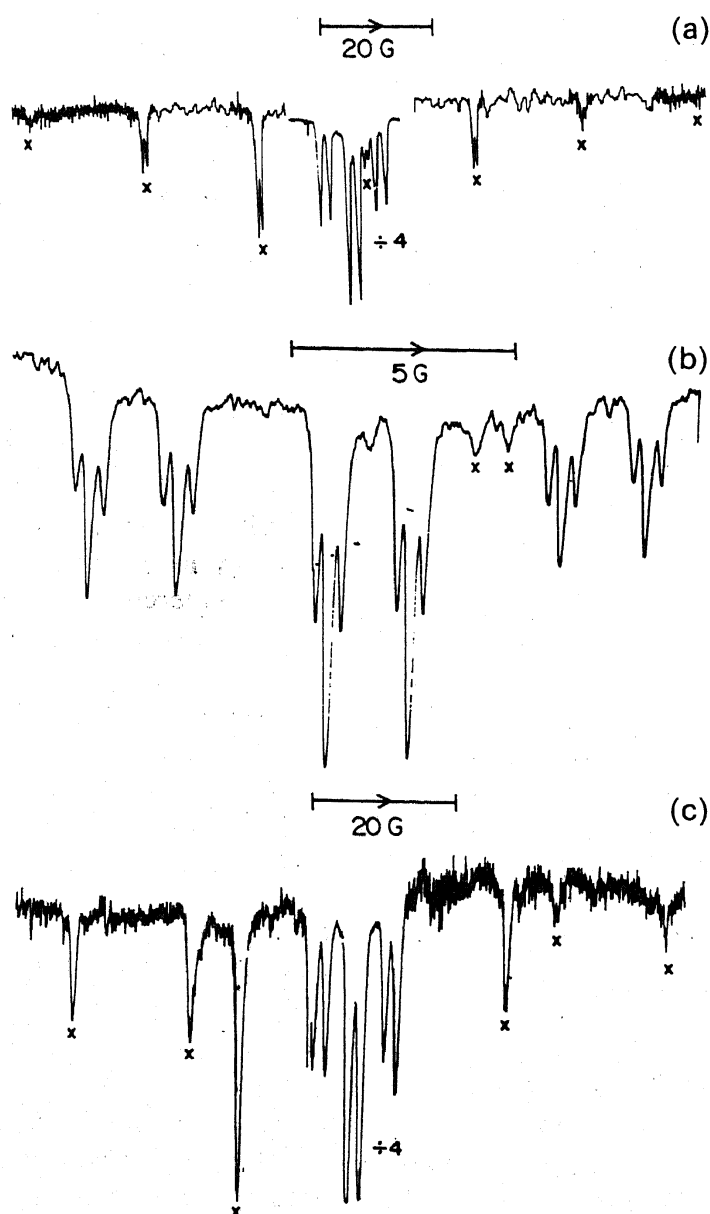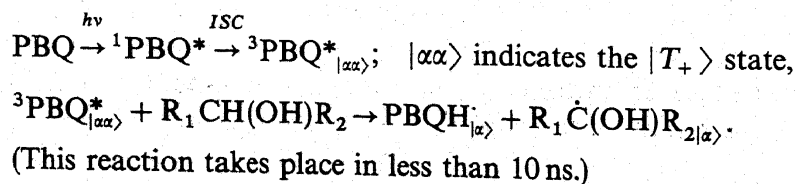
Figure 1. Emissively polarized ESR spectrum of 5mM of *p*-benzoquinone in isopropanol (a and b) and in ethanol (c). (a) 1·5 to 2·0 μs, (b) 3·0 to 3·5 μs, (c) 0·5 to 1·0 μs after the laser flash. The central doublet of the triplet in (a) and (c), shown in reduced gain, is the spectrum of the benzosemiquinone radical. ESR lines due to the hydroxy-isopropyl radical, $(CH_3)_2\dot{C}OH$, in (a) and (b) are marked with a cross ($\times$). Similarly, the ESR lines due to the hydroxyethyl radical, $CH_3\dot{C}HOH$, in (c) are marked with a cross ($\times$). (b) shows only the semiquinone spectrum along with the central doublet (marked $\times$) of the $(CH_3)_2\dot{C}OH$ radical.

With ethanol, the pattern is very similar and the hydroxyethyl radical, $CH_3\dot{C}HOH$, lines together with the lines of *p*-benzosemiquinone radical, are mainly in emission (figure 1c). From these studies we derive that the reaction is:

$$PBQ \xrightarrow{h\nu} {}^1PBQ^* \xrightarrow{ISC} {}^3PBQ^*_{|\alpha\alpha\rangle}; \quad |\alpha\alpha\rangle \text{ indicates the } |T_+\rangle \text{ state,}$$

$$^3PBQ^*_{|\alpha\alpha\rangle} + R_1CH(OH)R_2 \rightarrow PBQH^{\cdot}_{|\alpha\rangle} + R_1\dot{C}(OH)R_{2|\alpha\rangle}.$$

(This reaction takes place in less than 10 ns.)

This is one of the rare cases, as far as we know, where hydroxyalkyl radicals from alcohols have been found to give totally emissive ESR signals. It should be noted that we mainly or solely see the neutral semiquinone radical along with the hydroxyalkyl radical confirming that hydrogen abstraction is the primary step following the photoexcitation of quinone. The presence of the semiquinone anion radicals is not seen in our spectra. The semiquinone anion radical, which has been reported to be formed under similar reaction conditions (Pedersen *et al* 1975), could be formed at later times and may not be spin-polarized. Since our method of detection relies on spin-polarization for its sensitivity, resulting in enhanced intensities of the ESR spectra, it is possible that the anion radical spectra may not be observed here. The benzosemiquinone anion radical may be formed from subsequent reactions, like the deprotonation of the semiquinone (Pedersen *et al* 1975) or an electron-transfer reaction from the hydroxyalkyl radical to benzoquinone as in the case of duroquinone (Willson 1971). Our observations also rule out the formation of semiquinone anion by electron transfer from alcohol to the triplet excited quinone (McLauchlan and Sealy 1976) or electron transfer to excited quinone from alcohol with a deprotonation of the alcohol cation in a single-step process as proposed by Noda *et al* (1982). Studies are in progress with isopropanol-OD and ethanol-OD to confirm the site from which the hydrogen atom is abstracted.

Acknowledgement

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