Electron Transfer vs. Hydrogen Abstraction in Photoreduction of Quinones. An Application of Chemically Induced Dynamic Electron Polarization[1]

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Abstract: Flash photolysis electron spin resonance spectroscopy has been applied to answering the fundamental question in the photoreduction of 1,4-naphthoquinone, whether primarily involving electron transfer to or hydrogen abstraction by the excited triplet state. Hydrogen abstraction has been found to dominate in the pure 2-propanol or 2-butanol, as well as in the presence of pyridine. 1,4-Dihydronaphthoquinone is even a better hydrogen donor. Electron transfer has been shown, however, to be dominant in the presence of triethylamine in alcohol solutions. The effect of chemically induced dynamic electron polarization (CIDEP) must be exploited to solve the problem.

Although the photoreduction of aromatic ketones[2] and quinones[3] has been extensively investigated, the fundamental question, whether primarily involving electron transfer to or hydrogen abstraction by the photochemically excited triplet state, is not always clear and may be very difficult to distinguish. Electron spin resonance (ESR) steady-state studies have usually provided clear-cut evidence for the production of ketyl (semiquinone) anionic or neutral radicals as intermediates[4] in the reaction, while flash photolysis has allowed for the detection and recognition of the precursor of these radical intermediates as the triplet. Flash photolysis studies enjoy the advantages of high sensitivity and fast time response but often suffer from equivocal identification of transients; steady-state ESR studies provide clear-cut identification of intermediates but have little judgement on whether these are primary or secondary. To distinguish between electron transfer and hydrogen abstraction as the primary act of the photochemical reaction requires both unequivocal chemical and kinetic identification of two competing intermediates. Our approach has been to compromise by taking the advantage of the recently established coupling of the two above techniques, flash photolysis ESR spectroscopy[5] (fpesr). The very question was raised by Bridge and Porter[7] in their flash photolysis studies of quinones and dyes nearly 20 years ago but has never answered satisfactorily and remains controversial. They showed in this early study that the neutral semiquinone radical was the primary species and that the anion radical was derived from deprotonation in the photolysis of duroquinone in 98% ethanol solution. That early study also claimed that the photoactive state was the singlet state. This last claim had generated much controversy until recently. It is generally believed now that the photoactive state is the triplet.[8-10]

It has been established by fpesr studies of quinones that a strong photochemically induced dynamic electron polarization may be observed.[11-16] By this means the enhancement of the ESR sensitivity can be increased by more than one order of magnitude.[14-17] Furthermore, the mechanism of CIDEP in the systems has been proven to occur by the photochemical triplet mechanism,[13] the consequence (effect) of which will be resorted to solve the set problem. We have chosen 1,4-naphthoquinone in this preliminary work to demonstrate that this is feasible.

Experimental Section

1,4-Naphthoquinone (Aldrich) was recrystallized from methanol and then further purified by sublimation. 1,4-Dihydronaphthoquinone (K&K) was recrystallized successively from 95% ethanol, hot water, and benzene with a small amount of water. Other chemicals or solvents were of highest purity commercially available; pyridine and triethylamine were further purified by distillation.

The sample solutions contained in 4-mm o.d. suprasil tubes were deoxygenated by purging with nitrogen and then sealed off. The technique of flash photolysis electron spin resonance (fpser) has been generally discussed previously by Bolton and Warden.[5] A Varian E-12 X-band spectrometer using 100-kHz field modulation was employed and the time response of the system has been improved to be about 30 μs by widening the band pass in the "low pass filter". The pulsed light source used (Model 610) was developed here in the Photochemistry Unit and now manufactured by Photochemical Research Associate Inc. A Nicolet 1072 computer of average transient coupled with a Biomation 610B transient recorder was used for collecting and averaging data. For this work 16-64 transients were sufficient for an ESR kinetic curve. For steady-state photolytic ESR studies a 1-kW high-pressure Xe-Hg dc lamp was employed. The ESR spectra of the photoinduced naphthosemiquinone neutral radicals and anion radicals have been described previously.[12,14] All the major hyperfine components of the spectra have been looked at. It should be noted that while the spectra of the two radicals overlap at some filed positions the central component of anion radicals is free from interference from the neutral species, whereas the outmost components of the neutral radicals are free from interference from the anionic species.

Results

Steady-state ESR photolysis of a deoxygenated solution of 1,4-naphthoquinone (NQ) in 2-propanol or 2-butanol at room temperature produced mainly 1,4-naphthosemiquinone neutral radicals NHQ·. Flash photolysis ESR kinetic studies confirmed the previously observed chemically induced dynamic electron polarization (CIDEP) emission for all hyperfine lines[11,12] (Figure 1). The enhancement factor as a measured by the magnitude of emission over that of thermalized absorption signal was increased after a long irradiation. No emission from the anion (NQ⁻·) could be detected. Addition of 1,4-dihydronaphthoquinone to the original solution increased the CIDEP emission. When pyridine (~0.5 M) was added to the solution, the steady-state irradiation gave mainly the signals due to corresponding semiquinone radical anions. Fpesr studies of the anions did *not* reveal emission as shown in Figure 2 while the weaker steady-state neutral radicals on monitoring showed strong emission. When triethylamine (>0.1 M) replaced pyridine, the steady-state irradiation revealed again only anions. In this case, however, strong emission from the anion was discovered in the fpesr studies and the enhancement factor was *larger* than that of NHQ· in the original solution (Figure 3). In contrast the NHQ· escaped detection in the amine solution.

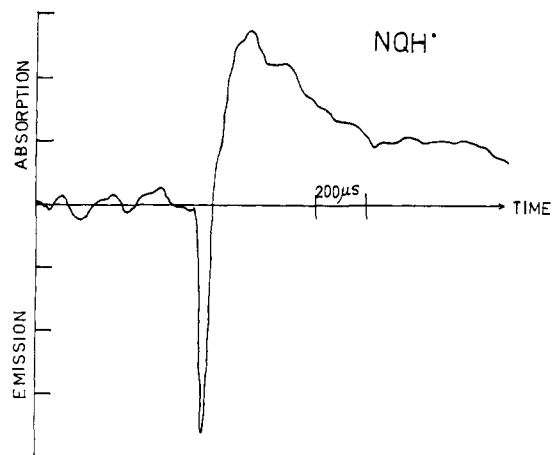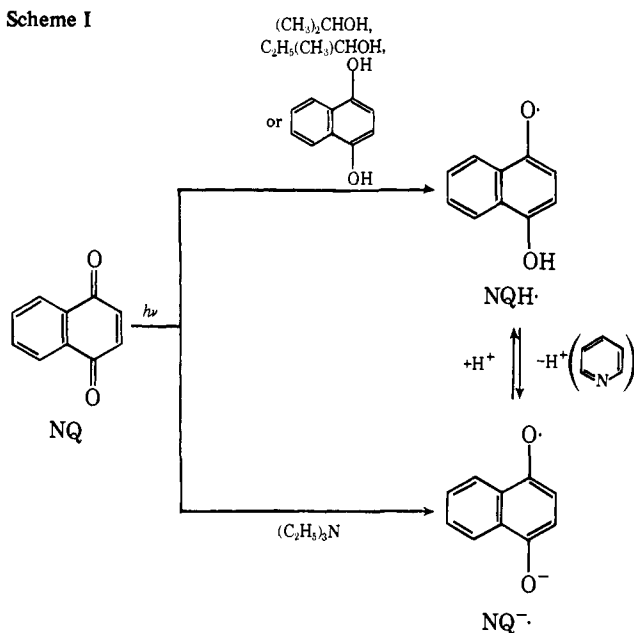## Discussion

Scheme I is sufficient for discussing the results.

Figure 1. Time dependence of ESR signal of 1,4-naphthosemiquinone neutral radicals from flash photolysis of 1,4-naphthoquinone in 2-butanol.

Figure 2. Time dependence of ESR signal of 1,4-naphthosemiquinone anion radical from flash photolysis of 1,4-naphthoquinone in 2-butanol in the presence of pyridine (~0.5 M).

Scheme I

Figure 3. Time dependence of ESR signal of 1,4-naphthosemiquinone anion radical from flash photolysis of 1,4-naphthoquinone in 2-butanol in the presence of triethylamine (~0.2 M).

The spin polarization observed here in the semiquinone neutral radical or anion arises from the spin population trapping[18] on the spin polarized triplet quinone by rapid hydrogen abstraction or electron transfer, respectively. The spin polarization of the triplet quinone is believed to be a consequence of the spin selective intersystem crossing from the excited singlet. The faster the hydrogen abstraction (or electron transfer) the better the spin population trapping and the larger the enhancement factor of the doublet radicals as the rate of the chemical reaction competes with the spin–lattice relaxation of the polarized triplet.[13,17] If the rate of the electron transfer were faster than that of hydrogen abstraction in alcohols we would, unless the anion protonation were extremely fast compared to the spin–lattice relaxation of anion, have observed the spin polarized anion. This proviso may hold in neutral media as the thermal equilibrium is toward NQH· from the steady-state study. However, in the presence of pyridine, the equilibrium is now in favor of NQ⁻·, as witnessed by the steady-state experiment; yet, the emission of the anions could not be observed in contrast to the now less thermodynamically stable species NQH·. The hydrogen abstraction must, nonetheless, dominate the electron-transfer reaction in the alcohols. The observation of larger emission for NQH· on prolonged photolysis of the quinone in alcohol solution is due to the
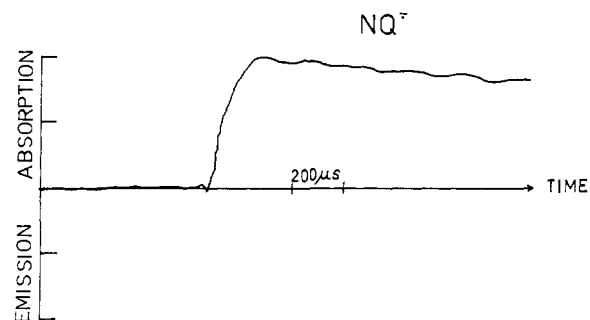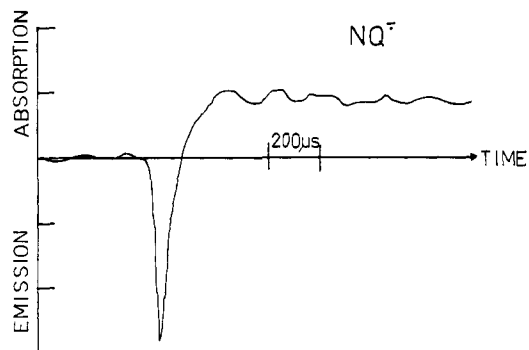
presence of the product of photoreduction, 1,4-dihydro-naphthoquinone, which is a much better hydrogen donor than the alcohols. In agreement, larger emission was observed following the prior addition of 1,4-dihydronaphthoquinone.

When triethylamine was present in the solution the neutral semiquinone radical could not be observed either in the steady-state situation or in kinetic modes. It could be that the hydrogen abstraction to produce NQH· was the faster primary reaction and NQH· was then rapidly converted to the anion under the influence of the much stronger base—triethylamine. This would result in the spin population trapping by deprotonation to generate NQ⁻· in emission as observed. However, in such a mechanism the enhancement factor of NQ⁻· by spin population trapping must always be *smaller* than that of NQH·; the observation is just the reverse. The only conclusion remaining is that electron transfer dominates in the presence of triethylamine in the primary reaction of the triplet 1,4-naphthoquinone with the amine as the electron donor.[20]

To put the present study in perspective, it is appropriate to review and to comment briefly on the recent works in answering this fundamental question. Very recently Scheerer and Gratzel,[21] in a nanosecond flash photolysis study of duroquinone, confirmed that the reactive state was indeed the triplet, but they found that the triplet state of duroquinone in a 2:1 v/v mixture of water–ethanol does not abstract hydrogen but an electron, in contrast to the finding of Porter. Gratzel supported his claim by a flash conductance measurement. The discrepancy is probably caused by "different" solvents; apparently larger amounts of water favor electron-transfer reaction. Steady photolysis ESR studies of *p*-benzoquinone and duroquinone in various solvents revealed the semiquinone neutral radicals as the only or the major paramagnetic species, thus confirming Porter's claim.[22,23] A combined CIDEP and CIDNP study of the photolysis of *p*-benzoquinone in 2-propanol[14] was in agreement with the predominating hydrogen

abstraction mechanism. These CIDNP results were confirmed by Buchachenko et al.[24] very recently. These authors, however, showed that in contrast to *p*-benzoquinone, or its derivative with electron-donor substituents, which reacts with alcohols by abstracting an α-H as the first step, 2,6-diphenylbenzoquinone reacts with alcohols with electron transfer as the first step. Pedersen et al.[25] made a CIDEP study of the photolysis of *p*-benzoquinone is ethylene glycol. They found that the neutral semiquinone has a larger emission than the coexisting anionic semiquinone and concluded that the former radical is the precursor of the latter. After the completion of this work, Yoshida et al.[26] reported a detailed ESR study of the continuous photolysis of a flow solution of *p*-benzoquinone in absolute ethanol. From varying the concentration of *p*-benzoquinone and the flow rate, as well as the previous results on the effect of the wavelength of light, they concluded that electron transfer was induced from ethanol to *p*-benzoquinone. While that work presented a more careful steady-state ESR study, unfortunately it neglected the possible complication from CIDEP effect of the system. The weaker signal of the neutral radical might be due to the cancellation of the initial emission signal and the relaxed residue absorption signal. In other words, in a system where CIDEP effect operates the ESR signal is not a simple measure of concentration because of the nonequilibrium of the spin system and, therefore, further testing is required.

It is worthwhile mentioning here the effort by Roth et al.[27-29] using CIDNP techniques to distinguish between the electron-transfer reaction and the hydrogen abstraction reaction in the photoreduction of aromatic ketones and quinones by amines. They took advantage of the effects of the relatively larger differences in electron g factors of aminoalkyl radicals and aminium radical ions and that of the difference in the hyperfine coupling patterns of the neutral radicals and the radical ions of amine for these studies. In the case of aromatic ketones hydrogen abstraction is shown to be dominating when the amine is aniline or triethylamine as the resulting radical pair is responsible for the CIDNP. When the amine is 1,4-diazabicyclo[2.2.2]octane (Dabco) the electron transfer dominates as the radical ion pair is responsible for the CIDNP. When *N,N*-diethyl-*p*-toluidine is used, they found evidence for both a net hydrogen abstraction from the production of ethyl-*p*-tolylvinylamine and an electron-transfer process from the regeneration of the starting amine by reverse electron transfer. However, the authors conceded that the results obtained in the ketone–amine systems did not lend themselves to answer question whether these intermediates are formed independently from a common precursor or whether the aminoalkyl radicals are formed in a two-step process initiated by electron transfer. Roth[29] has a more definite answer to the above question in his CIDNP studies of photoreduction of *p*-benzoquinone and anthraquinone by triethylamine. While the neutral radical and radical ion reactions were detected simultaneously in these systems, in the case of *p*-benzoquinone in CD_3CN the CIDNP effect of the product diethylvinylamine, which must be formed via the neutral aminoalkyl radical, could only be accounted for by considering the contribution from the radical ion pair. Thus he concluded that the net hydrogen abstraction in this case is a two-step process.

It is quite clear that this preliminary application of the technique of fpesr coupled with CIDEP effect does not provide a general conclusion with regard to the primary reaction in the photoreduction of quinones under various conditions discussed

above but promises a more direct experimental solution of a specific problem. It appears also that CIDNP provides the other facet of the same problem. While CIDEP monitors the free radical, which escapes from the radical pair after photoreaction, CIDNP studies the diamagnetic products (or reactants) which carry the information about the radical pair. Whether they (CIDEP and CIDNP) are always correlated or not is under active investigation.[30] Nevertheless, the photoreduction of quinones not only presents a fundamental and difficult problem for itself but also provides a photochemical system for correlation studies for CIDEP and CIDNP.

References and Notes

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