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MAGNETIC FIELD EFFECT ON THE PHOTOINDUCED ELECTRON TRANSFER REACTION BETWEEN DUROQUINONE AND AROMATIC AMINES IN SDS MICELLAR SOLUTION

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The magnetic field effect($<$80 mT) on the photoinduced electron transfer reaction between duroquinone and aromatic amines in SDS micellar solutions was studied by a nanosecond laser flash photolysis technique. The relative yield of diphenylamine cation free radical increases about 5 % at 79 mT, while that of triphenylamine cation free radical is almost magnetic field independent.

Recently increasing interest is being shown in the study of magnetic field effects on photochemical reactions.1)-7) As for electron transfer reaction, only few photo-redox systems such as pyrene - N-substituted anilines,2),3) and thionine - halogen-substituted anilines4) have been known in homogeneous solutions and there is no study in micellar (micro-heterogeneous) solutions, where the reaction is also important in relation to light energy utilization.

In this paper, we have studied the magnetic field effect on the photoinduced electron transfer reaction between duroquinone and aromatic amines in sodium dodecylsulfate(SDS) micellar solutions by a nanosecond laser flash photolysis technique. In the presence of a magnetic field(79 mT), the yield of diphenylamine cation radical($DA^{\dot{+}}$), generated from the reaction, increases about 5 %, while that of triphenylamine cation radical($TA^{\dot{+}}$) is almost magnetic field inde-

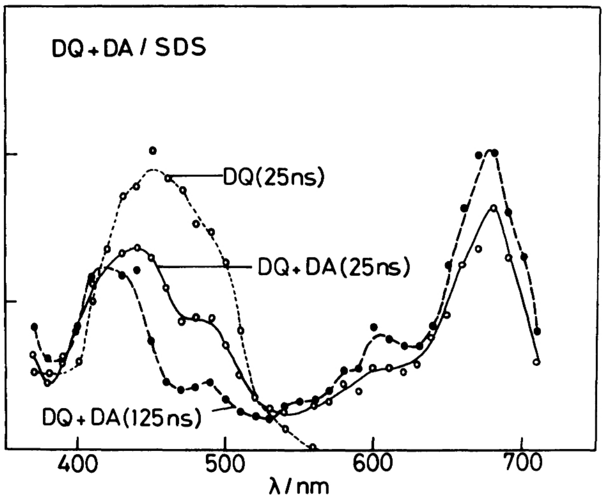


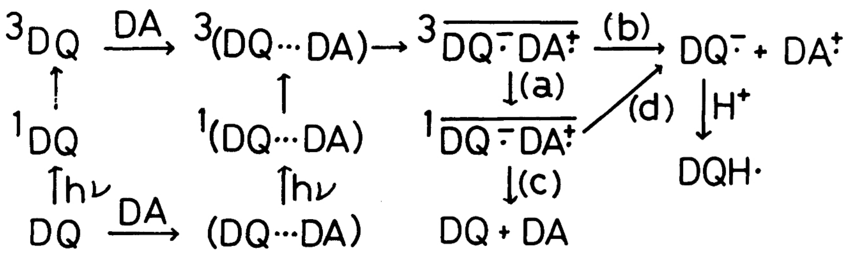
Fig. 1 Transient absorption spectra of air-saturated SDS micellar solution of DQ and DA. Concentrations of SDS, DQ, and DA are 0.4, 8×10^{-3}, and 5×10^{-3} mol dm^{-3}, respectively. --o-- , in the absence of DA at 25 ns delay after laser excitation; —o— , in the presence of DA at 25 ns delay; --●-- , in the presence of DA at 125 ns delay.

pendent.

The laser flash photolysis measurements were made at room temperature by using a Molectron UV-12 N_2 laser as an exciting source.[5)]

Figure 1 shows transient absorption spectra of the laser photolysis of the SDS micellar solution of duroquinone(DQ) and diphenylamine(DA). In the absence of DA, the T-T absorption of DQ appears at the 450 nm region. By the addition of DA to the solution, new transients appear both at 420 and 680 nm, which are assigned to durosemiquinone radical(DQH·) and diphenylamine cation radical($DA^{+\cdot}$), respectively, from comparison with the literature.[8)] Scheme 1 shows the reaction mechanism for the interpretation of the present data.

SCHEME 1



By the addition of DA into the SDS micellar solution of DQ, the ground-state absorption band at the 300-400 nm region slightly increases in intensity; a complex of DQ and DA, (DQ...DA), is probably formed in the ground state. Actually, upon laser excitation, the absorption of $DA^{+\cdot}$ at 680 nm shows an "immediate" ($\leq$20 ns) and a "slow" (~200 ns) growth in intensity. The former is probably due to the formation of the triplet radical ion pair, $^{3}\overline{DQ^{-\cdot}DA^{+\cdot}}$, by direct photoexcitation of the ground-state complex, (DQ...DA). The latter probably corresponds to the generation of $DA^{+\cdot}$ via the excited-state complex formation, ^{3}(DQ...DA), between the triplet state of DQ(^{3}DQ) and DA followed by rapid electron transfer, since the $DA^{+\cdot}$ signal grows up with the rate comparable to the decay of ^{3}DQ. The triplet-singlet intersystem crossing(ISC) (Path a) of the triplet pair, $^{3}\overline{DQ^{-\cdot}DA^{+\cdot}}$, and the separation(Path b) into $DA^{+\cdot}$ and $DQ^{-\cdot}$ free radicals take place competitively. Durosemiquinone(DQH·) is probably generated via rapid protonation of $DQ^{-\cdot}$ free radicals. In the singlet pair, $^{1}\overline{DQ^{-\cdot}DA^{+\cdot}}$, the reverse-electron transfer(Path c) to form DQ and DA and the separation(Path d) of radicals may also take place competitively. Since the absorption spectrum of $DA^{+\cdot}$ in the radical ion pair is very close to that of the free radical ion, the absorption intensity observed immediately after laser excitation is a sum of all $DA^{+\cdot}$ species in the scheme. At a few hundred nanosecond after laser excitation, the intensity is mostly due to the $DA^{+\cdot}$ free radicals.

The magnetic field effect was measured on the transients at 680 nm due to $DA^{+\cdot}$, since the absorption in the 400 nm region is rather complex because of the spectral overlap between the T-T and DQH· absorption bands. The relative yield, $\phi(H)$, of the amine cation free radical formation at several magnetic fields, H, was determined from the transient absorption intensity of cation radicals at 400 ns delay after laser excitation, where the intensity reached its plateau. The change of the yield, R, is defined by the following equation:

$$R = (\phi(H) - \phi(0))/\phi(0) \times 100. \qquad (1)$$

Figure 2a shows the magnetic field dependence of R for $DA^{\dot{+}}$. As is clear from the figure, the change of the $DA^{\dot{+}}$ yield, R, gradually increases with increasing a magnetic field from zero to 79 mT(R = ~5 % at 79 mT), though data points were rather scattered.

On the other hand, transients of the photolysis of DQ and triphenylamine(TA) in SDS micellar solution were similar to those of DQ and DA. The reaction mechanism of this system may be similar to that shown in Scheme 1. The magnetic field dependence of the yield of triphenylamine cation free radical, $TA^{\dot{+}}$, is shown in Fig. 2b. The R values for $TA^{\dot{+}}$ do not show any appreciable increase with increasing a magnetic field(R = ~1 % at 79 mT) within experimental errors.

According to the radical pair model of CIDNP,[9)] the triplet-singlet ISC of a radical ion pair occurs by electron-nuclear hyperfine interaction. At zero magnetic field, triplet sublevels(T_+, T_0, and T_-) of the pair degenerate with the singlet state(S), while, in the presence of a weak magnetic field, only T_0 remains to degenerate with S because of the Zeeman splitting of two other sublevels; the triplet-singlet ISC of a radical ion pair is therefore reduced in the presence of a weak magnetic field. The yield of the $DA^{\dot{+}}$ free radical ion observed seems to

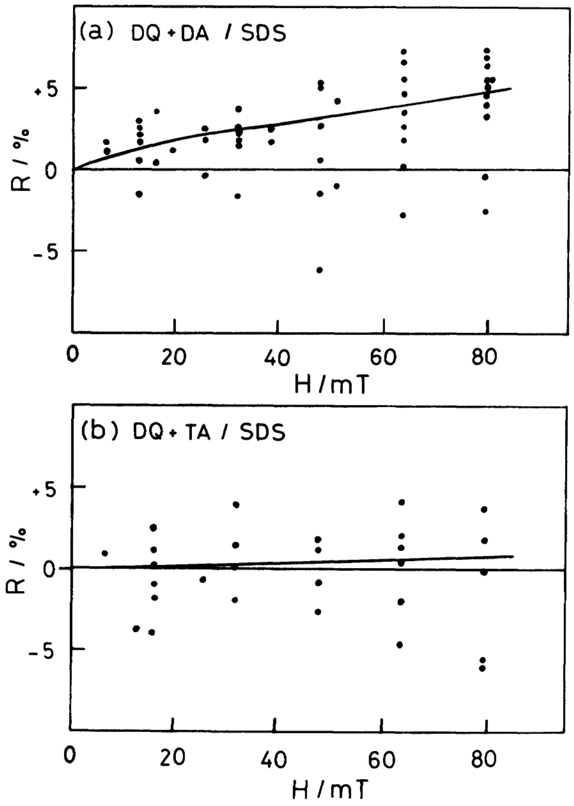


Fig. 2 Magnetic field dependence of R for aromatic amine cation radicals in nitrogen-gas-saturated SDS micellar solution. One data point is an average of five oscillograms. Concentrations of SDS and DQ are 0.4 and 8 x 10^{-3} mol dm^{-3}, respectively. (a) Diphenylamine cation radical observed at 680 nm. Concentration of DA is 5 x 10^{-3} mol dm^{-3}. (b) Triphenylamine cation radical observed at 650 nm. Concentration of TA is 6 x 10^{-4} mol dm^{-3}. For definition, see text.

increase at the expense of the reduction of the competing triplet-singlet ISC rate(Path a). Furthermore, in the present reaction, the two competing processes from the triplet pair, $^{3}\overline{\mathrm{DQ}^{\overline{\cdot}}\,\mathrm{DA}^{\dot{+}}}$, i.e., separation of component radicals(Path b) and triplet-singlet ISC(Path a) followed by the reverse-electron transfer(Path c), take an important role in the appearance of the magnetic field effect; a remarkable effect is observable only when the rates of both processes are comparable to each other. In the photoinduced hydrogen abstraction of benzoquinones,5) anthraquinones,6) and benzophenones7) in SDS micellar solutions, where both rates are comparable to each other, the yield of semiquinone and ketyl free radicals has increased more than 30-40 % at ~80 mT. The triplet-singlet ISC rate is proportional to the weighted sum of hyperfine coupling constants of a radical pair. However, the triplet-singlet ISC of the present pairs does not seem to be much slower than that of other radical pairs mentioned above from comparison of their hyperfine coupling constants estimated. Therefore, small magnetic field effect observed in the present system may be attributable to the slow reverse-electron transfer(Path c), resulting in the generation of free radicals from the singlet pair(Path d). This fact implies the reduction of the magnetic field effect. Actually, the reverse-electron transfer of $\mathrm{TA}^{\dot{+}}$ is expected to be slower than that of $\mathrm{DA}^{\dot{+}}$, as ionization potentials of TA and DA are 6.86 and 7.25 eV, respectively;10) this consideration is parallel with the finding that the magnitude of the effect on $\mathrm{TA}^{\dot{+}}$ yield is smaller than that of $\mathrm{DA}^{\dot{+}}$.

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