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

Yoshifumi TANIMOTO,* Katsuko SHIMIZU, Hiroko UDAGAWA, and Michiya ITOH

Faculty of Pharmaceutical Sciences, Kanazawa University,

Takara-Machi, Kanazawa 920

The magnetic field effect(<80 mT) on the photoinduced elec-
tron 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 triphenyl-
amine 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 anilines[4] 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 diphenyl-
amine cation radical(DA$^+$), generated from the reaction, increases about 5 %,
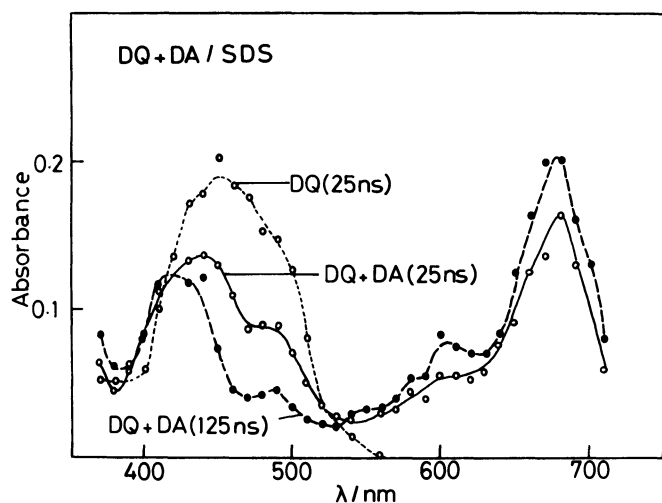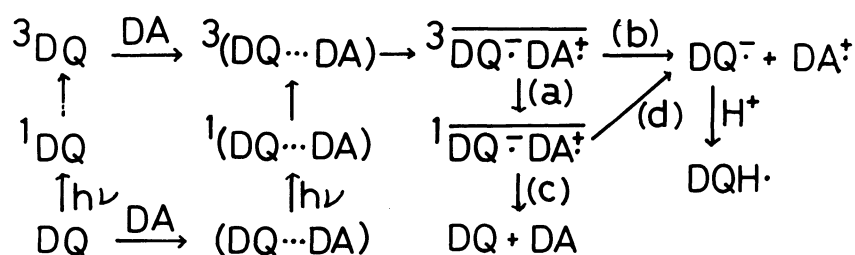while that of triphenylamine cation radical(TA$^+$) is almost magnetic field inde-

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 x 10^{-3}, and 5 x 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 pres-
ence 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^+), respectively, from comparison with the literature.[8] Scheme 1 shows the reaction mechanism for the interpretation of the present data.

SCHEME 1

$$^3DQ \xrightarrow{DA} {}^3(DQ\cdots DA) \to {}^3\overline{DQ^{\overline{\cdot}}DA^{+}} \xrightarrow{(b)} DQ^{\overline{\cdot}} + DA^{+}$$

$$\uparrow \qquad\qquad \uparrow \qquad\qquad \downarrow(a) \qquad\nearrow{(d)}\ \downarrow H^+$$

$$^1DQ \qquad {}^1(DQ\cdots DA) \qquad {}^1\overline{DQ^{\overline{\cdot}}DA^{+}} \qquad\qquad DQH\cdot$$

$$\uparrow h\nu_{\ DA} \qquad \uparrow h\nu \qquad\qquad \downarrow(c)$$

$$DQ \xrightarrow{DA} (DQ\cdots DA) \qquad DQ + DA$$

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^+ at 680 nm shows an "immediate" ($\leqslant 20$ ns) and a "slow" (~ 200 ns) growth in intensity. The former is probably due to the formation of the triplet radical ion pair, $^3\overline{DQ^{\overline{\cdot}}DA^{+}}$, by direct photoexcitation of the ground-state complex, (DQ...DA). The latter probably corresponds to the generation of DA^+ 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^+ 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, $^3\overline{DQ^{\overline{\cdot}}DA^{+}}$, and the separation(Path b) into DA^+ and $DQ^{\overline{\cdot}}$ free radicals take place competitively. Durosemiquinone(DQH·) is probably generated via rapid protonation of $DQ^{\overline{\cdot}}$ free radicals. In the singlet pair, $^1\overline{DQ^{\overline{\cdot}}DA^{+}}$, 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^+ 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^+ species in the scheme. At a few hundred nanosecond after laser excitation, the intensity is mostly due to the DA^+ free radicals.

The magnetic field effect was measured on the transients at 680 nm due to DA^+, 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 rad-
icals 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^+.   As is clear from the
figure, the change of the DA^+ yield, R, gradually increases with increasing a mag-
netic 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 mech-
anism 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^+, is shown
in Fig. 2b.   The R values for TA^+ do not show any appreciable increase with in-
creasing 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 mag-
netic 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
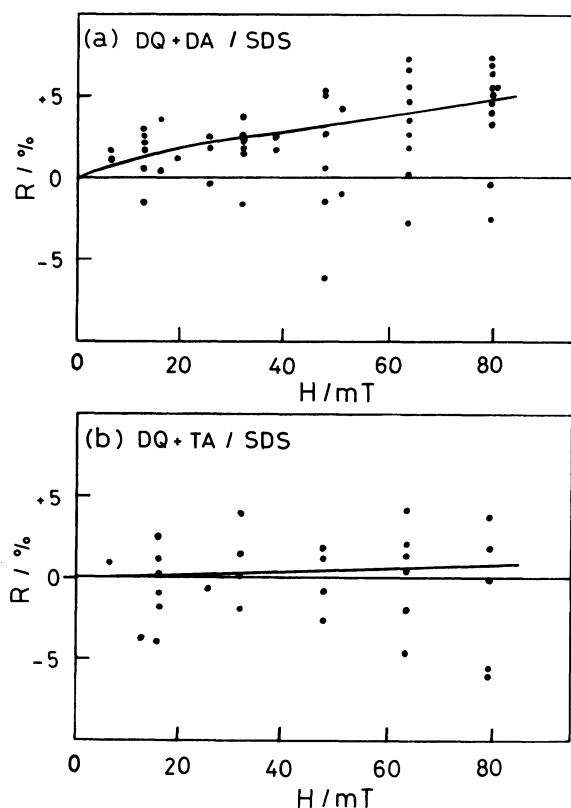a weak magnetic field.   The yield of the DA^+ free radical ion observed seems to

Fig. 2   Magnetic field dependence
of R for aromatic amine cation rad-
icals 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 8×10^{-3} mol dm^{-3}, respec-
tively. (a) Diphenylamine cation
radical observed at 680 nm. Concen-
tration of DA is 5×10^{-3} mol dm^{-3}.
(b) Triphenylamine cation radical
observed at 650 nm. Concentration
of TA is 6×10^{-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, $^3\overline{DQ^-\cdot DA^+}$, 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 benzophenones[7] 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 TA^+ is expected to be slower than that of DA^+, 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 TA^+ yield is smaller than that of DA^+.

References
1) For reviews: Yu. N. Molin, R. Z. Sagdeev, and K. M. Salikhov, Soviet Sci. Rev., Sect. B, Chem. Rev., 1, 1 (1979); N. J. Turro and B. Kraeutler, Acc. Chem. Res., 13, 369 (1980).
2) K. Schulten, H. Staerk, A. Weller, H.-J. Werner, and B. Nickel, Z. Physik. Chem., N. F., 101, 371 (1976).
3) M. E. Michel-Beyerle, R. Haberkorn, W. Bube, E. Steffens, H. Schröder, H. J. Neusser, and E. W. Schlag, Chem. Phys., 17, 139 (1976).
4) U. Steiner, Z. Naturforsch., 34a, 1093 (1979).
5) Y. Tanimoto and M. Itoh, Chem. Phys. Lett., 83, 626 (1981); Y. Tanimoto, H. Udagawa, Y. Katsuda, and M. Itoh, submitted to J. Phys. Chem.
6) Y. Tanimoto, H. Udagawa, and M. Itoh, J. Phys. Chem., in press.
7) Y. Sakaguchi, S. Nagakura, and H. Hayashi, Chem. Phys. Lett., 72, 420 (1980).
8) R. Scheerer and M. Grätzel, J. Am. Chem. Soc., 99, 865 (1977); J. Kiwi and M. Grätzel, J. Am. Chem. Soc., 100, 6314 (1978).
9) R. Kaptein, J. Am. Chem. Soc., 94, 6251 (1972).
10) J. L. Franklin, J. G. Pillard, H. M. Rosenstock, J. T. Herron, K. Droxl, and F. H. Field, Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions, NSRDS-NBS, No. 26, National Bureau of Standards, Washington D. C., 1964.