

A CIDEP Study on the Photoreaction Mechanism of *o*-Quinones

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CIDEP spectra of several *o*-quinone anion radicals generated from the photolyses in the presence of amines have been measured. The T_1 states associated with the reaction were assigned to the $\pi\pi^*$ state for 1,2-naphthoquinone and 9,10-phenanthrenequinone and the $n\pi^*$ for acenaphthenequinone in character.

Time-resolved ESR technique is very useful to study photochemical reaction mechanisms, since the CIDEP spectra observed give information about the character of the excited states taking part in the reaction as well as the produced radical species with a short lifetime. There has been few studies on the photochemistry of *o*-quinones in the light of mechanistic consequence while a number of works on *p*-quinones have been done.^{1,2)} In the present paper, CIDEP spectra obtained from the photolysis of several *o*-quinones in the presence of amines are reported. The quinones are 3,5-di-*t*-butyl-*o*-benzoquinone (*o*-BQ), 1,2-naphthoquinone (1,2-NQ), acenaphthenequinone (AcQ), and 9,10-phenanthrenequinone (9,10-PQ). Electronic structure of the excited triplet states is discussed and photosensitization effects are also mentioned.

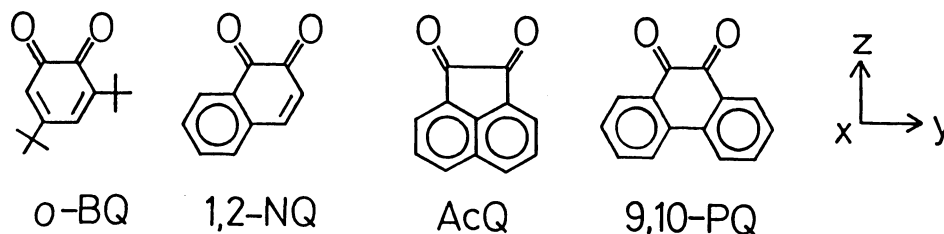


Fig. 1. Molecular structures and axes[†] of *o*-quinones.

[†]In-plane molecular axes for 1,2-NQ are ambiguous because of its low symmetrical structure.

Commercial *o*-quinones (Fig.1) were purified by recrystallization and then sublimation. All sample solutions were prepared at concentration of 5×10^{-3} mol dm⁻³ for *o*-quinones and 0.25 mol dm⁻³ for amines in acetonitrile. Triethylamine was mainly used as electron donor and triphenylamine was partially adopted. The same results were obtained from these amines in the present systems. Sample

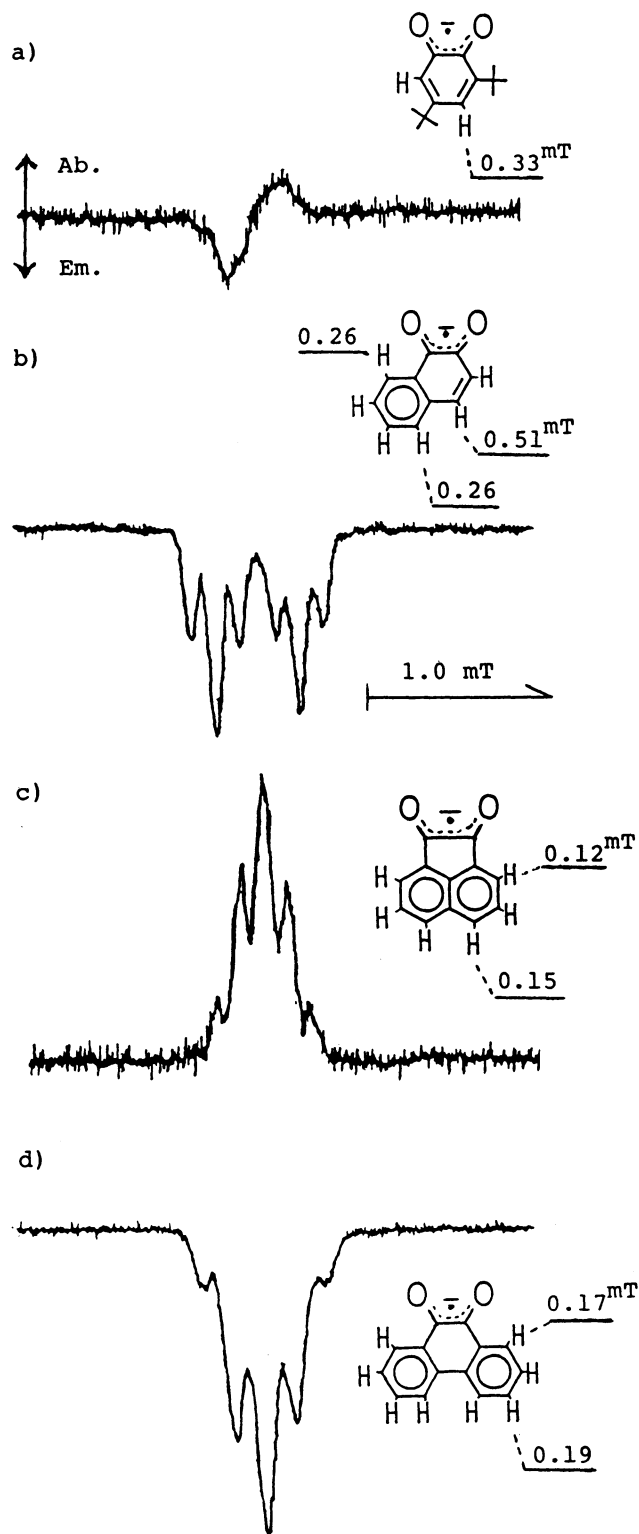


Fig. 2. CIDEP spectra of *o*-quinone anion radicals observed at 1 μ s after excitation of CH_3CN solution in the presence of Et_3N at -30°C .

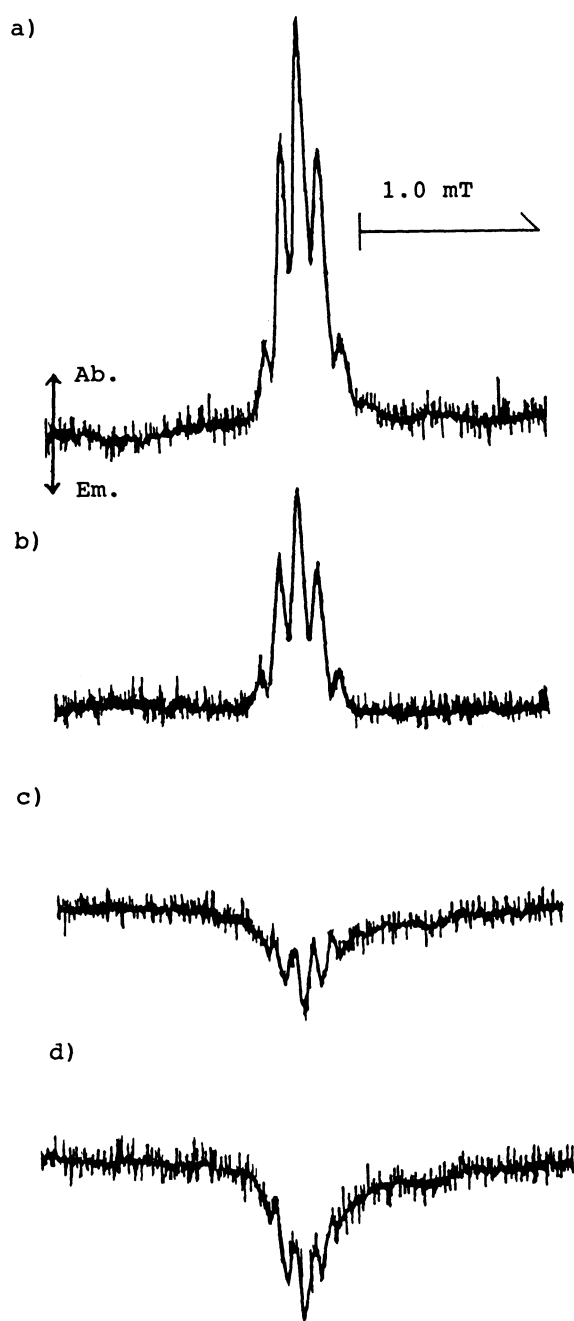


Fig. 3. Effect of benzophenone on the CIDEP spectrum of acenaphthenequinone anion radical. Spectra were observed at 1 μ s after pulse at -30°C . The concentrations of benzophenone are 0.01 (a), 0.02 (b), 0.05 (c), and 0.08 mol dm⁻³ (d), respectively.

solutions were deoxygenated by bubbling with argon gas before the flow measurements. The solutions were flowed in a quartz tube within the cavity of a Varian E 109E X-band EPR spectrometer. Transient ESR signal was directly detected and taken into a boxcar integrator (NF BX-531) at arbitrary times after the laser pulse. An excimer laser (Lumonics HE-420, XeCl) was used as the light source.

Figure 2 shows CIDEP spectra observed at a time delay of 1 μ s after excitation of a mixture of *o*-quinones and triethylamine in CH_3CN at -30°C . The generated radicals were easily assigned to the corresponding anion radicals from the hyperfine splitting (hfs) constants shown in Fig. 2.³⁾ Cation radical of triethylamine was not observed in these systems probably because of the short relaxation time. The spin polarization patterns are E(emission)/A(absorption) for *o*-BQ, total E for 1,2-NQ and 9,10-PQ, and total A for AcQ. These results clearly indicate that electron is transferred from amine to the excited triplet state of the quinone because the CIDEP spectra can be interpreted in terms of triplet RPM (radical pair mechanism) for *o*-BQ and pure TM (triplet mechanism) for the others. The pure RPM observed in *o*-BQ is probably due to the short electron spin relaxation time in the T_1 state. It is interesting that the phase of spin polarization of TM depends on the species in the present systems. Electronic structure of the T_1 states of these *o*-quinones are discussed as follows.

Recently, triplet ESR spectra of 1,2-NQ and 9,10-PQ were measured in glassy matrices at low temperature by using time-resolved ESR method.⁴⁾ In polar solvents, the T_1 states of these quinones were assigned to $\pi\pi^*$ in character from the results that relatively small D values (0.13 cm^{-1} for 1,2-NQ and 0.10 cm^{-1} for 9,10-PQ) and sharp line width of the triplet ESR component were observed. The spin polarization pattern of E EEA/EAA observed in these quinones suggested that the highest spin sublevel is preferentially populated in the $S_1 \rightarrow T_1$ intersystem crossing (ISC) process. It has been reported for *o*-quinones that the S_1 state is $n\pi^*$ (B_1 symmetry) and the lowest level of the $\pi\pi^*$ states has B_2 symmetry.^{5,6)} Therefore, in 1,2-NQ and 9,10-PQ, a dominant $^1n\pi^*(B_1) \rightarrow ^3\pi\pi^*(B_2)$ ISC for T_z sublevel ($Z // C_{2v}$ axis) is expected from theory, since direct spin orbit coupling (SOC) mixes $S_1(n\pi^*)$ only with the T_z sublevel in the $\pi\pi^*$ state. These suggest the order of spin sublevels in $^3\pi\pi^*$ of *o*-quinones to be T_z , T_y , and out-of-plane T_x from the top. Thus, the E-polarization observed in 1,2-NQ and 9,10-PQ anion radicals is consistent with the interpretation that the photo-reduction is induced from $^3\pi\pi^*$ of the quinones, in which the spin preferentially occupies the highest T_z sublevel.

On the other hand, $^3n\pi^*$ is implied as the T_1 state in AcQ, since total A CIDEP pattern was observed in this system. It is known that the energy separation between the $^3n\pi^*$ and $^3\pi\pi^*$ levels is very small in *o*-quinones such as 1,2-NQ and 9,10-PQ. In AcQ, the $^3\pi\pi^*$ state may be closely located above the $T_1(n\pi^*)$ state. Then, ISC ($^1n\pi^* \rightarrow ^3\pi\pi^*$) induced by SOC causes a preferential population of the T_z sublevel in $T_2(\pi\pi^*)$, followed by the subsequent internal conversion with spin conservation leading to a large population of the T_z sublevel in $T_1(n\pi^*)$ of AcQ. It can be deduced from the observation of A CIDEP in AcQ that the order of spin sublevels in the $^3n\pi^*$ state is different from that of the $^3\pi\pi^*$ state. Probably,

out-of-plane T_X sublevel is the highest one in the $^3n\pi^*$ state. It can be thus assumed that the sign of D value in $T_1(n\pi^*)$ of AcQ is positive in the present axis system. Similar result was reported by Grant and McLauchlan,⁷⁾ who observed A CIDEP for the neutral semiquinone radical of AcQ. It is interesting that the $^3n\pi^*$ state in AcQ has a positive D value in contrast to the negative value in p -quinones.⁸⁾

Addition of benzophenone ($E_T = 247$ kJ/mol) to the CH_3CN solution of AcQ (5×10^{-3} mol dm^{-3}) and Et_3N (0.25 mol dm^{-3}) caused a significant change of the CIDEP pattern. As shown in Fig. 3, an E polarization due to AcQ^\cdot was observed above the concentration of 0.05 mol dm^{-3} of benzophenone. Similar result was observed in the addition of 2-acetonaphthone ($E_T = 247$ kJ/mol). However, the addition of triphenylene ($E_T = 281$ kJ/mol) or phenanthrene ($E_T = 260$ kJ/mol) induced no effect on the spin polarization pattern of AcQ^\cdot though the intensity somewhat decreased. These results seem to indicate that the observed E polarization in the addition of benzophenone or 2-acetonaphthone is owing to an electron transfer from the polarized ketyl radical and not to a T-T energy transfer.⁹⁾ The detailed study is in progress.

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