CIDEP Study of 1,4-Naphthosemiquinone in Alcohols

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A Chemically Induced Dynamic Electron Polarization (CIDEP) signal of 1,4-naphthosemiquinone (NQH·) was examined by intermittent-light irradiation to a system of 1,4-naphthoquinone (NQ) and phenol (PhOH) in toluene-2-propanol (2:3), toluene–ethanol (2:3), and neat 2-propanol. The enhancement factors of the initial polarization and the F-pair polarization of the systems were determined separately. From the unusual pattern of a time profile of the ESR signal with a CIDEP phenomenon observed on the photoirradiated NQ–PhOH system in ethanol, it is concluded that in ethanol the photoexcited NQ first abstracts a hydrogen to give NQH·, then NQH· releases a proton to form $NQ^{\overline{\cdot}}$.

Quinones are important compounds in biochemistry, especielly as a component of an acceptor or a carrier of electrons in an electron-transport system in photosynthesis. The photochemistry of quinones in alcohols has been extensively investigated. The primary process has been generally considered to be that of hydrogen abstraction from a solvent by photoexcited quinones. But, the anionic mechanism for the photoreduction of *p*-benzoquinone to the hydronquinone was proposed by Yoshida *et al.*[1] They also reported that when 1,4-naphthoquinone (NQ) in ethanol is photoirradiated, the ESR signal of two types of radicals, *i.e.* semiquinone anion ($NQ^{\overline{\cdot}}$) and semiquinone neutral radical (NQH·), are observed at the same time.[2] Each of these radicals is known to exhibit strong signals due to Chemically Induced Dynamic Electron Polarization (CIDEP) by selecting the conditions of their formation.[3–5]

In a previous paper,[6] we treated a system of duroquinone and phenol (PhOH) in neat 2-propanol or in various organic solvents mixed with 2-propanol and detected the CIDEP signal of durosemiquinone (using a sector system and the usual ESR spectometer with a 100 kHz field modulation). In this paper, we report on a separate determination of the initial polarization (V^{I}) and the F-pair polarization (V^{F}) of NQH· which is produced photochemically from NQ and PhOH in a mixed solvent of alcohols and toluene and in neat 2-propanol. We also report on the reaction mechanism of the photoreduction of NQ with PhOH in alcohols (ethanol and 2-propanol) by taking advantage of a CIDEP phenomenon observed on its semiquinone.

Experimentals

Materials. NQ (Nakarai Chemical Co., G. R. grade) was refined by a sublimation method after being recrystallized from methanol. PhOH, ethanol and 2-propanol (Wako Junyaku, G. R. grade) were used without further purification.

Procedures. The concentrations of NQ and PhOH in alcohols were fixed to 0.05 (or sometimes 0.08) and 2.0 mol dm^{-3}, respectively. The temperature upon irradiation was −40 °C. The CIDEP observation system was almost the same as that used in a previous paper[6] except that a Boxcar integrator (NF Model BX-531 with PB-10 Sampling unit) online with a microcomputer (NEC PC-8001) and a plotter (Watanabe Model WX-4675) were used instead of a minicomputer (JEOL EC-6) and the recorder used in the previous study, respectively. The electronic absorption spectra were taken with a Hitachi 228 double-beam spectrophotometer.

Results and Discussion

Aspects of Absorption Spectra. In order to observe the outline of the photoreaction of NQ in alcohols, the absorption spectra of the systems and their change upon irradiation were observed. A typical example is shown in Fig. 1-a. The difference spectrum (spectrum (4)) obtained from the spectrum (1) (0.05 mol dm^{-3} NQ and 2.0 mol dm^{-3} PhOH in 2-propanol) and (2) (0.05 mol dm^{-3} NQ in 2-propanol) has a new peak at 360 nm. This indicates that an interaction takes place between NQ and PhOH in their ground states. When the light from a high-pressure mercury lamp was irradiated without a filter, the absorption spectrum of the 2-propanol solution containing NQ and PhOH changed with isosbestic points at 346 and 402 nm. Except for the unknown weak band appearing at 420—430 nm, the general feature of the spectral change reflected a decrease of NQ, accompanied with an increase of dihydronaphthoquinone or naphthalenediol (NQH_2), as shown in Fig. 1-b.

ESR Spectra and Its Time Profile. Some examples of the observed ESR spectra are shown in Fig. 2. When 2-propanol was used as a solvent, only the NQH· signal was observed in the photostationary state in cases with or without PhOH. When ethanol was used, the $NQ^{\overline{\cdot}}$ signal was detected overlapping that of NQH·. Especially, in the system containing PhOH, the $NQ^{\overline{\cdot}}$ signal predominated. The hf coupling constants of protons were determined to be 0.324 mT (2H) and 0.064 mT (4H) for $NQ^{\overline{\cdot}}$ and 0.701 mT (1H) and 0.174 mT (3H) for NQH·. These values are consistent with those in the literatures[2,7] within the error limit. The time profile of the ESR signal was observed at magnetic fields fixed at several points along the resonance line. Typical examples are given in Fig. 3 for a NQ

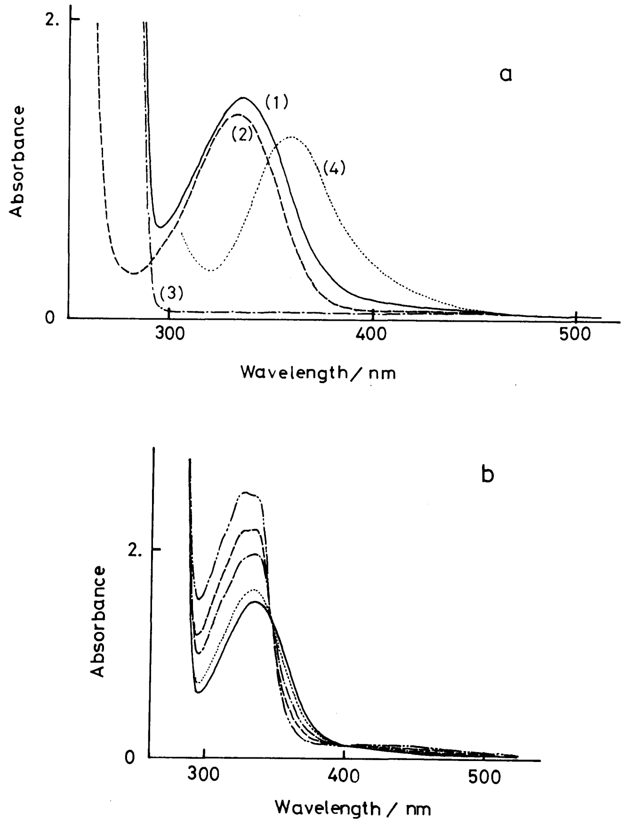

Fig. 1-a. Absorption spectra of CIDEP observation systems.
(1) 0.05 mol dm^{-3} NQ and 2.0 mol dm^{-3} PhOH, (2) 0.05 mol dm^{-3} NQ, and (3) 2.0 mol dm^{-3} PhOH in 2-propanol and (4) the difference between spectra (1) and (2) (the ordinate; × 1/5).
b. Spectral change with photoirradiation: before irradiation (——), 10 min (·······), 50 min (—·—), 100 min (———), and 220 min (-----) irradiation of 2-propanol solution containing 0.05 mol dm^{-3} NQ and 2.0 mol dm^{-3} PhOH by 100 W highpressure mercury lamp without filter.

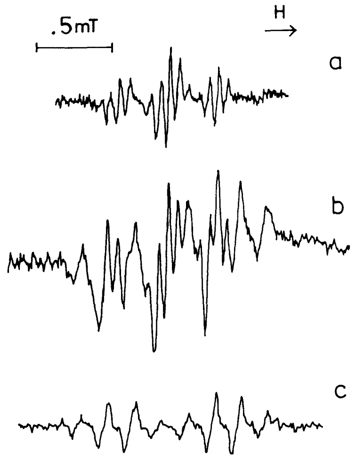

Fig. 2. ESR spectra observed in the photostationary state of the systems a: NQ+PhOH in ethanol at −40 °C, b: NQ in ethanol at −80 °C and c: NQ in 2-propanol at −40 °C.

and PhOH system in a toluene–2-propanol (2:3) mixed solvent. The fixed position of the magnetic field is pointed out by the arrows above the ESR spectrum in the figure. Since we chose 0.2 mT (or sometimes 0.08 mT) as the field-modulation width, the spectrum of NQH· formed a doublet of quartet with a broad linewidth and that of NQ$^{\bar{\cdot}}$ also became a broad triplet. At the end of the light-ON period, a steady state condition regarding radical concentration was achieved. The zero level of the signal intensity was determined by an analysis of the decay curve.[8]

The Enhancement Factor for NQH· Radical. Three kinds of solvent systems, *i.e.* toluene–2-propanol (2:3), toluene–ethanol (2:3) and neat 2-propanol systems, were used for the determination of the enhancement factors V^I and V^F. It is noteworthy that no NQ$^{\bar{\cdot}}$ signal was detected in the solvent systems containing toluene. V^I and V^F were calculated as follows.[8] First, I and I_0 were taken from the pettern in the figure as the difference between the zero level and level e, and that between the zero level and level a, respectively. The dimensionless quantity V' was defined to be $(I-I_0)/I_0$. This is represented as Eq. 1 by using V^I (net effect) and V^F (multiplet effect),

$$V' \equiv \frac{I-I_0}{I_0} = \frac{V^\mathrm{I}}{1+V^\mathrm{F}} \tag{1}$$

As the signal of NQH· radical had no hf line at the center of the spectrum, V^I and V^F were obtainied by using Eq. 2.

$$\left.\begin{aligned} V^\mathrm{I} &= 2\left(\frac{1}{V'(n)}-\frac{1}{V'(n')}\right)^{-1} \\ \bar{V}^\mathrm{F}(\mathrm{n}) &= \frac{\dfrac{1}{V'(n)}-\dfrac{1}{V'(n')}}{\dfrac{1}{V'(n)}+\dfrac{1}{V'(n')}} \end{aligned}\right\} \tag{2}$$

Here, n and n' are the numbers assigned to a pair of hf lines at the symmetric and mutually opposite positions to the center of the spectrum. $V'(n)$ is the value of V' at line n. $\bar{V}^F(n)$ is the mean value of $|V^F(n)|$ and $|V^F(n')|$, and was derived on the condition that $V^F(n)=-V^F(n')$. The time profile was observed at eight field points, each of which corresponded to the maximum or the minimum of hf lines 2, 3, 3′, and 2′, in Fig. 3. The velue of V' was found to be larger at higher field lines. This indicates the presence of a contribution from E/A type F-pair polarization in addition to initial polarization. By the method mentioned above, V^I and V^F values were separately estimated for three solvent systems containing 2.0 mol dm^{-3} PhOH, as listed in Table 1. These values are, however, the apparent enhancement factors. In order to obtain V^I values which can be compared with the values for other solvent systems, the corrections for the radical halflife $t_{1/2}$ and for the spin-lattice relaxation time of the radical T_1 must be made.[9,10] $t_{1/2}$ was evaluated from an analysis of the decay curve after light-OFF in Fig. 3.[8] As T_1 was considered to be independent of a solvent, $\bar{V}^{I}_{av}\ t_{1/2}$ values were calculated and were found to be in good agreement among three solvent systems (see Table 1). When toluene is mixed with the solvent, the viscosity decreases. Consequently, the radical lifetime $t_{1/2}$ becomes shorter. The fact results in an observation of the larger V' (Table 1). Further the intrinsic $\bar{V}^{I}_{av}t_{1/2}$ value was determined in a toluene–2-propanol system to be 7.1 ms by extrapolating the concentration of PhOH to infinite,[9] as shown in Fig. 4. If we borrow a T_1 value of $\approx$10 μs from the data by Frydkjear and Muus,[5] the intrinsic enhancement factor V^{∞}_{int} is calculated to be -7.1×10^2. According to the Eq. 14 of the previous paper,[6] (DK+3EI)$=-0.3\ \mathrm{cm}^{-1}$ is obtained. Here, D and E are zero-field splitting constants, and K and I are parameters showing anisotropy of $S_1\rightarrow T_n$ intersystem crossing rate. (S_1: the excited singlet state, T_n: the n'th excited triplet state). Although the value is based on many assumptions, it seems to be reasonable and be in good agreement with the date obtained by Murai *et al.*[11] They estimated the D and E of the 1,4-naphthoquinone triplet state to be -0.330 and $0.019\ \mathrm{cm}^{-1}$, respectively, by observing the time-resolved ESR spectrum of the triplet state in glassy matrices at 77 K. The longitudinal relaxation time ${}^3T_1$ of the triplet NQ was estimated to be 13 ns from the slope of the plot in Fig. 4, using the value of k_q (the NQ triplet quenching rate constant by PhOH)$=0.58\times10^8$ $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$.[12]

V^F values are given in Table 1 as the form of the ratios of $\bar{V}^F/\bar{V}^I_{av}$ to exclude the effect of the exciting light intensity. The ratio of $\bar{V}^F{}_2/\bar{V}^F{}_3$ is a little larger than the theoretical one based on the radical pair mechanism[13] ($\approx$1.3 by rough estimation) but is reasonable in comparison with the literature.[5]

Mechanism of Photoreduction in Ethanol. The broad triplet line obtained by the use of the modulation of 0.2 mT was assigned to the signal of a NQ$^{\cdot-}$ radical. To take the time profiles, the magnetic field was fixed at a minimum and a maximum signal points of each resonance line of the derivative curve. All six patterns that were recorded were unusual when we assumed the presence of only one radical species. Among them, two most unusual patterns concerning the central resonance line are shown in Fig. 5. At the field point (1) in Fig. 5-a, the absorption of the photostationary signal is represented by the downward one. If the emission of NQ$^{\cdot-}$ occurs immediately after irradiation, the signal level should move upwards. In addition to this, runs both during light-ON and after light-OFF were not simple. These unusual facts can be understood by considering that in this system, first NQH· is formed and it changes to NQ$^{\cdot-}$ during the time scale of the measurement. The following is an explanation for the observation: the *g*-value of NQ$^{\cdot-}$ is a little larger than

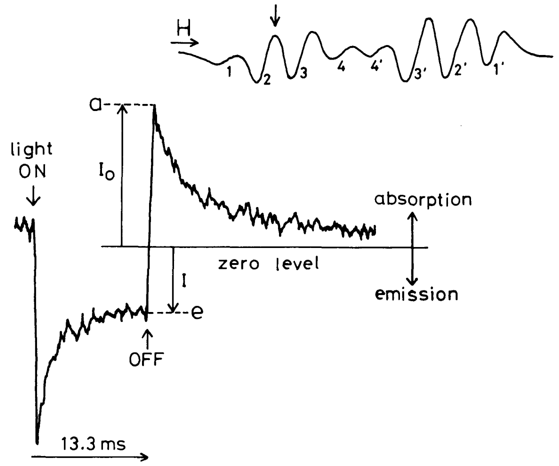

Fig. 3. Time profile of ESR signal intensity observed on NQ and PhOH system in toluene–2-propanol (2:3) mixed solvent.

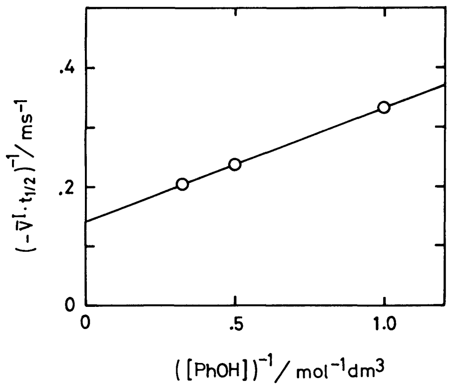

Fig. 4. Effect of PhOH concentration on $\bar{V}^{I}\ t_{1/2}$ of NQH· in toluene–2-propanol (2:3) mixed solvent at −40 °C.

Table 1. Enhancement factors for NQH· radical[a)]

Solvent	$\bar{V}_2{}^{I}$	$\bar{V}_3{}^{I}$	$\bar{V}_{av}{}^{b)}$	$\bar{V}_2{}^F/\lvert\bar{V}_{av}{}^I\rvert$	$\bar{V}_3{}^F/\lvert\bar{V}_{av}{}^I\rvert$	$t_{1/2}$/ms	$\bar{V}_{av}{}^I\cdot t$/ms
Toluene–*i*-PrOH(2:3)	−1.49	−1.50	−1.50	−0.055	−0.022	2.8	−4.2
Toluene–EtOH(2:3)	−1.69	−1.73	−1.71	−0.068	−0.012	2.4	−4.1
i-PrOH	—	—	−0.96	≈0	≈0	4.4	−4.2

a) The system of [NQ]=0.05 mol dm^{-3} and [PhOH]=2.0 mol dm^{-3}. b) The avearage of $\bar{V}_2{}^I$ and $\bar{V}_3{}^I$. Subscripts 2 and 3 indicate the magnetic field position depicted in Fig. 3.

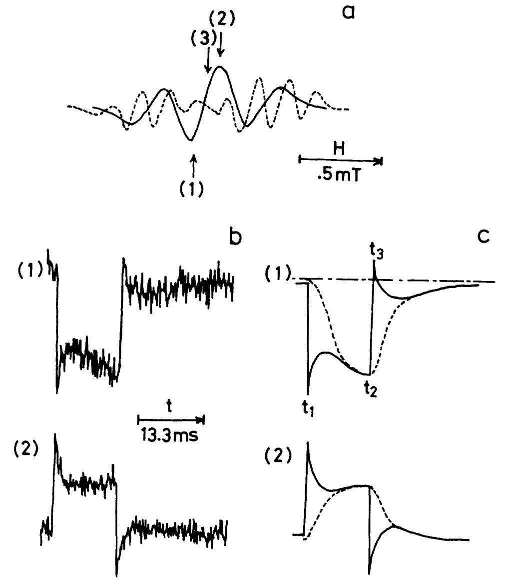

Fig. 5. Time profile observed on NQ and PhOH system in ethanol.
a: The overlapping relation between ESR spectrum of NQ· radical (——) and that of NQH· radical (······).
The arrows numbered (1)—(3) are the fixed tion of the magnetic field.
b: The unusual time profiles. The numbers (1) and (2) correspond to those in a.
c: The time profiles extracted from the runs (1) and (2) in b.

that of NQH·; thus, their spectra overlap with each other as shown in Fig. 5-a. The feature of the run was extracted and is depicted in Fig. 5-c. At time t_1, almost all radical species present were the polarized naphthosemiquinone, NQH·*. Thus, this level is only a reflection of the amount of NQH·*. At t_2, the signal level comprizes those from NQH·*, NQH· (in thermal equilibrium) and NQ$^{\dot{-}}$ (in thermal equilibrium, produced from NQH·). At t_3, the level is the sum of those of NQH· and NQ$^{\dot{-}}$, both in thermal equilibrium. Thus, the following relation holds for these levels:

$$\mathrm{level}(t_2) - \mathrm{level}(t_1) = \mathrm{level}(t_3) \qquad (3)$$

The zero level of this run is determined by Eq. 3, as shown by the horizontal line in the figure. Further, we can infer the time dependence of the formation and disappearance of NQ$^{\dot{-}}$ qualitatively. It may be given by the broken line in the figure, if we assume that V'(NQH·)$=-1$ and the signal intensity ratio of NQH· to NQ$^{\dot{-}}$ at t_2 is -1. The circumstances are the same as with those mentioned above in the case of the field position (2), except that the level movement is upside-down (Fig. 5-c).

In order to make clear that NQ$^{\dot{-}}$ exhibited no CIDEP signal, we carefully chose a field position where NQH· had a zero signal intensity ((3) in Fig. 5-a) and examined the time profile there. The run had much noise but no CIDEP signal appeared. There was some time-lag before a riseup of the signal and the shape of the signal-decay after light-OFF was also unusual. The facts may support the idea that NQ$^{\dot{-}}$ is not formed initially but second in the reaction sequence. Thus, it is concluded that in ethanol photoexcited NQ abstracts a hydrogen atom from PhOH first and changes to NQH·. Then NQH· promptly releases a proton to convert to NQ$^{\dot{-}}$. This is the reason why the NQ$^{\dot{-}}$ signal is observed with continuous light irradiation and no CIDEP signal for NQ$^{\dot{-}}$ is detected in ethanol. In 2-propanol, NQH· does not release a proton. The difference in the behavior of NQH· might be attributed to the slight difference in the dielectric constants of the two alcohols. The idea is consistent with the fact that no NQ$^{\dot{-}}$ signal appeared in a toluene–ethanol system. NQ$^{\dot{-}}$ may be more stabilized in a polar media than NQH·. This conclusion is in contrast to that of Wong,4) who also observed a CIDEP signal of NQH· produced photochemically in 2-propanol or 2-butanol. In his case, the reductant was a solvent. By the addition of pyridine to the solution, NQH· changed to NQ$^{\dot{-}}$, which exhibited no CIDEP signal.

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