Effect of Water on the Photo-Induced Electron Transfer from Hydroquinone to p-Benzoquinone in Solution. Study by Means of ESR and CIDNP.

By

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Abstract

Photo-induced reaction of p-benzoquinone with hydroquinone in solution was investigated by means of ESR and CIDNP. Water present in the solution affected much the relative amount of "free" radical species, quinone anion radical and semiquinone neutral radical which were detected by the ESR signals. Diagnosis of the electron transfer in a solvent cage was done by the CIDNP phenomena. It was concluded that the reaction of this photo-excited redox system was initiated with electron transfer from hydroquinone to p-benzoquinone followed by proton transfer, but not with hydrogen abstraction from hydroquinone.

Introduction

Quinones such as plastoquinone and ubiquinone are well-known electron carriers in the biological redox processes including the photosynthesis. Because of their wide distributions in plants and animals as well as their outstanding biological activities, quinones have attracted many investigators.[1]

Photochemistry of quinones has been a subject of the intensive studies in our laboratory. Especially, the photochemical hydrogen abstraction reactions of p-benzoquinone derivatives,[2] naphthoquinone derivatives,[2] and phenanthrenequinone derivatives[3] have been widely examined. These hydrogen abstraction reactions from hydrogen donors proceed majorly via the in-cage process. In addition, with olefins [$2\pi + 2\pi$] cycloaddition is widely accepted as general trends in the photochemical reactions of quinones.[4] However, substitution reaction of halogenated quinones with olefins induced by initial electron transfer from olefins to photo-excited quinones has been disclosed by the present authors.[5]

An activity of quinones as electron acceptors is the most important role in the biological processes of living things.[6] These electron transfer processes of living things could proceed in a medium in which a lot of water would be present. It is well known that hydroquinone (H_2Q)-p-benzoquinone (Q) system forms one of the typical charge transfer complexes; quinhydrone. The details of its redox process especially in its excited states, however, still remain to be clarified. Using this simple quinone-hydroquinone system we investigated photo-induced electron transfer followed by proton transfer by means of CIDNP and ESR in the presence of a small amount of water in organic solvent.

Since by means of CIDNP radical or electron-transfer process in cage and by means of ESR behavior of "free" radicals out of cage could be disclosed, we applied these methodology to the present investigation. It was confirmed by the present investigation that in the dark electron transfer or even proton exchange could not occur from H_2Q to Q in solution,[7] but upon irradiation electron transfer followed by proton transfer did occur. The reaction courses were profoundly influenced by the amount of added water into organic medium; 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF). Effects of other protic additives; alcohols, on the reaction course were similarly investigated and the structure of lipophilic moiety of the alcohols gave a profound influence on the relative concentrations of radical species.

The problem of structure and properties of water has been attracted the interest of many investigators, especially in the field of physical or biological chemistry.[8] The present work will give an impact to the investigators in the fields.

Results

ESR Spectra and CIDNP Spectra Observed during Irradiation of Hydroquinone (H_2Q)-p-Benzoquinone (Q) System.
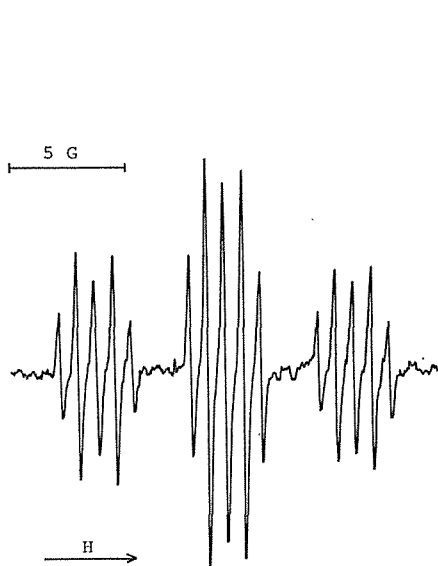

Fig. 1. ESR spectrum observed during irradiation of p-benzoquinone in dry DME.
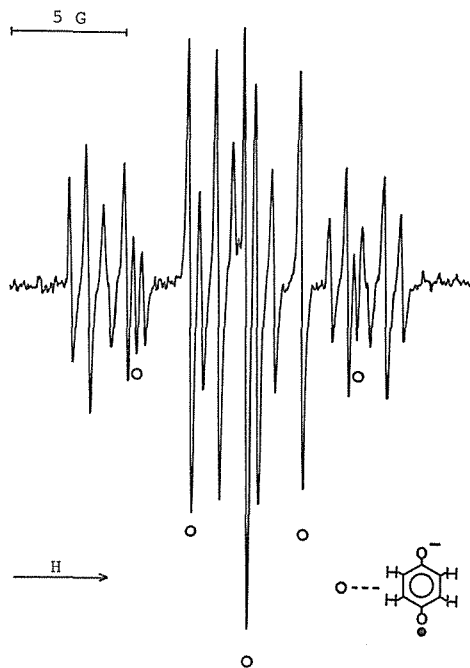p-Benzoquinone; 0.1 M
room temperature.

Fig. 2. ESR spectrum observed during irradiation of a dry DME solution of p-benzoquinone and hydroquinone.
p-Benzoquinone; 0.1 M
Hydroquinone ; 0.2 M
room temperature.

Upon irradiating p-benzoquinone $(5 \times 10^{-8}$ Einsteins/sec.) dissolved in dry DME at room temperature (20°C), only ESR signals due to the semiquinone neutral radical (HQ̇) were observed as shown in Fig. 1. These signals are essentially the same as those reported previously.[9] On the other hand, when a dry DME solution of p-benzoquinone was irradiated in the presence of hydroquinone, both quinone anion radical (Q⁻˙) and semiquinone neutral radical (HQ̇) were observed simultaneously as seen in Fig. 2.

(HQ̇)

$g = 2.0049$
$a_{OH} = 1.50$ G
$a_{H2} = 0.81$ G
$a_{H3} = 5.67$ G

(Q⁻)

$g = 2.0047$

$a_H = 2.36$ G
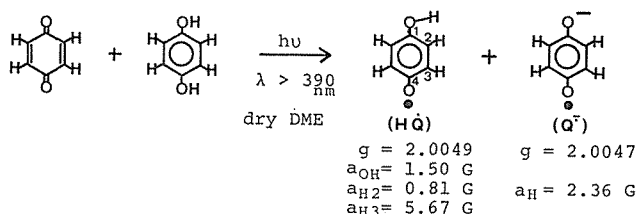
Immediately after turning out the light the ESR signals disappeared completely within 0.1 sec, which indicates the life-time of HQ̇ and Q⁻˙ are less than 0.1 sec. (see Fig. 3).
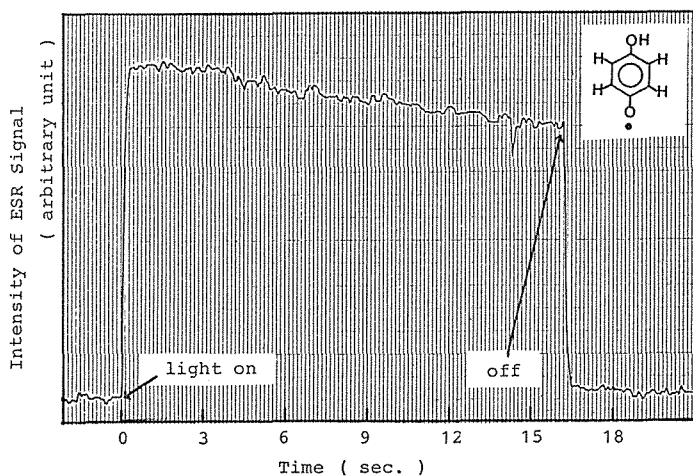

Fig. 3.   Intensity of ESR signal attributable to semiquinone neutral radical (HQ).

The CIDNP technique was applied to this system to investigate the details of the electronic behavior. When Q dissolved in dry DME was irradiated in the presence of H₂Q, the ring-H's of Q showed an enhanced emission signal, whereas the ring-H's of H₂Q an enhanced absorption signal (see Fig. 4).

According to Kaptein's rule,[10] these CIDNP signals clearly indicate that the electron transfer initially occurred from H₂Q to the triplet state of Q, giving a radical ion pair composed of quinone anion radical (Q⁻˙) and hydroquinone cation radical (H₂Q⁺˙). We came to this conclusion considering the following facts. The g-value of Q⁻˙ is determined to be 2.0047 under our experimental conditions, while that
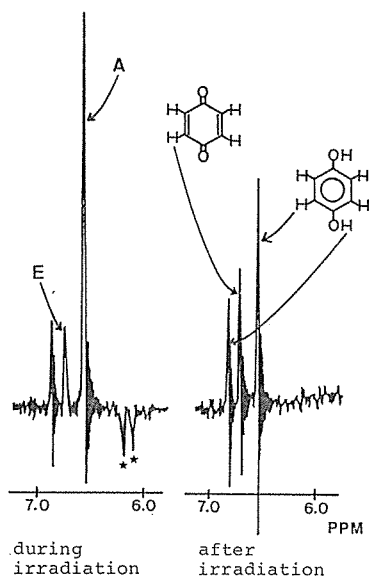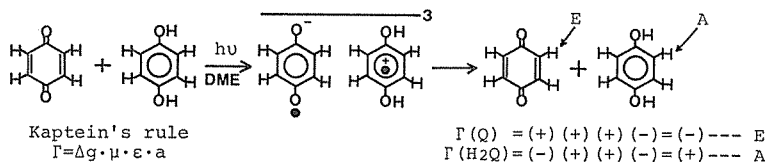
Fig. 4. CIDNP signals observed during irradiation
of a dry DME solution of p-benzoquinone
and hydroquinone.
p-Benzoquinone; 0.02 M
Hydroquinone ; 0.02 M
room temperature.
★ Signals due to minor products originat-
ed from hydrogen abstraction.[2]

of $H_2Q^{\cdot+}$ is reported to be 2.0034.[11] The hyperfine coupling constants (hfcc's) of the ring-H's of $Q^{\cdot-}$ are negative[12] and the hfcc's of ring-H's of $H_2Q^{\cdot+}$ are negative,[13] too. The multiplicity of the radical ion pair $(Q^{\cdot-}, H_2Q^{\cdot+})$ is assumed to be triplet, because Q photochemically excited will readily undergo intersystem crossing to give triplet state.[14]

$$\Gamma(Q) = (+)\ (+)\ (+)\ (-) = (-) \text{---} E$$
$$\Gamma(H2Q) = (-)\ (+)\ (+)\ (-) = (+) \text{---} A$$

Kaptein's rule
$\Gamma = \Delta g \cdot \mu \cdot \epsilon \cdot a$

Successive proton transfer to form stable $H\dot{Q}$ and $Q^{\cdot-}$ would be rather slow process compared with the initial electron transfer as will be described in the discussion below.

The relative concentrations of two stable radical species; $H\dot{Q}$ and $Q^{\cdot-}$, estimated by the intensities of the corresponding ESR signals were much dependent upon the amount of added water into the medium. Upon irradiation an amount of $H\dot{Q}$ and of $Q^{\cdot-}$ was observed in dry DME as shown in Fig. 2, but the relative concentration of $H\dot{Q}$ increased at the expense of $Q^{\cdot-}$, when the water content increased as shown in Fig. 5.

The amount of water in the organic solvent increased up to about 1 M, and then $Q^{\cdot-}$ could not be detected at all. However, the concentration of $Q^{\cdot-}$ increased again by adding water further into the solvent. On the other hand, the concentration of $H\dot{Q}$ increased once and decreased again with increasing the amount of water. Determined from the ESR signal, concentration of $H\dot{Q}$ reached its maximum at
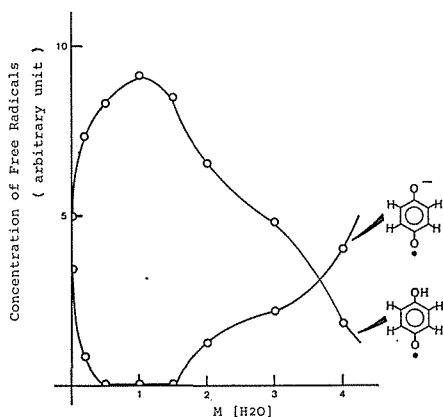
Fig. 5–1. Dependence of radical concentration upon the amount of water added into a dry DME solution of p-benzoquinone and hydroquinone (during irradiation).
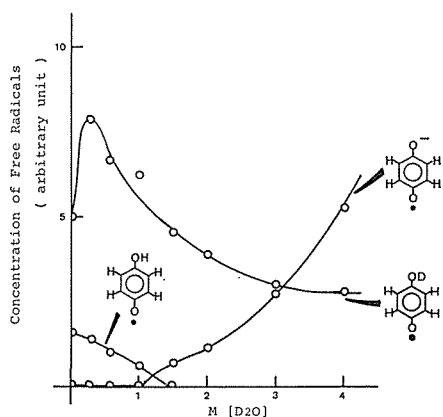p-Benzoquinone; 0.1 M
Hydroquinone ; 0.2 M
room temperature.

Fig. 5–2. Dependence of radical concentration upon the amount of deuterium oxide added into a dry DME solution of p-benzoquinone and deuterated hydroquinone (during irradiation).
p-Benzoquinone; 0.1 M
Deuterated hydroquinone; 0.2 M
room temperature.

nearly one molar of added water, while $Q^{\overline{\cdot}}$ disappeared in this region.   When THF was used as a solvent instead of DME, $Q^{\overline{\cdot}}$ and $H\dot{Q}$ were similarly observed during irradiation in the absence of water.   The dependency of the relative concentrations of two radical species upon the amount of added water showed a similar tendency as in the DME case (see Fig. 6).

Variation of H_2Q/Q dissolved in organic medium affects little on the relative concentrations of $Q^{\overline{\cdot}}$ and $H\dot{Q}$ as shown in Fig. 7.

Fig. 6. Dependence of radical concentration upon the amount of water added into a dry THF solution of p-benzoquinone and hydroquinone (during irradiation).
p-Benzoquinone; 0.1 M
Hydroquinone ; 0.2 M
room temperature.

Fig. 7. Dependence of radical concentration upon the amount of water added into a dry DME solution of p-benzoquinone and hydroquinone (during irradiation).
p-Benzoquinone; 0.1 M
room temperature.

Fig. 8–A

Fig. 8–C

p-Benzoquinone; 0.1 M
Hydroquinone ; 0.2 M
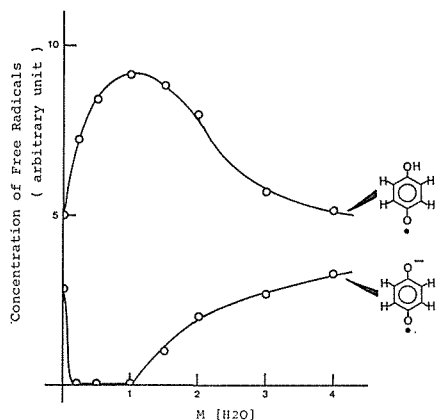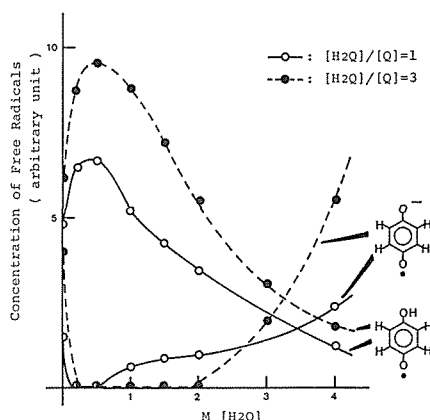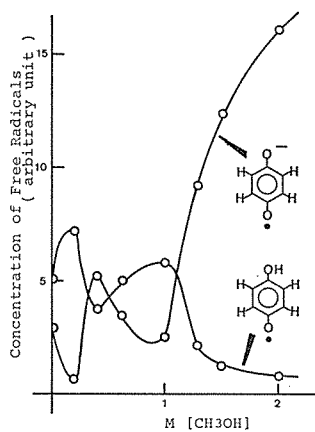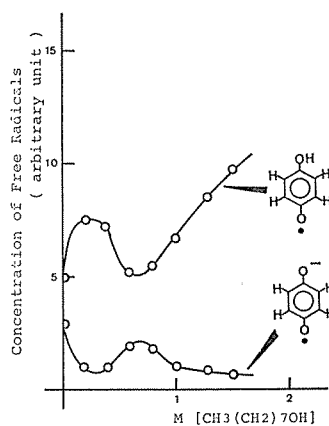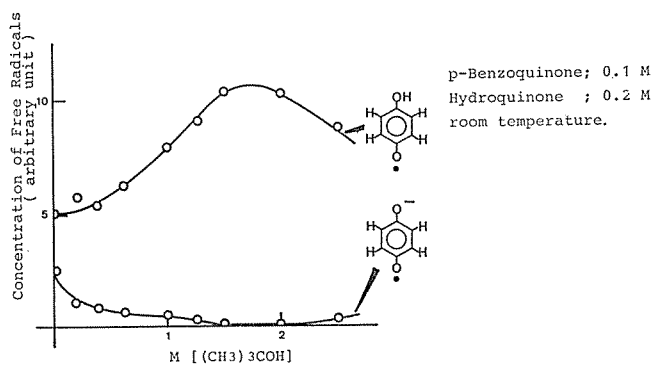room temperature.

Fig. 8–B   Dependence of radical concentration upon the amount of protic
additives added into a dry DME solution of *p*-benzoquinone and
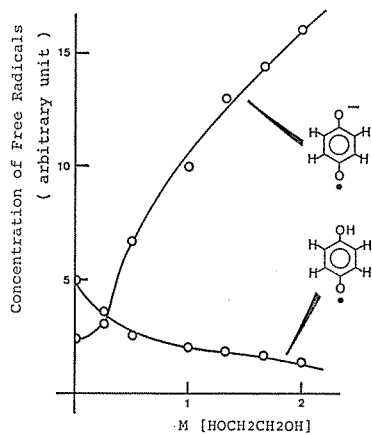hydroquinone (during irradiation).

Fig. 8–D
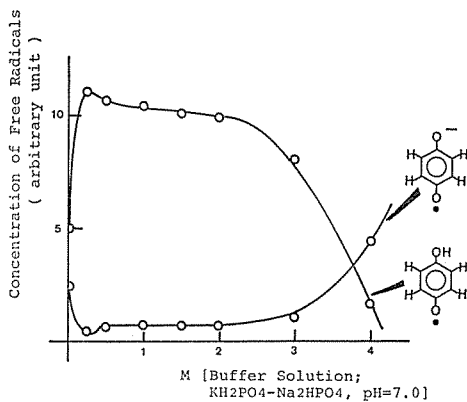
Fig. 8–E

The effect of other protic additives than water was similarly examined by ESR method. The used additives were methanol (Fig. 8–A), t butanol (Fig. 8–B), n-octanol (Fig. 8–C), ethylene glycol (Fig. 8–D), and a buffer solution of water (Fig. 8–E).

The shapes of Q^- vs HQ curves were quite dependent upon the structure of the additives. These facts clearly suggest formation of some sort of local micro-structure among H_2Q, Q, and a protic additive in solution as that depicted in Fig. 9. The reason of this will be discussed later.
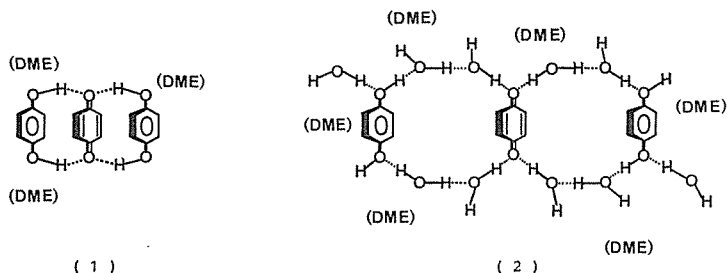
Fig. 9. Schematic presentation of hydrogen-bonded aggregation among hydro-
quinone, p-benzoquinone, and water.
(1) in the absence of water.
(2) in the presence of water.

The CIDNP signals of Q and H_2Q observed in a solution upon irradiation were also affected by adding water as shown in Fig. 10.
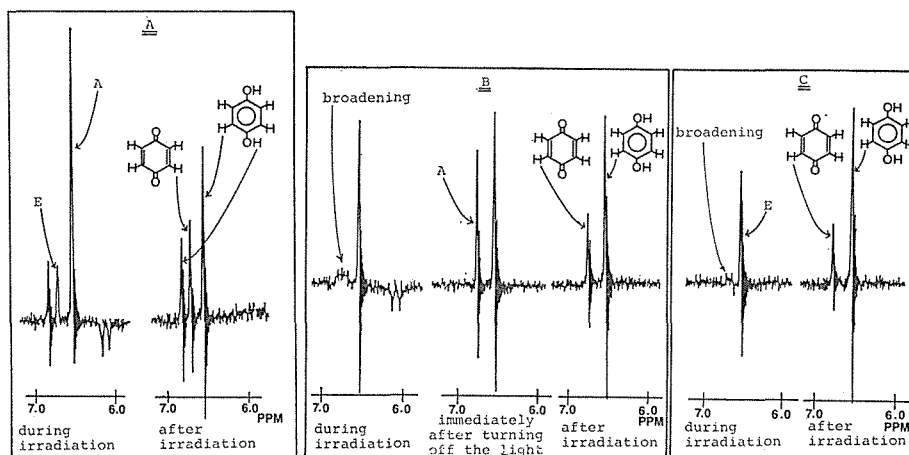
Fig. 10. CIDNP signals observed in the photochemical reaction of p-benzoquinone and hydro-
quinone. Dependence of signal intensity upon the amount of water added into a DME
solution.
p-Benzoquinone; 0.02 M,   A: [H_2O]= 0 M
Hydroquinone ; 0.02 M,   B: [H_2O]=1.0 M
room temperature.   C: [H_2O]=4.0 M

When a small amount of water (1 M) was added into the solution, the ring-H's of Q showed a broadening during irradiation indicating presence of long-lived "free" radicals, and an enhanced absorption immediately after stop of irradiation.[15] On

the other hand, under the conditions the ring-H's of H_2Q did not show any definite polarization as shown in Fig. 10–B. However, when the greater amount (>2 M) of water was added, the ring-H's of H_2Q showed again an enhanced emission instead of an enhanced absorption during irradiation as given in Fig. 10–C. In this case, the ring-H's of Q also showed a broadening during irradiation and an enhanced absorption immediately after stop of irradiation.

These results indicate that the course of the photo-induced electron and proton transfer processes of H_2Q–Q system is quite dependent upon the solvent composition. Using dry THF as a solvent we observed similar changes in the CIDNP signals of Q ring-H's and H_2Q ring-H's. Such the photo-induced electron transfers were confirmed similarly by means of CIDNP technique in several other combinations of H_2Q and Q with electron donating or attracting substituents.

p-Benzoquinone-Hydroquinone Systems with Electron Donating or Attracting Substituents.

Fig. 11. CIDNP signals observed during irradiation of a dry DME solution of chloranil and hydroquinone.
Chloranil   ; 0.02 M
Hydroquinone; 0.02 M
room temperature.

When a mixture of H_2Q and substituted p-benzoquinone with electron donating or attracting substituents dissolved in dry DME was irradiated, CIDNP signals due to both the ring-H's of H_2Q and the ring-H's of Q originated from H_2Q were observed.

By CIDNP;

R = Cl, CH3

Polarization

Upon irradiating a mixture of chloranil (tetrachloro-p-benzoquinone; Cl_4Q) and H_2Q strongly polarized enhanced absorption signal due to the ring-H's of Q and weakly polarized enhanced emission signal due to the ring-H's of H_2Q were observed as shown in Fig. 11.
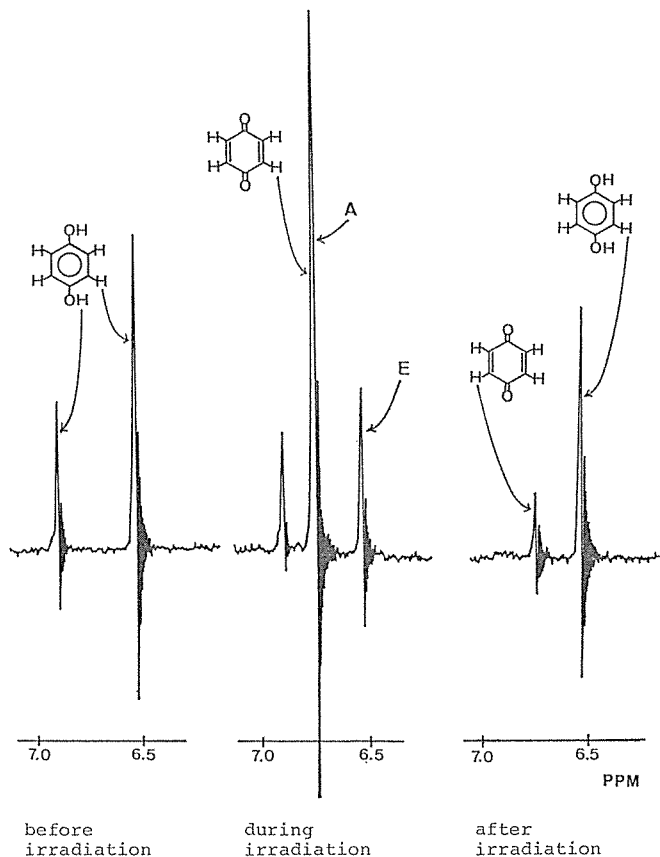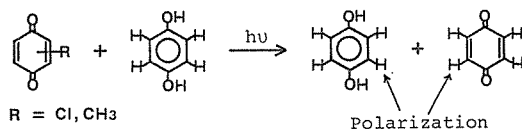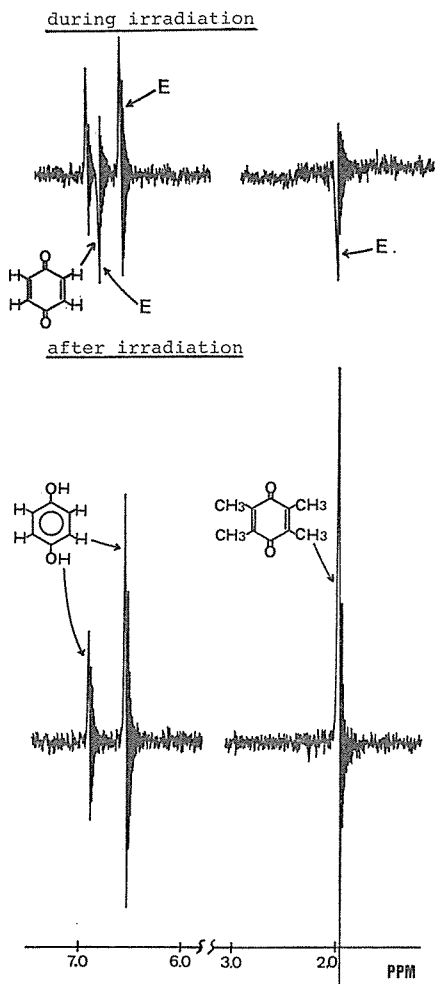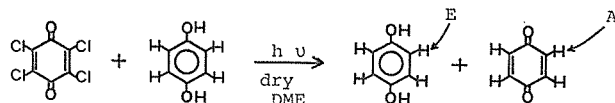

Fig. 12. CIDNP signals observed during ir-
radiation of a dry DME solution of
duroquinone and hydroquinone.
Duroquinone ; 0.02 M
Hydroquinone; 0.02 M
room temperature.

By CIDNP;

On the other hand, irradiation of a mixture cf duroquinone (tetramethyl-p-benzoquinone; Me_4Q) and H_2Q gave an enhanced emission signal due to the ring-H's of Q and an enhanced emission signal due to the ring-H's of H_2Q (see Fig. 12).

By CIDNP;
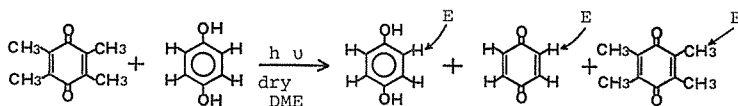
In the case, an enhanced emission signal due to the methyl-H's of duroquinone was observed simultaneously. CIDNP signals observed during irradiation in the reactions of mixtures of substituted p-benzoquinone and H_2Q were listed in Table 1.

Table 1.   Observed CIDNP signals during irradiation.   A DME solution of substituted p-benzoquinone and hydroquinone.

hydro-quinone H_2Q (0.02 M)	quinone Q (0.02 M)	Polarization			
		H_2O; 0 M		H_2O; 2 M	
		B Q	H_2Q	B Q	H_2Q
H_2Q	Cl_4Q	A	wE	E→A	A
	Cl_2Q	A	—		—
	BQ	wE	A	br.→A	
	Me_2Q	wE	—		
	Me_2Q	E	E	br.	E

E   ; strongly enhanced emission.
wE ; weakly enhanced emission.
A   ; strongly enhanced absorption.
wA ; weakly enhanced absorption.
—   ; no polarization.
br. ; broadening.
E→A ; initially enhanced emission and finally enhanced absorption during irradiation.
br.→A ; broadening during irradiation and enhanced absorption immediately after turn-
          ing off the light.
Cl_4Q ; Chloranil.
Cl_2Q ; 2,6-Dichloro-p-benzoquinone.
B Q ; p-Benzoquinone.
H_2Q ; Hydroquinone.
Me_2Q ; 2,6-Dimethyl-p-benzoquinone.
Me_4Q ; Duroquinone.
Solvent; dry DME,   room temperature.

When chloro-substituted p-benzoquinones (chloranil and 2,6-dichloro-p-benzoquinone) were used, Q was detected in the solution after irradiation, while none of it was detected in the solution if one used methyl-substituted p-benzoquinones (duroquinone and 2,6-dimethyl-p-benzoquinone).

The ESR signal observed during irradiation of chloranil-H_2Q system in dry DME was shown in Fig. 13.   Under this condition $H\dot{Q}$ was exclusively recognized, but none of chloranil anion radical or $Q^{\bar{\cdot}}$ was detectable.

Fig. 13.   ESR spectrum observed during irradiation of a dry DME solution of chloranil and hydroquinone.
Chloranil   ; 0.1 M
Hydroquinone; 0.2 M
room temperature.

By ESR;

$$a_{OH} = 0.36 \text{ G} \quad g = 2.0045$$
$$a_{Me2} = 0.97 \text{ G}$$
$$a_{Me3} = 5.63 \text{ G}$$
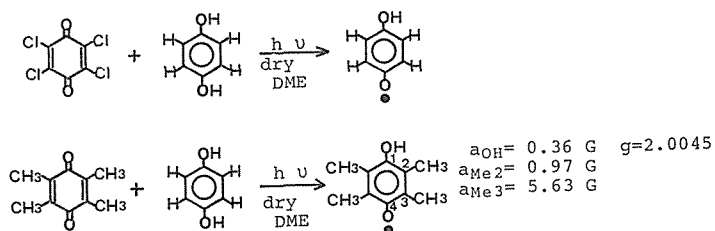
On the other hand, when duroquinone-H_2Q system was irradiated in dry DME, the ESR signal of durosemiquinone neutral radical was exclusively observed as shown in Fig. 14.

However, addition of water in the solutions changed the situations noticeably as shown in Figs. 15 and 16.

For example, at the presence of twenty times molar of water to chloranil (ten times to hydroquinone) into a DME solution of chloranil and H_2Q, one can recognize by ESR that a larger amount of chloranil anion radical ($Cl_4Q^{\bar{\cdot}}$) compared with $H\dot{Q}$ was formed upon irradiation (Fig. 15).   Similarly, addition of twenty times molar of water to duroquinone into a DME solution of duroquinone and H_2Q produces a greater amount of $Q^{\bar{\cdot}}$ and a smaller amount of durosemiquinone neutral radical ($Me_4\dot{Q}H$) and of $H\dot{Q}$ under irradiated conditions.

These phenomena were also reflected on the ^{1}H-CIDNP spectra.   In a dry DME solution of chloranil and H_2Q the strong ^{1}H-CIDNP (absorption) of Q and
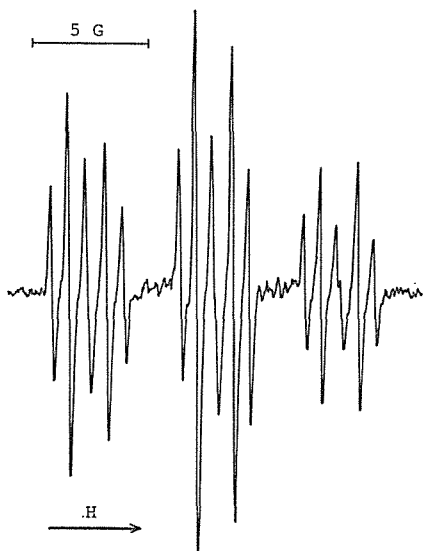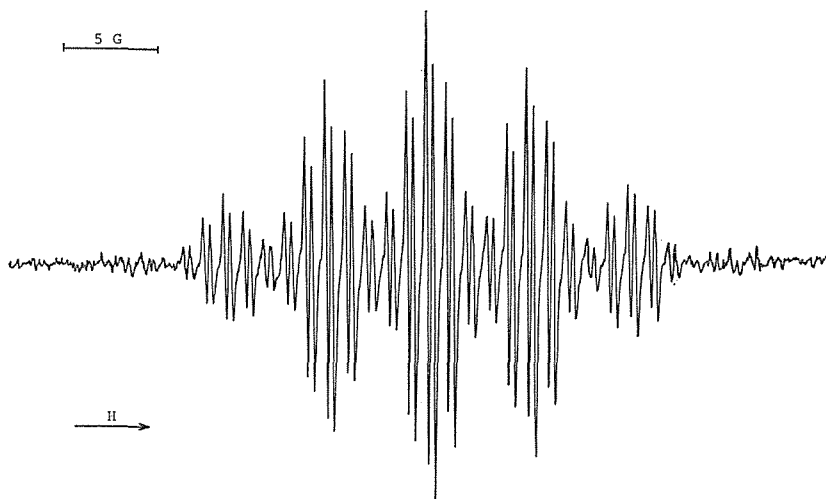
Fig. 14. ESR spectrum observed during irradiation of a dry DME solution of duroquinone
and hydroquinone.
Duroquinone ; 0.1 M
Hydroquinone; 0.2 M
room temperature.
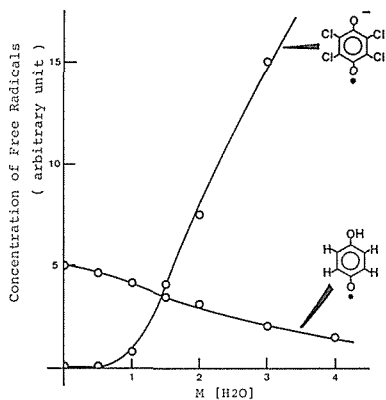
Fig. 15. Dependence of radical concentration
upon the amount of water added into
a dry DME solution of chloranil and
hydroquinone (during irradiation).
Chloranil ; 0.1 M
Hydroquinone; 0.2 M
room temperature.
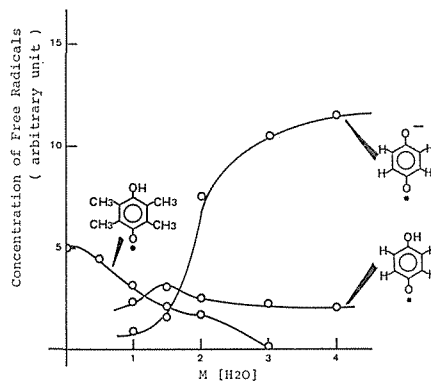
Fig. 16. Dependence of radical concentration
upon the amount of water added into
a dry DME solution of duroquinone
and hydroquinone (during irradiation).
Duroquinone ; 0.1 M
Hydroquinone; 0.2 M
room temperature.

the weak ^{1}H-CIDNP (emission) of H_2Q were observed as described above, while
in the presence of water (twenty times to chloranil) one can observe time-varying
^{1}H-CIDNP polarization from emission to absorption of Q and the inverted polariza-
tion of H_2Q (absorption) as given in Table 1. Variation in the ^{1}H-CIDNP of duro-
quinone-H_2Q system in a DME solution with and without water upon irradiation
was not so dramatic, but the ^{1}H-CIDNP of H_2Q became strong, and the ^{1}H-NMR
signals of Q and duroquinone showed broadening.

The results given in Table 1 as well as those observed by ESR indicate unambiguously that the initial process of the present photo-induced reactions is an electron transfer reaction.

Discussion

Schematic presentations of the present photo-induced electron transfer process between H_2Q and Q will be shown in Scheme 1 and 2.   The reasoning will be given below.

Q + H_2Q $\rightleftharpoons$ $(Q \cdot H_2Q)_{molecular\ complex}$ $\xrightarrow{h\upsilon}$ $(Q^{3*} \cdot H_2Q)_{molecular\ complex}$

e-transfer

$[Q^- , H_2Q^+]^3_{cage}$

H^+-transfer   free radical formation

$[H\dot{Q} , H\dot{Q}]_{cage}$ $Q^- + H_2Q^+$

free radical formation $[Q , H_2Q]_{cage}$ e-transfer

$2 H\dot{Q}$

disproportionation $Q + H_2Q$

——: detected by ESR.
══: showed ^1H-CIDNP.
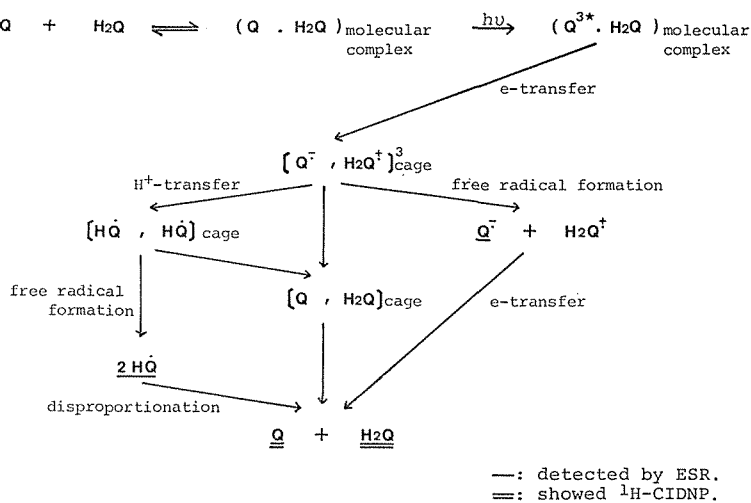
Scheme 1   In dry DME.

In highly wet DME.

Q + H_2Q + nH_2O $\rightleftharpoons$ $(Q \cdot nH_2O \cdot H_2Q)_{molecular\ aggregation}$

$h\upsilon$

$(Q^{3*} \cdot nH_2O \cdot H_2Q)_{molecular\ aggregation}$

e-transfer

$[Q^- , nH_2O , H_2Q^+]^3_{cage}$

free radical formation

$Q^- + H\dot{Q} + H_3O^+ + (n-1)H_2O$

——: detected by ESR.
══: showed ^1H-CIDNP.

$Q + H_2Q$
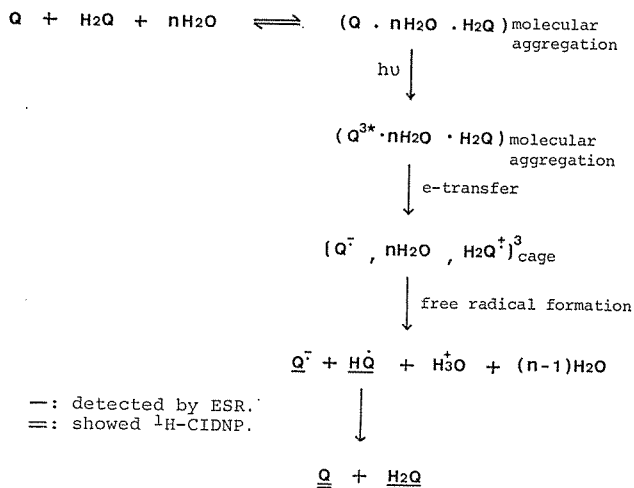
Scheme 2   In highly wet DME

When Q dissolved in dry DME was irradiated, excited triplet state of Q ab-
stracted hydrogen atom from DME, giving HQ̇ only as detected by ESR technique.
No electron transfer could be observed in this case. On the other hand, in the
presence of H_2Q the observed ESR spectrum was composed of a mixture of HQ̇ and
Q̇⁻ as shown in Fig. 2. These results show clearly the contribution of some other
processes than the hydrogen abstraction.

It is most probable that Q̇⁻ identified by the ESR was generated as the result of
an electron transfer from hydroquinone. As described in the Results, the initial
electron transfer from H_2Q to photo-excited Q is further supported by analyzing
direction of the CIDNP signals due to the relevant species. Upon irradiation of a
mixture of Q and H_2Q in DME we observed ^{1}H-CIDNP signals attributable to the
ring-H's of Q and H_2Q. Q showed an enhanced emission (E) signal and H_2Q
an enhanced absorption (A) signal. According to Kaptein's rule[10] the expected
polarization based on the electron transfer process predict us (E)-polarization for
Q and (A)-polarization for H_2Q, consisting with the experimental results. All of
the investigations examined by ^{1}H-CIDNP, which is summarized in Table 1 and
2, indicate that an initial electron transfer from hydroquinone to quinone is involved
as the major process in the photo-induced reaction.

Table 2. Observed CIDNP signals during irradiation.
A DME solution of p-benzoquinone and sub-
stituted hydroquinone.

quinone Q (0.02 M)	hydro-quinone H_2Q (0.02 M)	Polarization	
		BQ	H_2Q
	Cl_4H_2Q	A	A
	Cl_2H_2Q	A	A
B Q	H_2Q	wE	A
	Me_2H_2Q	—	wA
	Me_4H_2Q	wE	wA

E   ; strongly enhanced emission.
wE   ; weakly enhanced emission.
A   ; strongly enhanced absorption.
wA   ; weakly enhanced absorption.
—   ; no polarization.
Cl_4H_2Q ; Tetrachlorohydroquinone.
Cl_2H_2Q ; 2,6-Dichlorohydroquinone.
B Q   ; p-Benzoquinone.
H_2Q ; Hydroquinone.
Me_2H_2Q; 2,6-Dimethylhydroquinone.
Me_4H_2Q; Tetramethylhydroquinone.
Solvent ; dry DME, room temperature.

The electron transfer process is much dependent upon the amount of water added
into the solution. As shown in Fig. 5–1, the relative concentrations of two radical
species as observed by ESR technique, were changed with the amount of water.
With increasing the amount of added water the concentration of HQ̇ reached once

at the maximum ($[H_2Q]$: nearly 1 M) and decreased gradually, while that of $Q^{\overline{\cdot}}$ decreased at first to zero and increased again. Since the reproducibility of all experiments are quite good, this sort of interesting phenomena could indicate the existence of some regularity concerned with the relevant radical species in the solution. As given in Fig. 8–A, B, C, and D the shape of $Q^{\overline{\cdot}}$ vs $H\dot{Q}$ curves were quite dependent upon the structure of the protic additives, too. When deuterium oxide (D_2O) was used instead of water, the shape of $H\dot{Q}$ vs $Q^{\overline{\cdot}}$ curve changed greatly as depicted in Fig. 5–2, inducing left hand shift for the maximum of $D\dot{Q}$ curve. These facts make us imagine the existence of a local molecular aggregation among $Q^{\overline{\cdot}}$, water, $H\dot{Q}$, and their hydrated species. This idea is supported by the variation of the proton hyperfine coupling constants of $H\dot{Q}$ with the structure of the additives in solutions as given in Table 3.

Table 3. Hyperfine coupling constants of semiquinone neutral radical ($H\dot{Q}$).

Solvent	DME						CH_3CN	THF	Benzene
Additive (2 M)	H_2O	HOCH$_2$ CH$_2$OH	CH_3OH	$(CH_3)3COH$	$C_8H_{17}OH$	—	—	—	—
a_{OH} (G)	1.65	1.65	1.65	1.63	1.56	1.50	1.55	1.51	1.14
a_{H2}	0.56	0.56	0.60	0.65	0.69	0.81	0.70	0.78	1.10
a_{H3}	5.42	5.43	5.46	5.58	5.61	5.67	5.55	5.69	5.88
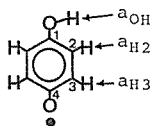
On the other hand, the polarization attributable to the ring-H's of Q and H_2Q as detected by CIDNP technique changed with increasing the amount of water. Although it is hard to come to the complete understanding of these phenomena, the present results might reflect the multiple character of water as a proton donor, a polarity-increasing agent, and a hydrogen bonding promoter. In a dry DME solution both of $Q^{\overline{\cdot}}$ and $H\dot{Q}$ were observed simultaneously by ESR technique, in which solution both the enhanced emission of ring-H's of Q and the enhanced absorption of ring-H's of H_2Q were detectable by CIDNP technique. However, as described in the Results water content in solution changes the situation drastically. In the region where the concentration of $H\dot{Q}$ reached its maximum and $Q^{\overline{\cdot}}$ could be hardly detected ($[H_2O]$: 1–2 M) by ESR, the ring-H's of Q showed a broadening and the ring-H's of H_2Q did not show a definite ^{1}H-CIDNP polarization. The broadening of ^{1}H-NMR signals is caused by existing "free" radicals in solutions, because of the shortening of T_2. Further, in the region where $Q^{\overline{\cdot}}$ became detectable again by ESR ($[H_2O] > 2$ M), the ring-H's of Q showed a broadening during irradiation and an enhanced absorption immediately after stop of irradiation, while the ring-H's of H_2Q showed an enhanced emission.

By analyzing with assistance of Kaptein's rule[10] the CIDNP signals observed in a irradiating dry DME solution of H_2Q and Q, we can conclude that the photo-

induced electron transfer proceeds by an in-cage process. Kaptein's rule[10] predicts an enhanced emission of the ring-H's of Q and an enhanced absorption of the ring-H's of H$_2$Q in agreement with the experimental results. However, the ring-H's of Q showed a broadening upon irradiation in the presence of water. Such a broadening of the CIDNP signal indicates the involvement of "free" radicals resulted from the out-of-cage reaction. With increasing the amount of water, the out-of-cage process would be involved overwhelmingly, resulting in the inversion of the polarization attributable to the ring-H's of Q and H$_2$Q as shown in Fig. 10.

In a dry DME solution, Q and H$_2$Q form molecular complex, judging from the change of the electronic spectra as given in Fig. 17.
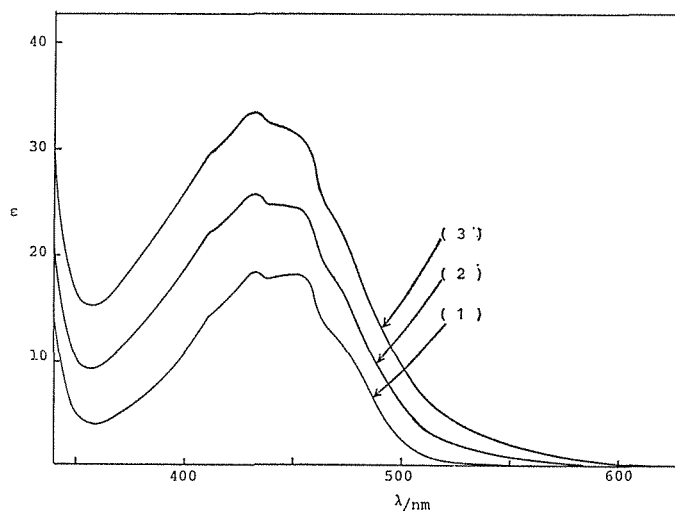

Fig. 17. Electronic absorption spectra of p-benzoquinone and hydroquinone
    system in dry DME.
    p-Benzoquinone; 0.1 M
    (1) Hydroquinone; 0 M
    (2) Hydroquinone; 0.2 M
    (3) Hydroquinone; 0.4 M

As depicted in Fig. 9, addition of an amount of water in the solution would induce both neutralization of Q$^-$ and a disorder for the molecular complex between Q and H$_2$Q by forming hydrogen bonding among water, H$_2$Q, and Q, making unfavorable for the in-cage reaction. With increasing the amount of water into the solution the molecular complexation between Q and H$_2$Q will be mostly destroy, while the polarity of the solvent increases. Thus, the out-of-cage electron transfer process would become favorable, where the CIDNP signals due to the species originated from the out-of-cage process as well as the strong ESR signal due to "free" Q$^-$ were detected. A sharp dependence of HQ̇ vs Q$^-$ curve upon the structure of other additives than water will support further the above arguments.

As for the photo-induced reactions of H$_2$Q with substituted p-benzoquinones or of substituted hydroquinones with Q the reaction courses become more complex, although the reaction will start with an initial electron transfer. As shown in Figs.

13 and 14 we can observe simply $H\dot{Q}$ in a dry DME solution of Cl_4Q–H_2Q system by ESR and simply $Me_4\dot{Q}H$ in a Me_4Q–H_2Q system, while the ^{1}H-CIDNP examinations of the corresponding systems confirm that all of the expected relevant quinones and hydroquinones exhibit polarization[16] as described in the Results (see Tables 1 and 2, too).   Since we can not recognize radical pair in a solvent cage but a "free" radical by ESR, the apparent differences in the results of the ESR and the ^{1}H-CIDNP examinations reflect the state of radicals in "in-cage" or "out-of-cage".   Addition of water in the reacting system gave a great influence on the composition of the radicals as shown in Figs. 15 and 16.   Water existing in the solution leads to a greater generation of "free" Cl_4Q^- in the Cl_4Q–H_2Q system and of "free" Q^- in the Me_4Q–H_2Q system.

In conclusion, it was clarified by means of CIDNP and ESR that the photo-induced electron transfer between H_2Q and Q proceeded and the courses of the reactions were influenced with the amount of water existing in the solution, probably by the local molecular aggregations among Q, H_2Q, and water.

Experimentals

Materials. p-Benzoquinone commercially available was further purified by sublimation.   Hydroquinone in guaranteed grade commercially available was used without further purification.   Chloranil and 2,6-dichloro-p-benzoquinone were commercially available, and were recrystallized from benzene and dried in vacuo before use.

2,6-Dimethyl-p-benzoquinone obtained by the oxidation of the corresponding phenol with Fremy's salt and duroquinone synthesized from durene were purified by sublimation.

ESR Measurements.   The ESR spectra of the transient semiquinone intermediates were observed at room temperature by the use of the JEOL PE3X spectrometer during continuous irradiation of the hydroquinone (0.2 M)-p-benzoquinone (0.1 M) systems in 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF) in the presence of a known amount of water.

DME used as a solvent was dried with metallic sodium and purified by distillation.   THF was prepared similarly.   Samples dissolved in a solvent were thoroughly degassed by freeze-thaw cycle and sealed.   The irradiation (5.0×10^{-8} Einsteins/sec.) was carried out with the light from a 500 W high pressure mercury arc lamp through the glass filter (Toshiba UV-39).

CIDNP Examinations.   Investigations of these photochemical reactions by CIDNP technique were performed using the JEOL PS-100 spectrometer, equipped with a modified NMR probe for the photo-irradiation.   The details of the method used were described elsewhere.[2]

A sample solution containing H_2Q (0.02 M) and Q (0.01 M) and a known amount of water was deoxygenated in a NMR tube by bubbling the solution with the commercially available argon gas (99.99%) just before irradiation.

The sample was irradiated at room temperature by a 500 W high pressure mercury arc lamp through the glass filter (Toshiba UV-39) and the ^{1}H-CIDNP signals were observed before, during, and after irradiation.

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(16) Polarization of chloranil could not be observed, because of the absence of hydrogen in the molecule.