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# CIDEP Study of Durosemiquinone Radical in Various Solvents

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F-pair polarization and triplet mechanism (TM) polarization of durosemiquinone radical produced by light irradiation of duroquinone–phenol systems were discriminated at 260 K in a simple way based on the analysis of the enhancement factors in the steady-state method with intermittent light irradiation. Both polarizations are not so sensitive to viscosity or polarity of solvents. TM enhancement factor is nearly constant (−0.8) in wide range of viscosity (2.5—25 cP, 1 cP = 0.001 Pa s). F-pair polarization is suppressed in some extent by halogenated solvents while TM polarization is not affected by such solvents.

Semiquinone radicals produced by light irradiation of quinones in the presence of reducing agents show Chemically Induced Dynamic Electron Polarization (CIDEP) arising from both the triplet mechanism (TM) and the radical pair mechanism (RPM).[1,2] The elementary descriptions of these mechanisms are as follows: The TM polarization arises from the anisotropic intersystem crossing from the lowest excited singlet state ($S_1$) to each spin sublevel of the triplet state ($T_n$) in a photoexcited molecule, and the RPM polarization comes from the magnetic interaction in radical pairs, which are formed from initial reactions of excited molecules or from random encounters among the radicals in the later stage. Then some fundamental questions arise. Is the magnitude of TM polarization varied by interaction with the external heavy atom because of the change in the anisotropy of the $S_1 \rightarrow T_n$ intersystem crossing as is observed in phosphorescence in solid phase at very low temperatures[3]? And, is the magnitude of RPM polarization influenced by the solvent viscosity, which the interacting period for two radicals is likely to depend upon?

In order to answer such questions, we chose duroquinone–phenol (DQ–PhOH) systems, because durosemiquinone radical produced by light irradiation shows polarizations caused by both mechanisms. Some halogenated solvents were used to see the external heavy atom effect and also used a variety of mixed solvents to change viscosity and polarity.

## Experimental

All chemicals were GR grade and used without further purification except 1-bromo-2-propanol, which was distilled under reduced pressure to remove the coloured component. But it remained containing 2-bromo-1-propanol (20%). No effect was observed for the experimental results by the addition of a small amount of water to *i*-PrOH dried over molecular sieves.

In ESR observations, DQ and PhOH concentrations were fixed to 0.1 mol dm$^{-3}$ and 2.2 mol dm$^{-3}$, respectively, and the temperature was kept at 260 K.

The CIDEP observation system is illustrated in Fig. 1. A JEOL PE-1X type ESR spectrometer using 100 KHz field modulation was improved to have sufficient short responce time (150 μs) to observe the rise and decay of neutral durosemiquinone radical (DQH·). The sample solution was irradiated intermittently by the sector whose light-ON and light-OFF periods were 13.3 and 26.7 ms, respectively. The light source was a 1 kW Ushio USH-1005D super-high-pressure mercury lamp. The temperature rise of about 1 K during irradiation was observed.

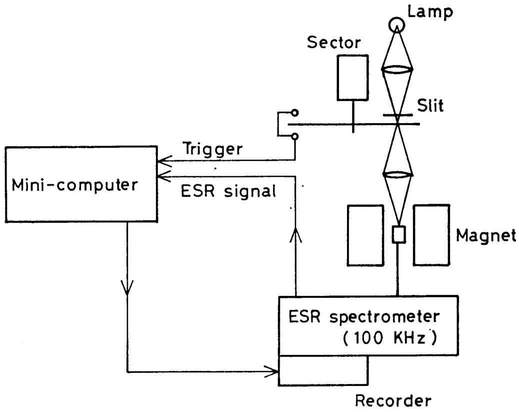

Fig. 1. Block diagram of CIDEP observation.

ESR signal was sampled at every 60 μs over 36 ms at a fixed magnetic field corresponding to one of the first derivative peak positions of DQH· spectrum. The time profile of the signal obtained in this way were accumulated 6000—20000 times with a JEOL EC-6 minicomputer (Fig. 2). The time required for accumulation was 5—16 min. Irradiation of this rather long time gave no change in the UV absorption spectra of the samples. The absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer.

## Analysis of the Time Profile

The steady-state enhancement factor $V_{ss}$ is defined as:

$$V_{ss} = \frac{I_{ss} - I_{ss.0}}{I_{ss.0}}, \qquad (1)$$

where $I_{ss}$ is the intensity of the ESR signal in the presence of CIDEP and $I_{ss.0}$ that in the absence of CIDEP.

It has been known that DQH· produced by light irradiation of DQ–PhOH systems show TM and F-pair polarization.[1,2] The latter is one type of RPM polarization caused by random encounters among DQH· radicals. It is possible that initial (or geminate) pair polarization occurs in the radical pair $\overline{DQH\cdot\ PhO\cdot}$ formed by the initial reaction

$$^3DQ^* + PhOH \longrightarrow \overline{DQH\cdot, PhO\cdot}, \qquad (I)$$

where $^3DQ^*$ is the excited triplet state of DQ and

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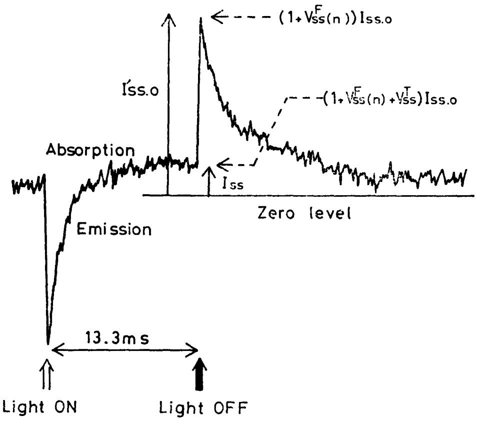

Fig. 2. Time profile of ESR signal intensity.

PhO· phenoxyl radical. As far as photochemically produced geminate radical pairs are concerned, there are few reports about initial pair polarization.[4,5] It is assumed that initial polarization observed in our experiment is due to TM only. We denote the enhancement factor for initial polarization as $V^T_{ss}$, which has no hyperfine dependence. The magnitude of F-pair polarization depends upon the nuclear spin state in DQH·. We denote the enhancement factor of F-pair polarization observed at the $n$th peak in ESR spectrum as $V^F_{ss}(n)$.

In the time profile shown in Fig. 2, the concentration of DQH· immediately after the light-OFF point is equal to the steady-state concentration reached in the light-ON period because of the slow decay of DQH· radical. Therefore the upward spike can be attributed to the rapid disappearance of TM polarization. From the definition (Eq. 1),

$$I_{ss} = (1+V_{ss})I_{ss.0} \tag{2}$$

Signal intensities immediately before and after the light-OFF point ($I_{ss}$ and $I'_{ss.0}$, respectively) can be written as follows:

$$I_{ss} = (1+V^F_{ss}(n)+V^T_{ss})I_{ss.0} \tag{3}$$

$$I'_{ss.0} = (1+V^F_{ss}(n))I_{ss.0}. \tag{4}$$

With our CIDEP observation system, absolute signal intensity can not be measured. Instead, the following dimensionless quantity, which is slightly different from the enhancement factor, is measured.

$$V'(n) = \frac{I_{ss}-I'_{ss.0}}{I'_{ss.0}} \tag{5}$$

From Eqs. 3 and 4, we obtain

$$V'(n) = \frac{V^T_{ss}}{1+V^F_{ss}(n)}. \tag{6}$$

Since the signal intensity at the center of the ESR spectrum is unaffected by F-pair polarization,[6] there exists the following relation.

$$V'(n)_{\text{center}} = V^T_{ss} \tag{7}$$

$V^F_{ss}(n)$ can be obtained from Eqs. 6 and 7.

Time dependence of signal intensity is written as Eq. 8 following Fessenden's treatment.[7]

$$I(t) = \left(\frac{V^F_{ss}(n)}{1+t/t_{1/2}}+1\right)\cdot\frac{I'_{ss.0}}{1+t/t_{1/2}}, \tag{8}$$

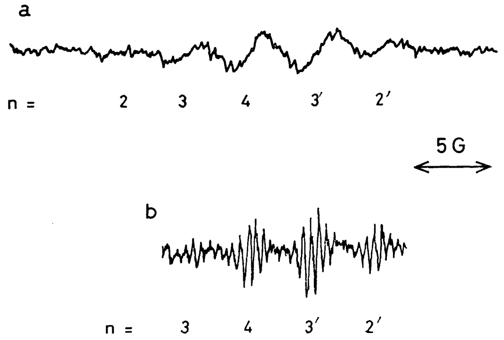

Fig. 3. ESR spectra of durosemiquinone radical DQH· in $i$-PrOH at 260 K.
Concentrations of DQ and PhOH are 0.1 and 2.2 mol dm$^{-3}$. Modulation width are 2.0 G (a) and 0.2 G (b).

where $t_{1/2}$ is the half-life of a radical. At the center line ($V^F_{ss}(n)=0$) Eq. 8 becomes simple second order decay. Signal zero level was so determined that the decay analysis in the light-OFF period gave the best fit to the second order kinetic. Decays of other lines were also well approximated by hyperbolas.

## Results and Discussion

*On the TM Enhancement Factor.* The ESR spectrum of DQH· is shown in Fig. 3. Only neutral radical was detected and durosemiquinone anion radical (DQ$^{\overline{\cdot}}$) was not observed. Hyperfine splitting constants of DQH· were 4.8 G (1 G=10$^{-4}$ T, 6H) and 0.6 G (6H). A modulation width of 2.0 G was used to make the spectrum large septet lines.

Light intensity dependence of $V^T_{ss}$ was studied to examine the reliability of our apparatus and to find whether the following relation, which had been given for $V^F_{ss}(n)$ by Fessenden,[7] could be applied to $V^T_{ss}$.

$$V_{\text{int}} = \frac{V_{ss}t_{1/2}}{T_1}, \tag{9}$$

where $V_{\text{int}}$ is the intrinsic enhancement factor independent of the radical concentration, and $T_1$ is the longitudinal relaxation time. $T_1$ of DQH· could not be measured because of the long responce time of the spectrometer. It is likely to be constant regardless of the light intensity. If that is the case, $V_{ss}t_{1/2}$ should be independent of the radical concentration, which depends on light intensity. A plot of $V^T_{ss}t_{1/2}$ *vs.* the square root of light intensity is shown in Fig. 4. Values of $V^T_{ss}$ were measured at the higher and the lower field peaks of the central resonance line ($n$=4). The numbering of the septet line is illustrated in Fig. 3. The average of four measurements at each line is taken and listed in Fig. 4.

$V^T_{ss}t_{1/2}$ is independent of the light intensity as expected. Therefore the Eq. 9 is valid for $V^T_{ss}$ as well as $V^F_{ss}(n)$. Fig. 4 also shows the square root dependence of $V^T_{ss}$ on the light intensity. This can be attributed to the disproportional radical decay:

$$\text{DQH}\cdot + \text{DQH}\cdot \longrightarrow \text{DQ} + \text{DQH}_2. \tag{II}$$

In the neat solvents except $i$-PrOH, DQH· was

TABLE 1. SOLVENT DEPENDENCE OF $V_{ss}^{T}$ AT 270 K[a)]

| Added solvent[b)] | Molar fraction[b)] | $-V_{ss}^{T}$ | $t_{1/2}$/ms | $-V_{ss}^{T}t_{1/2}$/ms | $\eta$/cP | $\varepsilon$[c)] |
|---|---|---|---|---|---|---|
| $CH_2Cl_2$ | 0.4 | 0.75 | 1.6 | 1.2 | 2.5 | 22 |
| Toluene | 0.4 | 0.83 | 1.4 | 1.2 | 2.5 | 11 |
| MeOH[d)] | 0.6 | 0.82 | 1.7 | 1.4 | 3.1 | 22 |
| Cyclohexane | 0.4 | 0.86 | 1.7 | 1.5 | 4.2 | 11 |
| (*i*-PrOH) | 0 | 0.76 | 2.0 | 1.5 | 8.6 | 18 |
| 1-Bromo-2-propanol | 0.2 | 0.76 | 2.3 | 1.8 | 11.0 | |
| Ethylene glycol | 0.2 | 0.79 | 2.2 | 1.8 | 14.3 | 20 |
| 1-Bromo-2-propanol | 0.4 | 0.74 | 2.4 | 1.7 | 16.9 | |
| 1-Bromo-2-propanol | 0.6 | 0.77 | 2.5 | 1.9 | 24.2 | |
| Ethylene glycol | 0.4 | 0.87 | 2.7 | 2.3 | 24.7 | 23 |

a) The light intensity was kept constant. b) Added solvents to *i*-PrOH and their content in molar fraction. c) Dielectric constants were calculated from volume ratio of added solvent and PhOH. d) Light intensity change was corrected using the relation (9).

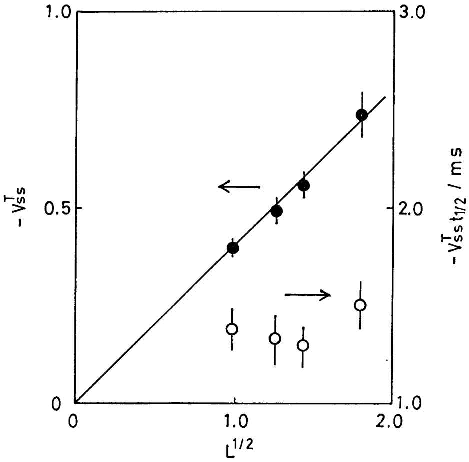

Fig. 4. Light intensity dependence of $V_{ss}^{T}$ and $V_{ss}^{T}t_{1/2}$. *L* denotes the relative light intensity.

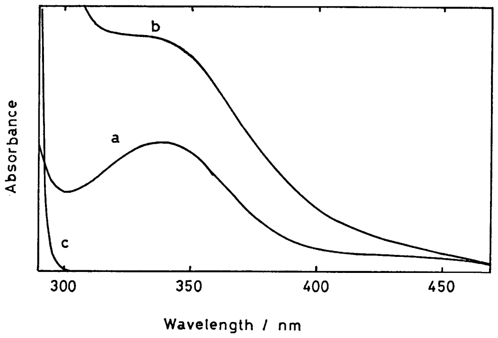

Fig. 5. Absorption spectra of a: DQ (0.07 mol dm$^{-3}$), b: DQ and PhOH (0.07 and 1.7 mol dm$^{-3}$) and c: PhOH (1.7 mol dm$^{-3}$) in *i*-PrOH at room temperature.

not detected. Thus, $V_{ss}^{T}$ was measured in the mixed solvents with *i*-PrOH. Results are listed in Table 1. The light intensity was kept constant.

Only a small change in $V_{ss}^{T}$ was observed with the change of dielectric constants of solvents from 11 to 23. Any simple correlation between $V_{ss}^{T}$ and $\varepsilon$ could not be found. Hence $S_1 \rightarrow T_n$ intersystem crossing in DQ* is thought to be unaffected by solvent polarity in spite of the near location of both (n,$\pi$*) and ($\pi$,$\pi$*) states with the lowest triplet state.[8)]

It must be noted that the addition of PhOH to the DQ solution gave an obvious change in absorption spectra (Fig. 5). This was referred previously by Elliot and Wan,[1)] and attributed to the change in hydrogen bonding characteristics as the addition of PhOH. However, similar spectral change was observed by the addition of other aromatic compounds such as benzene or toluene, but not with aliphatic additives such as cyclohexane or acetonitrile. Thus, the change of optical spectra is explained in terms of the interaction between aromatic rings of DQ and PhOH rather than the hydrogen bond.

Table 1 also indicates that $V_{ss}^{T}$ is not sensitive to solvent viscosity. $V_{int}^{T}$ was described by Wan and Elliot[1,2)] as follows:

$$\frac{1}{V_{int}^{T}} = \frac{1}{V_{\infty}^{T}}\left(1+\frac{1}{{}^{3}T_1 \times k_q[\mathrm{PhOH}]}\right), \tag{10}$$

where ${}^{3}T_1$ is the longitudinal relaxation time of $^3$DQ*, $k_q$ is the second order rate constant of the reaction (I), and $V_{\infty}^{T}$ is the limitting value of $V_{int}^{T}$ at infinite concentration of PhOH. $V_{ss}^{T}$ was expected to be sensitive to solvent viscosity because of the viscosity dependences of $T_1$, ${}^{3}T_1$, and $k_q$. But noticeable dependence of $V_{ss}^{T}$ on solvent viscosity was not observed.

There is a correlation between $V_{ss}^{T}t_{1/2}$ and the viscosity. To discuss this, Eqs. 9 and 10 are combined to give

$$V_{ss}^{T}t_{1/2} = \frac{1}{{}^{3}T_1^{-1}\cdot k_q^{-1} \times [\mathrm{PhOH}]^{-1}+1}\cdot V_{\infty}^{T}\cdot T_1 \tag{11}$$

If cancellation occures between the effect of ${}^{3}T_1$ and $k_q$, the denominator of the right hand side of Eq. 11 is insensitive to the viscosity. This seems to be the case found in the report on DQ$^{\overline{\cdot}}$, which was given by Atkins as shown in Table 2.[9)] Values of $k_q\cdot{}^{3}T_1$ are nearly constant except in methanol. From the same reason, $k_q\cdot{}^{3}T_1$ is likely to be insensitive to viscosity variation in our systems. Then, if we assume that $V_{\infty}^{T}$ is independent of solvent viscosity, from Eq. 11 viscosity dependence of $V_{ss}^{T}t_{1/2}$ is attributed to that of $T_1$, and from the values of $V_{ss}^{T}t_{1/2}$ it turns out that $T_1$ increases about twice as the viscosity

TABLE 2. RATE CONSTANT $k_q$ OF THE REACTION $^3DQ^* + (C_2H_5)_3N \rightarrow DQ^{\cdot -} + (C_2H_5)_3N^{\cdot +}$ AND LONGITUDINAL RELAXATION TIMES IN SOME SOLVENTS, BY ATKINS, *et al.*[9]

| Solvent | $\eta$ / cP | $k_q \times 10^{-8}$ / $mol^{-1} dm^3 s^{-1}$ | $^3T_1$ / ns | $^2T_1$ / μs | $^3T_1 / {^2T_1}$ | $k_q {^3T_1}$ / $mol^{-1} dm^3$ |
|---|---|---|---|---|---|---|
| $CH_3OH$ | 0.61 | 2.7 | 2.7 | 2 | $1.4\times10^{-3}$ | 0.73 |
| $(CH_3)_2CHOH$ | 2.2 | 3.6 | 9.7 | 8 | $1.2\times10^{-3}$ | 3.5 |
| $(CH_3)_3COH$ | 4.8 | 3.9 | 7.1 | 9 | $0.9\times10^{-3}$ | 3.0 |
| *cyclo*-$C_6H_{11}OH$ | 57 | 1.9 | 17 | 18 | $0.9\times10^{-3}$ | 3.2 |

TABLE 3. SOLVENT DEPENDENCE OF $V^F_{ss}$ AT 270 K

| Added solvent | Molar fraction | $V^F_{ss}(3) / \lvert V^T_{ss}\rvert$ | $V^F_{ss}(3') / \lvert V^T_{ss}\rvert$ | $-V^T_{ss}$ | $t_{1/2}$ / ms | $\eta$ / cP |
|---|---|---|---|---|---|---|
| Toluene | 0.4 | −0.44 | 0.46 | 0.79 | 1.8 | 2.9 |
| Cyclohexane | 0.4 | −0.43 | 0.47 | 0.82 | 1.7 | 4.2 |
| (*i*-PrOH) | 0 | −0.40 | 0.43 | 0.86 | 1.7 | 8.6 |
| Ethylene glycol | 0.2 | −0.36 | 0.43 | 0.93 | 2.0 | 14.3 |
| Ethylene glycol | 0.4 | −0.36 | 0.31 | 0.70 | 2.6 | 24.7 |
| Bromobenzene | 0.4 | −0.29 | 0.27 | 0.75 | 1.7 | 4.0 |
| $CCl_4$ | 0.4 | −0.26 | 0.34 | 0.54 | 2.7 | 4.7 |
| 1-Bromo-2-propanol | 0.2 | −0.16 | 0.14 | 0.93 | 2.1 | 11.0 |
| 1-Bromo-2-propanol | 0.4 | −0.10 | 0.13 | 0.92 | 2.3 | 16.9 |
| 1-Bromo-2-propanol | 0.6 | −0.10 | 0.15 | 0.80 | 2.9 | 24.2 |
| 1,3-Dibromo-2-propanol | 0.4 | −0.27 | 0.25 | 0.64 | 3.7 | 36.9 |

changes from 2.5 to 24.7 cP, and $V^T_{int}$ is independent of viscosity.

The above assumption that $V^T_\infty$ is not influenced by solvent viscosity can be rationalized as follows. The enhancement factor $V^T_{int}$ can be written as Eq. 12 using the theoretical equation for the magnetization $\langle S_z\rangle$ of a radical polarized due to TM given by Atkins and Evans (Ref. 10, Eq. 5—3).

$$V^T_{int} = \frac{\langle S_z\rangle - \langle S_{z.e}\rangle}{\langle S_{z.e}\rangle} \simeq \frac{\langle S_z\rangle}{\langle S_{z.e}\rangle}$$
$$= \frac{(DK+3EI)}{1+k_T^{-1}\cdot{^3T_1^{-1}}} \cdot \frac{2}{15}\left(\frac{4\omega_0\tau_2^2}{1+4\omega_0^2\tau_2^2} + \frac{\omega_0\tau_2^2}{1+\omega_0^2\tau_2^2}\right)$$
$$\cdot \frac{1}{\langle S_{z.e}\rangle} \tag{12}$$

where $\langle S_{z.e}\rangle$ is the thermal magnetization of the radical, $k_T$ is the triplet quenching rate which can be substituted by $k_q\cdot$[PhOH] in our case, $D$ and $E$ are zero-field splitting constants, $K$ and $I$ are parameters showing anisotropy of $S_1 \rightarrow T_n$ intersystem crossing rate, $\omega_0$ is angular frequency of the microwave, and $\tau_2$ is the rotational correlation time. In the derivation of $\langle S_z\rangle$, isotropic rotational diffusion and the unity yield of intersystem crossing are assumed. The latter condition is valid for DQ.[11] Then we get Eq. 13 from Eq. 10.

$$V^T_\infty = \frac{2}{15}\left(\frac{4\omega_0\tau_2^2}{1+4\omega_0^2\tau_2^2} + \frac{\omega_0\tau_2^2}{1+\omega_0^2\tau_2^2}\right)\cdot\frac{DK+3EI}{\langle S_{z.e}\rangle} \tag{13}$$

If we adopt the Debye's relation $\tau = 4\pi\eta r^3/3kT$ for $\tau_2$ (assuming $r = 4$ A), Eq. 13 reduces to Eq. 14 because $\omega_0\tau_2 \gg 1$.

$$V^T_\infty = \frac{4}{15}\cdot\frac{DK+3EI}{\langle S_{z.e}\rangle}\cdot\frac{1}{\omega_0} \tag{14}$$

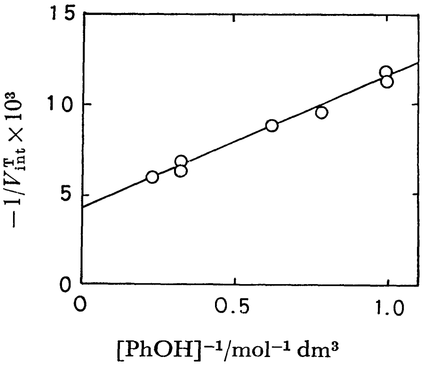

Fig. 6. Effect of phenol concentration on $V^T_{int}$ of DQH· in *i*-PrOH at 260 K.

Consequently $V^T_\infty$ does not depend on viscosity.

The value of $V^T_\infty$ can be obtained by extrapolating the plot of $(V^T_{int})^{-1}$ *vs.* $[PhOH]^{-1}$ according to Eq. 10 and the value $(DK+3EI)$ of $^3DQ^*$ in liquid phase is calculable from $V^T_\infty$. This plot was carried out for the PhOH concentration range from 1 to 4 mol $dm^{-3}$ using $T_1$ values of $DQ^{\cdot -}$ in ethanol reported by Rengan *et al.*[12] The plot was linear and $V^T_\infty$ was obtained to be −240, as shown in Fig. 6. By using Eq. 14, we obtain $(DK+3EI) = -0.1\ cm^{-1}$. This is a reasonable value for an aromatic compound. Also $^3T_1$ of $^3DQ^*$ was estimated to be 2.6 ns from the slope of the plot using the value of $k_q = 2\times10^8$ $mol^{-1} dm^3 s^{-1}$.[1]

With aromatic carbonyls in solid phase, $D$, $E$ and the rate of intersystem crossing are remarkably influenced by the nature of host and the external heavy atom.[3] On the other hand in liquid phase, the addition of nonpolar or viscous solvents to the DQ–

PhOH system does not affect the TM enhancement factor as discussed above. The addition of halogenated solvents to the system also gives little change in $V^{\mathrm{T}}_{\mathrm{ss}}$ (see Table 1).

*On the RPM Enhancement Factor.* In various solvents, $V^{\mathrm{F}}_{\mathrm{ss}}(3)$ and $V^{\mathrm{F}}_{\mathrm{ss}}(3')$, together with $V^{\mathrm{T}}_{\mathrm{ss}}$ were measured. Table 3 lists the ratios of $V^{\mathrm{F}}_{\mathrm{ss}}(n)/V^{\mathrm{T}}_{\mathrm{ss}}$ which are intrinsic value independent of the light intensity:

$$V^{\mathrm{F}}_{\mathrm{ss}}(n)/V^{\mathrm{T}}_{\mathrm{ss}} = \frac{V^{\mathrm{F}}_{\mathrm{ss}}(n)t_{1/2}}{T_1} \Bigg/ \frac{V^{\mathrm{T}}_{\mathrm{ss}}t_{1/2}}{T_1} = V^{\mathrm{F}}_{\mathrm{int}}(n)/V^{\mathrm{T}}_{\mathrm{int}}. \tag{15}$$

This ratio can be regarded as the reflection of the solvent dependence of $V^{\mathrm{F}}_{\mathrm{int}}$, because $V^{\mathrm{T}}_{\mathrm{ss}}$ or $V^{\mathrm{T}}_{\mathrm{int}}$ is nearly independent of solvents as discussed. The sign of $V^{\mathrm{F}}_{\mathrm{ss}}(3)$ is negative (emission) and the one of $V^{\mathrm{F}}_{\mathrm{ss}}(3')$ positive (enhanced absorption). Absolute values of $V^{\mathrm{F}}_{\mathrm{ss}}(3)$ and $V^{\mathrm{F}}_{\mathrm{ss}}(3')$ of each sample were equal, which is consistent with the theory of RPM.(6) This fact gives a support to the validity of the simple method of the analysis we adopted.

In the first five lines in Table 3, results on samples without heavy atoms are listed. In spite of the wide change in viscosity ranging from 2.9 to 24.7 cp, the deviation of the ratio is within 25%. As mentioned previously, the change in viscosity is expected to vary the period of magnetic interaction between radicals within the radical pair $\overline{\mathrm{DQH}\cdot\ \mathrm{DQH}\cdot}$, so that the enhancement factor of RPM is likely to be sensitive to solvent viscosity. The result is contrary to this expectation. The value of $V^{\mathrm{F}}_{\mathrm{ss}}(n)/V^{\mathrm{T}}_{\mathrm{ss}}$ decreases slightly with increasing viscosity.

$V^{\mathrm{F}}_{\mathrm{ss}}(n)/V^{\mathrm{T}}_{\mathrm{ss}}$ is remarkably small when the sample contains 1-bromo-2-propanol, as shown in the lower part of Table 3. Other halogenated solvents have the similar effect to 1-bromo-2-propanol, however the magnitude is small. Two possible .causes for this effect are considered. (1) The yield or the rate of the reaction (II), which is the origin of F-pair polarization, decreases for the participation of such solvents. (2) There is the external heavy atom effect on the F-pair polarization, *i.e.*, the reduction of the singlet-triplet mixing in the radical pair $\overline{\mathrm{DQH}\cdot\ \mathrm{DQH}\cdot}$. A possible mechanism for (1) is that a considerable amount of DQH· decays through a process other than (II). This mechanism, however, fails to explain that the half-life of DQH· is unaffected by halogenated solvents. Although the cause (2) cannot explain quantitatively the difference in magnitude of the effect among halogenated solvents, it is likely to exist. A probable mechanism of cause (2) is a suppression of the interaction between radicals by another interaction between radicals and halogenated solvents.

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