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# Electron Transfer Reaction in the Triplet State. Role of Ferrocene as an Electron Donor

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Quenching of the triplet state of methylene blue by ferrocene and *p*-phenylenediamine in ethanol has been investigated by an emission-absorption flash technique. The triplet dye is quenched by ferrocene and *p*-phenylenediamine at a diffusion-controlled rate, yielding the semi-reduced dye. Efficiency of the semi-reduced dye formation is 0.09 and 1.0 for ferrocene and *p*-phenylenediamine, respectively. Since the triplet level of the dye is lower than that of ferrocene, quenching of the triplet dye by ferrocene seems to occur through the charge (electron) transfer interaction.

Many triplets of aromatic compounds are quenched by ferrocence (F) at a diffusion-controlled rate.[1-3] However, the quenching mechanism has not been elucidated because the triplet level of F[4-6] remained obscure.

Fry *et al.*[1] studied the quenching rate of some triplets by F with a conventional flash technique, and presumed that quenching is due to the formation of a short-lived charge transfer complex, because they could not observe any transient absorption attributable to the addition of F.

We measured quenching rate constants by F for several triplets with levels located in the range 8000—23800 $\mathrm{cm^{-1}}$,[7] and studied the triplet energy transfer for the eosin-tetracene-ferrocene mixed system. It was concluded that the triplet level of F is $15000 \pm 1000\ \mathrm{cm^{-1}}$ and the lifetime of triplet F shorter than 1 μs. Thus, it is obvious that the triplet with level higher than 15000 $\mathrm{cm^{-1}}$ is mainly quenched by triplet energy transfer to F and that with level lower than 15000 $\mathrm{cm^{-1}}$ is quenched by some other mechanism. Since the oxidation potential of F is low,[8] it is anticipated that charge transfer interaction plays an important role.

In order to show this role, quenching of the lowest triplet state of methylene blue ($^3D^+$) by F has been studied by an emission-absorption flash technique.[9] Since the dye ($D^+$) has a low reduction potential[10] and a triplet level lower than that of F, it is considered to be the most appropriate for the purpose. Quenching by *p*-phenylenediamine (P) has been also studied for comparison.

## Experimental

*Materials.* Ferrocene (G. R. grade, Tokyo Kasei) was recrystallized from benzene, zone refined, and sublimated. Methylene blue (G. R. grade, Merck) was recrystallized from *n*-butanol. *p*-Phenylenediamine (E. P. grade, Tokyo Kasei) was recrystallized twice from ethanol and used immediately after sublimation. Ethanol (G. R. grade, Wako Jun-yaku) was used without further purification.

*Apparatus and Procedure.* Flash energy was controlled in the range 56—130 J its half duration being about 10 μs. A Toshiba V-O51 filter was used for exciting the dye only. A Q-switched ruby laser provides a 15 ns pulse of about 0.15 J. All measurements were made at room temperature. Ethanol solutions were degassed by repeating bulb-to-trap-distillation in vacuum.

## Results and Discussion

Two transient absorption spectra obtained when the deaerated solution of the dye was flashed are shown in Fig. 1. Spectrum (a) is attributed to the T–T absorption of the dye because of its close resemblance to the spectrum in literature.[11,12] The decay is nearly of first order, but its rate increases with increasing dye concentration. This is apparently due to the D–D mechanism given by Koizumi *et al.*[13] The result is consistent with that of steady light illumination.[14] The observed rate constant is linear with respect to dye concentration (Fig. 2).

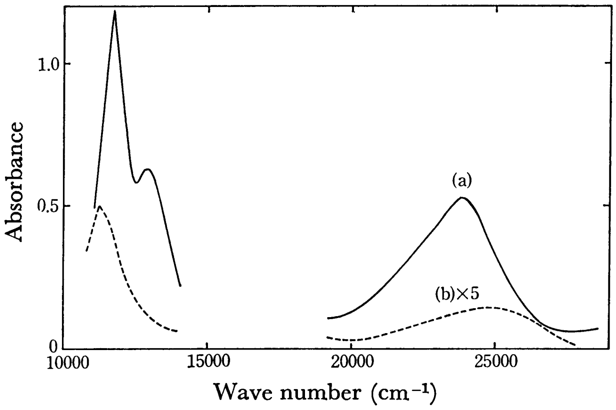
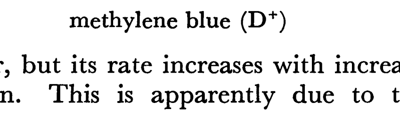


Fig. 1. Transient absorption spectra of methylene blue in deaerated ethanol ($10^{-5}$ M). (a) triplet, (b) long-lived intermediate (5 ms after flashing).



methylene blue ($D^+$)

$$k_{\mathrm{obsd}} = k_t = k_0 + k[\mathrm{D}]$$

From the intercept and the slope we obtain

$$k_0 = 2.2 \times 10^3\ \mathrm{s^{-1}}$$

$$k = 4.5 \times 10^8\ \mathrm{M^{-1} \cdot s^{-1}}.$$

Spectrum (b) (Fig. 1) was observed after the disappearance of the T–T absorption spectrum (a) and seems to be that of the protonated semireduced dye ($\mathrm{DH^{\dot{+}}}$), since the spectral shape accords substantially with the

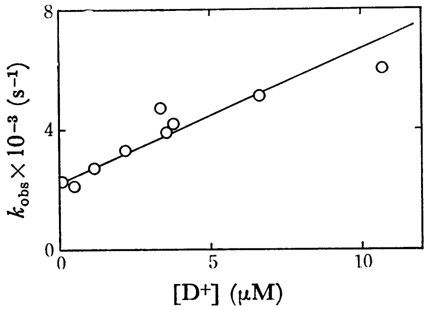


Fig. 2. The dependence of the observed first order decay constant of the triplet methylene blue on dye concentration.

reported one.[15] The decay of $DH^{\cdot +}$ is not reproducible, and the lifetime is much longer than 1 ms. The absorption spectrum of the dye changes slightly with repeated flashing.

The decay rate constant of the triplet dye increases linearly with F concentration.

$$k_{obsd} = k_t + k_F[F]$$

From the slope we obtain

$$k_F = 4.5 \times 10^9\ M^{-1} \cdot s^{-1}.$$

For F concentrations higher than $10^{-4}$ M (Fig. 3), quite a different spectrum (a) completely replaces the T–T absorption spectrum. The spectrum decays as a first order process to produce a long-lived absorption spectrum (b), but the decay rate is not reproducible.

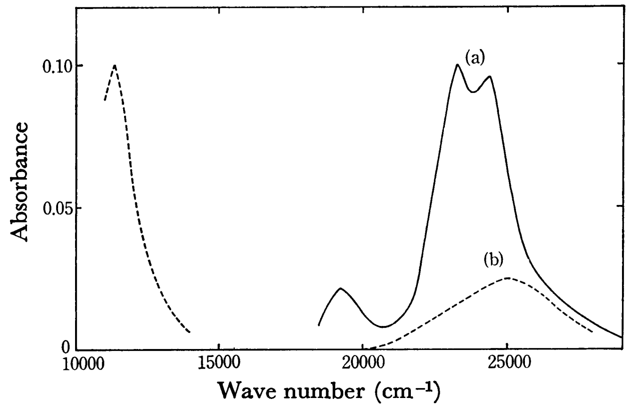


Fig. 3. Transient absorption spectra of methylene blue ($5 \times 10^{-6}$ M) in ethanol containing $10^{-4}$ M ferrocene. (a) immediately after flashing, (b) 1 ms after flashing.

With the addition of an efficient electron donor, P, the decay of the triplet dye also increases. For P concentrations higher than $10^{-4}$ M (Fig. 4), spectrum (a) was observed instead of the T–T absorption spectrum. The spectrum decays in first order, giving a long-lived absorption spectrum (b). The decay of the long-lived absorption is not reproducible.

The transient absorption spectrum (a) in Fig. 3 is similar to the spectrum of the semireduced dye (D·) in a basic solution.[11,15] The transient absorption spectra (a) shown in Figs. 3 and 4 resemble each other, the latter having an additional absorption peak at *ca.* 500 nm. The absorption spectrum of P cation radical ($P^{\cdot +}$)[16] was obtained by flashing the aerated ethanol solution of P (Fig. 4(c)). It is obvious that the spectrum (Fig. 4(a)) consists of the superposition of D· and $P^{\cdot +}$.

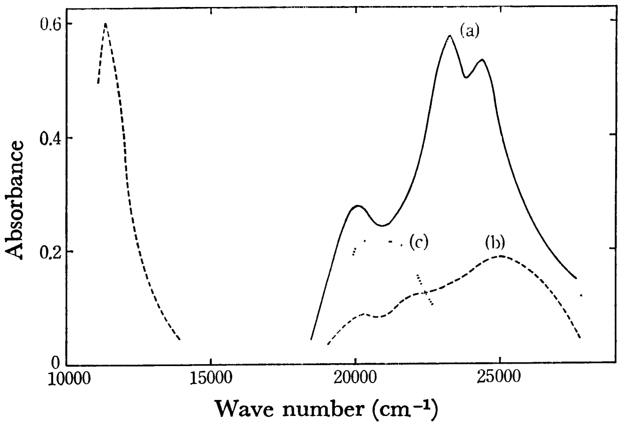


Fig. 4. Transient absorption spectra of methylene blue ($5 \times 10^{-6}$ M) in ethanol containing $10^{-4}$ M*p*-phenylenediamine. (a) immediately after flashing, (b) 1 ms after flashing. (c) The spectrum of *p*-phenylenediamine cation radical in ethanol is drawn for comparison.

The spectra (b) shown in Figs. 1, 3, and 4 are similar to the spectrum of $DH^{\cdot +}$. Since $pK_a$ of D· is 9.0,[15] it might be protonated in ethanol as in other basic compounds such as proflavine.[17] Thus, spectra (a) and (b) in Fig. 3 can be assigned respectively to D· and $DH^{\cdot +}$, since the contribution of F added to absorbance in this wavelength region is negligible owing to the small molar extinction coefficients of F and its cation radical ($F^{\cdot +}$).[18] The absorbance of $DH^{\cdot +}$ increases at the expense of that of D·, implying that the protonation is the main decay process of D·. The fact that the decay rate of D· is not reproducible can be interpreted as a result of unregulated proton concentration. No transient absorption was observed by flashing the aerated solution of the dye. However, the transient absorption spectra (a) in Figs. 3 and 4 were observed in the aerated solution containing F and P, respectively. These spectra decay as a second order process to reproduce the dye. The spectrum of $DH^{\cdot +}$ was not observed in either case. The results suggest that D· is stable against oxygen, and that $DH^{\cdot +}$ may react with oxygen as follows,

$$DH^{\cdot +} + O_2 \longrightarrow D^+ + HO_2\cdot$$

The absorption and fluorescence spectra are not affected by the addition of F or P. Hence, the reaction state of the dye is the lowest triplet state alone. The scheme can thus be summarized as follows.

$$\begin{array}{lll}
(1) & D^+ \xrightarrow{I_{ab}\phi_{ST}} {}^3D^+ & \\
(2) & {}^3D^+ \longrightarrow D^+ & \left.\right\} k_t \quad \left.\right\} k_{dt} \\
(3) & {}^3D^+ + D^+ \longrightarrow D\cdot + D^{\cdot ++} & \\
(4) & {}^3D^+ + O_2 \longrightarrow D^+ + {}^1O_2^* & k_0[O_2] \\
(5) & {}^3D^+ + F \longrightarrow D\cdot + F^{\cdot +} & k_F{}^r \quad \left.\right\} k_F \\
(6) & {}^3D^+ + F \longrightarrow D^+ + F & \\
(7) & {}^3D^+ + P \longrightarrow D\cdot + P^{\cdot +} & k_P{}^r \quad \left.\right\} k_P \\
(8) & {}^3D^+ + P \longrightarrow D^+ + P &
\end{array}$$

The semi-oxidized dye ($D^{\ddagger +}$) produced by process (3) has an absorption peak at *ca.* 520 nm.[11] This may interpret the fact that spectrum (b) in Fig. 1 is significantly swelled at about 500 nm compared with spectrum (b) in Fig. 3.

The yield of D· at the end of a flash is related with the total quantity of light absorbed during one flash by

$$\int \mathrm{d}[\mathrm{D}] \equiv [\mathrm{D}\cdot]_0 = \phi_{\mathrm{ST}}\cdot\frac{k_{\mathrm{Q}}{}^{\mathrm{r}}[\mathrm{Q}]}{k_{\mathrm{dt}}+k_{\mathrm{Q}}[\mathrm{Q}]}\cdot\int I_{\mathrm{ab}}\mathrm{d}t \qquad (1)$$

where Q indicates F or P and the subscript "0" stands for the quantity immediately after flashing. The time integrated fluorescence intensity measured at $\lambda'$ during a flash is given by

$$\int I_{\mathrm{f}}(\lambda')\mathrm{d}t = \alpha\phi_{\mathrm{f}}\int I_{\mathrm{ab}}\mathrm{d}t \qquad (2)$$

When Q is F, the transient absorption spectrum (a) in Fig. 3 is entirely attributable to D·. Thus, from Eqs. (1), (2), and the relation

$$D_0(\lambda) = \varepsilon(\lambda)[\mathrm{D}\cdot]_0 d \qquad (3)$$

we obtain

$$\frac{\int I_{\mathrm{f}}(\lambda')\mathrm{d}t}{D_0(\lambda)} = \frac{\alpha\phi_{\mathrm{f}}}{\varepsilon(\lambda)\mathrm{d}\cdot\phi_{\mathrm{ST}}}\cdot\frac{k_{\mathrm{F}}}{k_{\mathrm{F}}{}^{\mathrm{r}}}\left(1+\frac{k_{\mathrm{dt}}}{k_{\mathrm{F}}}\cdot\frac{1}{[\mathrm{F}]}\right) \qquad (4)$$

where $D(\lambda)$ and $\varepsilon(\lambda)$ are the absorbance and the molar extinction coefficient of D· at wavelength $\lambda$, respectively, and $d$=10 cm. When Q is P, the transient absorption is composed of D· and $\mathrm{P}^{\ddagger}$. As the concentration of $\mathrm{P}^{\ddagger}$ is equal to that of D·, the following relation holds instead of Eq. (3).

$$\begin{aligned} D_0(\lambda) &= \{\varepsilon(\lambda)[\mathrm{D}\cdot]_0+\varepsilon'(\lambda)[\mathrm{P}^{\ddagger}]_0\}d \\ &= \{\varepsilon(\lambda)+\varepsilon'(\lambda)\}[\mathrm{D}\cdot]_0 d \qquad (5)\end{aligned}$$

where $\varepsilon'(\lambda)$ is the molar extinction coefficient of $\mathrm{P}^{\ddagger}$ at $\lambda$. $\int I_{\mathrm{f}}(720)\mathrm{d}t$ and $D_0(420)$ were measured at various F and P concentrations. The results are given in Table 1. $\int I_{\mathrm{f}}(\lambda')\mathrm{d}t/D_0(\lambda)$ is plotted against the reciprocals of F and P concentration in Fig. 5. From the plots we have

$$k_{\mathrm{dt}}/k_{\mathrm{F}} = 7.4 \times 10^{-4}\,\mathrm{M} \qquad (6)$$

$$k_{\mathrm{dt}}/k_{\mathrm{P}} = 7.3 \times 10^{-4}\,\mathrm{M} \qquad (7)$$

TABLE 1. YIELDS OF THE SEMIREDUCED DYE AND TIME INTEGRATED FLUORESCENCE INTENSITY

| | $D_0(420)$ | $\int I_{\mathrm{f}}(720)\mathrm{d}t$ | $\int I_{\mathrm{f}}(720)\mathrm{d}t/D_0(420)$ |
|---|---|---|---|
| [F] | | | |
| $1.02\times10^{-4}$M | $0.013_8$ | 5.7 | $41_3$ |
| $2.0 \times10^{-4}$ | $0.023_4$ | 5.7 | $24_4$ |
| $3.06\times10^{-4}$ | $0.030_0$ | 5.7 | $19_0$ |
| $4.0 \times10^{-4}$ | $0.041_6$ | 5.6 | $13_4$ |
| $5.1 \times10^{-4}$ | $0.043_5$ | 5.5 | $12_6$ |
| $6.0 \times10^{-4}$ | $0.048_1$ | 5.4 | $11_2$ |
| [P] | | | |
| $8.87\times10^{-5}$ | 0.096 | 5.5 | $57._3$ |
| $1.43\times10^{-4}$ | $0.15_4$ | 5.5 | $35._7$ |
| $2.21\times10^{-4}$ | $0.20_8$ | 5.4 | $25._9$ |
| $4.44\times10^{-4}$ | $0.29_4$ | 5.0 | $17._0$ |
| $9.53\times10^{-4}$ | $0.41_6$ | 4.5 | $10._8$ |
| $1.33\times10^{-3}$ | $0.47_6$ | 4.3 | $9._0$ |

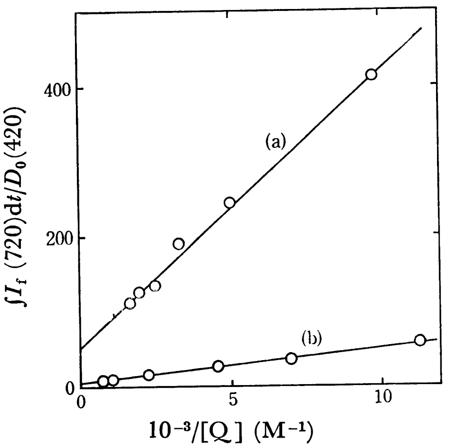


Fig. 5. The plot of $\int I_{\mathrm{f}}(\lambda')\mathrm{d}t/D_0(\lambda)$ *vs.* 1/[Q].
(a) Q: ferrocene, (b) Q: *p*-phenylenediamine.

The decay rate of the triplet dye in the aerated solution was measured by using a Q-switched ruby laser.

$$k_{\mathrm{dt}} = k_{\mathrm{t}} + k_{\mathrm{o}}[\mathrm{O}_2] = 3.7 \times 10^6\,\mathrm{s}^{-1} \qquad (8)$$

From Eqs. (6), (7), and (8), we have

$$k_{\mathrm{F}} = 5.0 \times 10^9\,\mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$$

$$k_{\mathrm{P}} = 5.1 \times 10^9\,\mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$$

The value of $k_{\mathrm{F}}$ agrees with that ($k_{\mathrm{F}}=4.5\times10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) obtained from the effect of F concentration on the triplet decay.

It should be noted that the yield of D· is larger for P than for F (Table 1). This indicates that the rate constant of the formation of D·, $k_{\mathrm{P}}{}^{\mathrm{r}}$, is larger than $k_{\mathrm{F}}{}^{\mathrm{r}}$, because the rate constants of the triplet quenching by P and F are nearly equal.

The efficiency of D· formation, $k_{\mathrm{P}}{}^{\mathrm{r}}/k_{\mathrm{P}}$ and $k_{\mathrm{F}}{}^{\mathrm{r}}/k_{\mathrm{F}}$, was estimated as follows. In the deaerated solution, the absorbance of the T–T absorption immediately after flashing is expressed by

$$\left[\frac{D_0{}^{\mathrm{T}}(\lambda)}{\int I_{\mathrm{f}}(\lambda')\mathrm{d}t}\right] = \varepsilon^{\mathrm{T}}(\lambda)\mathrm{d}\cdot\frac{\phi_{\mathrm{ST}}}{\alpha\phi_{\mathrm{f}}} \qquad (9)$$

where $D^{\mathrm{r}}(\lambda)$ and $\varepsilon^{\mathrm{T}}(\lambda)$ are the absorbance and the molar extinction coefficient of the T-T absorption, respectively. For F concentration higher than $10^{-4}$ M, the T–T absorption spectrum is replaced by the spectra of D·, because the triplet dye reacts rapidly with F ($k_{\mathrm{F}}[\mathrm{P}]\gg k_{\mathrm{dt}}$). The following relation is then obtained from Eqs. (4) and (9).

$$\frac{k_{\mathrm{F}}{}^{\mathrm{r}}}{k_{\mathrm{F}}} = \frac{[D_0(\lambda)/\int I_{\mathrm{f}}(\lambda')\mathrm{d}t]_{\mathrm{F}}}{[D_0{}^{\mathrm{T}}(\lambda)/\int I_{\mathrm{f}}(\lambda')\mathrm{d}t]}\cdot\frac{\varepsilon^{\mathrm{T}}(\lambda)}{\varepsilon(\lambda)} \qquad (10)$$

For P concentration higher than $10^{-4}$ M, we have also

$$\frac{k_{\mathrm{P}}{}^{\mathrm{r}}}{k_{\mathrm{P}}} = \frac{[D_0(\lambda)/\int I_{\mathrm{f}}(\lambda')\mathrm{d}t]_{\mathrm{P}}}{[D_0{}^{\mathrm{T}}(\lambda)/\int I_{\mathrm{f}}(\lambda')\mathrm{d}t]}\cdot\frac{\varepsilon^{\mathrm{T}}(\lambda)}{\varepsilon(\lambda)+\varepsilon'(\lambda)} \qquad (11)$$

The molar extinction coefficients were obtained by completely converting the dye into the triplet state or D·.

$$\varepsilon^{\mathrm{T}}(825) = 1.6_5 \times 10^4\,\mathrm{M}^{-1}\cdot\mathrm{cm}^{-1}$$

$$\varepsilon(420) + \varepsilon'(420) = 1.1 \times 10^4\,\mathrm{M}^{-1}\cdot\mathrm{cm}^{-1}$$

The molar extinction coefficient of D· was estimated by correcting the absorption of $P^{\dagger}$.

$$\varepsilon(420) = 9._4 \times 10^3\,\mathrm{M^{-1}\cdot cm^{-1}}$$

$D_0(420)$ and $D_0^{\mathrm{T}}(825)$ are plotted against $\int I_f(720)\mathrm{d}t$ in Fig. 6. From the slope of the plots, we have

$$[D_0(420)/\int I_f(720)\mathrm{d}t]_{\mathrm{F}} = 0.009$$

$$[D_0(420)/\int I_f(720)\mathrm{d}t]_{\mathrm{P}} = 0.12$$

$$[D_0^{\mathrm{T}}(825)/\int I_f(720)\mathrm{d}t] = 0.18$$

From these values and the molar extinction coefficients obtained above and with the aid of Eqs. (10) and (11), we obtain

$$k_{\mathrm{P}}^{\mathrm{r}}/k_{\mathrm{P}} = 1.0$$

$$k_{\mathrm{F}}^{\mathrm{r}}/k_{\mathrm{F}} = 0.09$$

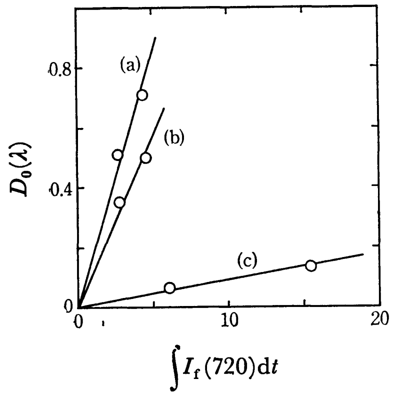


Fig. 6. The plot of $D_0(\lambda)$ and $D_0^{\mathrm{T}}(\lambda)$ *vs.* $\int I_f(\lambda')\mathrm{d}t$.
(a) $D_0^{\mathrm{T}}(825)$, (b) $D_0(420)$: *p*-phenylenediamine, (c) $D_0(420)$: ferrocene.

It was suggested[7] that quenching of the triplet whose level is lower than 15000 $\mathrm{cm^{-1}}$ by F is due to the charge transfer interaction. However, we could not directly demonstrate quenching by the charge transfer interaction, since all the triplets studied did not give any new transient absorption in the case of quenching by F. The triplet level of the dye is 11650 $\mathrm{cm^{-1}}$ [19] and its reduction potential 0.008 V (*vs.* S.C.E.)[10] in aqueous solution at pH=7. The oxidation potentials of F and P in acetonitrile are 0.30[8] and 0.185 V (*vs.* S.C.E.),[20] respectively. According to the method of Rehm and Weller,[21] the changes of free enthalpy ($\Delta G$) involved in the electron transfer reaction from F and P to the triplet dye were estimated both as $\Delta G < -20$ kcal/mol. The result suggests that the triplet dye must be quenched by F and P at a diffusion-controlled rate, which agrees well with the experimental results described above. In addition, the electron transfer reaction from F to the triplet dye, though its efficiency is small, has been confirmed. It can thus be shown that the charge (electron) transfer interaction plays an important role on the triplet quenching by F. The fact that the efficiency of electron transfer reaction from F to the triplet dye is small suggests that the lifetime of encounter complex of the triplet dye and F is too short to react. It can therefore be supposed that the triplet quenching of an aromatic compound whose triplet level is lower than 15000 $\mathrm{cm^{-1}}$ by F is ascribed to the instantaneous formation of the charge transfer complex.

Consequently, F can act as an electron donor for the triplet quenching by charge transfer interaction, but the efficiency of the electron transfer reaction is generally very small.

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