

## QUENCHING OF EXCITED 2,5-DIPHENYLOXAZOLE BY $\text{CCl}_4$

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(Received March 14, 1980)

### Summary

The interactions between the ground and excited states of 2,5-diphenyloxazole and  $\text{CCl}_4$  were investigated in cyclohexane at 23 °C. Distinct complex formation was not observed either in the ground or in the excited states. The quantum yields of fluorescence and intersystem crossing were determined to be 0.85 and 0.12 respectively. The fluorescence is quenched and the photobleaching is extremely enhanced by the addition of  $\text{CCl}_4$ . The excited singlet and triplet states are deactivated by  $\text{CCl}_4$  with rate constants  $k_q = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{qt} = 7.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  respectively. Using the emission-absorption flash technique it was found that the fluorescence quenching by  $\text{CCl}_4$  is caused by the photochemical reaction ( $k_r$ ), intersystem crossing ( $k'_{ST}$ ) and physical quenching ( $k_d$ ) with the relative rates  $k_r:k'_{ST}:k_d = 1:0.4:21$ . The deactivation of the triplet by  $\text{CCl}_4$  is the result of physical quenching.

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### 1. Introduction

Carbon tetrachloride ( $\text{CCl}_4$ ) is known to be an efficient fluorescence quencher for several fluorescent compounds. The quenching ability of  $\text{CCl}_4$  is much stronger than those of  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  for the fluorescence of aliphatic ketones [1] and aromatic compounds [2, 3]. The fluorescence quenching by  $\text{CCl}_4$  has been explained in terms of exciplex formation which may cause the photochemical reaction and the intersystem crossing [4, 5].

The fluorescence of 2,5-diphenyloxazole (PPO) is also quenched by  $\text{CCl}_4$  [2]. The quantum yield  $\Phi_F^0$  of fluorescence of PPO in cyclohexane has been reported to be 1.0 at room temperature [6]. Therefore PPO seems to be suitable for obtaining direct evidence of the enhancement of the intersystem crossing due to fluorescence quenching by  $\text{CCl}_4$ . In the present work we investigate the interaction between  $\text{CCl}_4$  and PPO in the ground and the excited singlet and triplet states in order to clarify the quenching mechanism.

## 2. Experimental

### 2.1. Materials

Scintillation grade PPO (Nakarai) and anthracene (Tokyo Yushi) were used without further purification. Ferrocene (G.R. grade, Tokyo Kasei) was recrystallized from benzene, was zone refined twice and was sublimed twice.  $\text{CCl}_4$  was treated five times with alcoholic sodium hydroxide for  $\frac{1}{2}$  h at 50 - 60 °C, was washed with water, with concentrated sulphuric acid and again with water, was dried over calcium chloride and was distilled over phosphorus pentoxide. Chloroform was treated with concentrated sulphuric acid, was washed with dilute sodium hydroxide and with water, was dried over calcium chloride, was distilled and was passed through activated alumina. 1,1'-Dichloroethane (G.R. grade, Wako Junyaku) was used without further purification. Cyclohexane was purified by a standard method [7].

### 2.2. Apparatus and procedure

Absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer. Fluorescence spectra were measured with a modified Hitachi EPU spectrophotometer the spectral response of which was calibrated in units of relative quanta per wavenumber using quinine sulphate in 1.0 N sulphuric acid, 4-dimethylamino-4'-nitrostilbene in *o*-dichlorobenzene [8] and 2-aminopyridine in 1.0 N sulphuric acid [9]. Lifetime measurements were made with a phase fluorimeter modulated at 10.7 MHz. An NEC He-Cd laser (325 nm) was used for the modulated light source. The flash energy was usually 130 J and full width at half-maximum was about 20  $\mu\text{s}$ . A Toshiba UV-D25 filter and a Pyrex glass filter were used for excitation. A Toshiba SHL-100 UV high pressure mercury lamp was used for the steady light photolysis. Monochromatic light of wavelength 313 nm was taken out through a filter system consisting of a Toshiba UV-D25 filter and an approximately  $5 \times 10^{-4}$  M  $\text{K}_2\text{CrO}_4$  aqueous solution filter. The intensity of the 313 nm light was measured using a potassium ferrioxalate actinometer. Sample solutions were degassed by freeze-pump-thaw cycles unless otherwise stated. All measurements were made at 23 °C.

## 3. Results and discussion

### 3.1. Absorption spectrum

Absorption spectra of PPO in cyclohexane at various concentrations of  $\text{CCl}_4$  are shown in Fig. 1. The spectrum does not change up to a  $\text{CCl}_4$  concentration of about 1 M. Further increase in the  $\text{CCl}_4$  concentration causes a progressive red shift of the spectrum, but no isosbestic point is observed. This shift is a consequence of the general solvent effect.

### 3.2. Fluorescence spectrum, yield and lifetime

It should be noted that, when  $\text{CCl}_4$  is contained in the sample solution, accurate measurements of the fluorescence spectrum, the yield and the

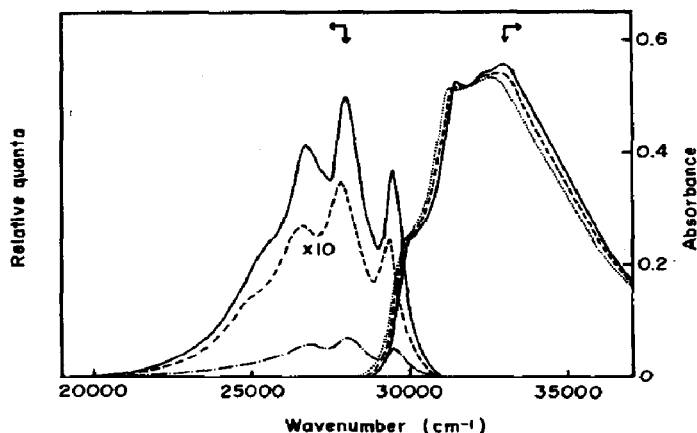


Fig. 1. Absorption and fluorescence spectra of PPO in cyclohexane at various  $\text{CCl}_4$  concentrations: —, 0 M; - - -, 2 M; - · - ·, 4 M; · · ·, 8 M.

lifetime are difficult because of fast photobleaching. The fluorescence spectrum of PPO does not change with the addition of  $\text{CCl}_4$  up to a concentration of about 2 M, but shows a progressive red shift above 2 M as shown in Fig. 1. The fluorescence spectral shape does not depend on the excitation wavelength over the  $\text{CCl}_4$  concentration range studied.

The quantum yield of fluorescence  $\Phi_F^0$  was determined to be 0.85 relative to quinine sulphate in 1.0 N sulphuric acid ( $\Phi_F = 0.546$  at 298 K [10]) as a standard solution, which is in good agreement with the results of Birks [4].

A Stern-Volmer plot of the fluorescence quenching by  $\text{CCl}_4$  is shown in Fig. 2. The plot is linear up to a  $\text{CCl}_4$  concentration of 2 M for both deaerated and aerated solutions:

$$\Phi_F^0/\Phi_F = 1 + K_Q[\text{CCl}_4] \quad (1)$$

From the slope we obtain a quenching constant  $K_Q$  of  $3.0 \text{ M}^{-1}$ . Since the plot does not depend on the excitation wavelength above 265 nm, distinct complex formation between  $\text{CCl}_4$  and PPO in the ground state is not observed, which is in contrast with the case of anthracene [11, 12]. The upward deviation of the plot from the straight line for  $\text{CCl}_4$  concentrations above 2 M can be attributed to the transient effect, which is a result of the non-stationary concentration of quencher molecules around an excited molecule.

The fluorescence lifetime  $\tau_0$  in cyclohexane was measured to be 1.3 ns, which agrees with the value of 1.4 ns reported by Berlman [6]. The fluorescence decay rate  $1/\tau$  increases linearly with increasing  $\text{CCl}_4$  concentration as shown in Fig. 3:

$$1/\tau = 1/\tau_0 + k_q[\text{CCl}_4] \quad (2)$$

From the slope we obtain  $k_q = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The values  $\tau_0 = 1.3 \text{ ns}$  and  $k_q = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  give  $K_Q = k_q\tau_0 = 2.6 \text{ M}^{-1}$  which is consistent with the value just obtained using the steady state method. The diffusion-controlled

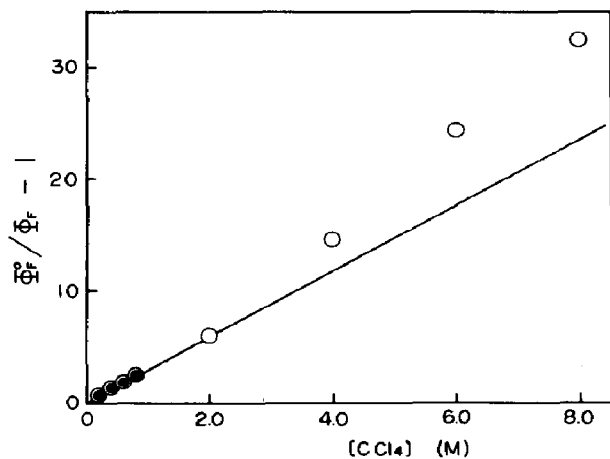


Fig. 2. A Stern-Volmer plot for aerated (○) and deaerated (●) solutions.

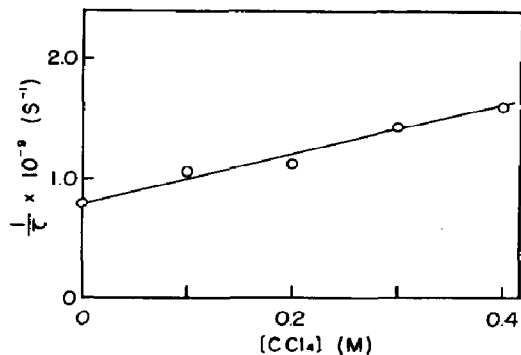


Fig. 3. A plot of  $1/\tau$  vs.  $[\text{CCl}_4]$ .

bimolecular rate constant is calculated to be  $7.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in cyclohexane at  $23^\circ \text{C}$  using the modified Debye equation ( $8RT/3000\eta$  [13]), so that one of every five collisions between PPO in the excited singlet state  $^1\text{PPO}^*$  and  $\text{CCl}_4$  causes the deactivation.

The fluorescence of PPO is not quenched by the addition of either 1.24 M  $\text{CHCl}_3$  or 1.26 M  $\text{C}_2\text{H}_4\text{Cl}_2$  in cyclohexane. Therefore the fluorescence quenching by  $\text{CCl}_4$  cannot be attributed to the heavy atom effect of the chlorine atoms in  $\text{CCl}_4$ .

### 3.3. Steady light photolysis

Photobleaching of PPO essentially does not occur in cyclohexane, but is extremely enhanced by the addition of  $\text{CCl}_4$ . Typical changes in the absorption spectra caused by irradiation of the deaerated and aerated solutions containing 0.2 M  $\text{CCl}_4$  are shown in Fig. 4. Two isosbestic points appear at 269 and 340 nm in the deaerated solution and at 266 and 340 nm in the aerated solution; the formation of the photoproduct is proportional to the decrease of PPO in both the deaerated and aerated solutions. The photoproduct in the deaerated solution is not necessarily identical with that in the aerated solution, as can be seen from the spectral change above 350 nm upon irradiation. Attempts to identify the photoproduct have not yet been successful.

Plots of  $\ln(e^{\epsilon cd} - 1)$  versus time are linear for both the deaerated and aerated solutions containing  $\text{CCl}_4$ ; the rate of the photoreaction is proportional to the light quanta absorbed. The quantum yield  $\Phi_R$  of the photobleaching was determined from the slope. Plots of  $1/\Phi_R$  versus  $1/[\text{CCl}_4]$  for the deaerated and aerated solutions are linear as shown in Fig. 5:

$$1/\Phi_R = C_1 + C_2/[\text{CCl}_4] \quad (3)$$

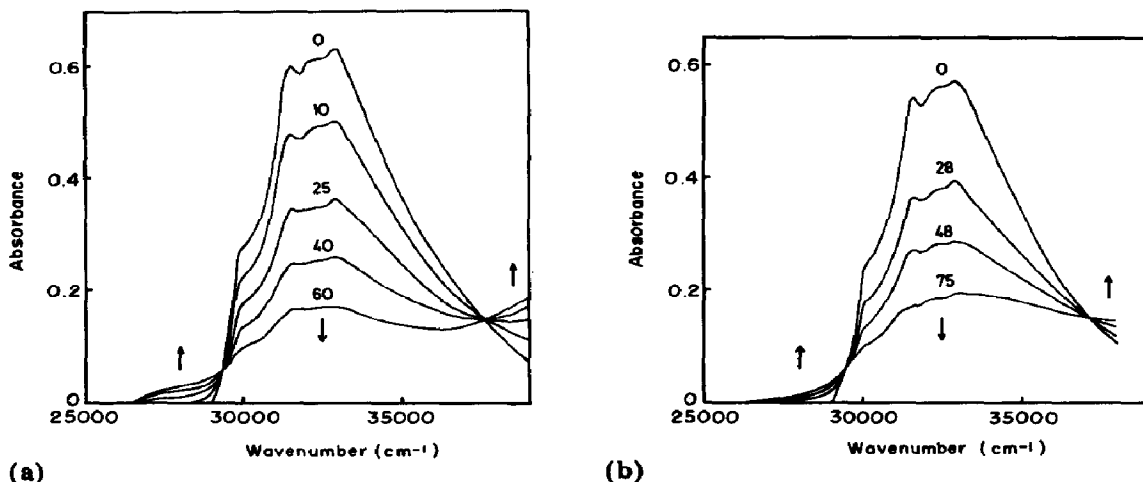


Fig. 4. Spectral changes of PPO upon 365 nm irradiation: (a) an aerated solution containing 0.2 M  $\text{CCl}_4$ ; (b) a deaerated solution containing 0.2 M  $\text{CCl}_4$ .

From the intercepts and slopes we obtain  $C_1 = 22.0$  and  $C_2 = 7.7$  M for the deaerated solution and  $C_1 = 7.0$  and  $C_2 = 2.5$  M for the aerated solution respectively. It should be noted that  $\Phi_R$  of the aerated solution is larger than that of the deaerated solution for the same concentration of  $\text{CCl}_4$ .

$\Phi_R$  is not altered by the addition of 0.1 mM ferrocene which is known [14, 15] to be an effective triplet quencher. This result suggests that the lowest triplet state  $^3\text{PPO}$  does not participate in the photoreaction.

### 3.4. Flash photolysis

Figure 6(a) shows the transient absorption spectrum observed in cyclohexane; it is similar to the triplet-triplet (T-T) absorption spectrum of PPO in ethanol [16]. Since further triplet energy transfer from this transient to anthracene was observed, it is attributed to the T-T absorption spectrum of PPO. The decay constant observed is expressed as follows:

$$k_{\text{obsd}}^{\circ} = k_{\text{dt}} = k_1 + k_2[{}^3\text{PPO}] \quad (4)$$

where  $k_1 = 6.0 \times 10^2 \text{ s}^{-1}$  and  $k_2/\epsilon_T = 3.5 \times 10^5 \text{ s}^{-1} \text{ cm}$  at 500 nm. The molar extinction coefficient  $\epsilon_T$  of the T-T absorption was determined to be  $1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 500 nm from the triplet energy transfer from PPO to anthracene; an emission-absorption flash technique [17, 18] and  $\epsilon_T(\text{anthracene}) = 6.47 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 425 nm in cyclohexane [19] were used. Hence,  $k_2$  is determined to be  $4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

The quantum yield  $\Phi_{\text{ST}}^{\circ}$  of intersystem crossing of PPO in cyclohexane was determined using an emission-absorption flash technique. The following equation was used [18]:

$$\frac{\Phi_{\text{ST}}^{\text{P}}}{\Phi_{\text{ST}}^{\text{A}}} \frac{\epsilon_{\text{T}}^{\text{P}}(\lambda^{\text{P}})}{\epsilon_{\text{T}}^{\text{A}}(\lambda^{\text{A}})} = \left[ \frac{\{\alpha(\lambda')\Phi_{\text{F}}\}^{\text{P}}}{\{\alpha(\lambda')\Phi_{\text{F}}\}^{\text{A}}} \right] \frac{\{D_0^{\text{P}}(\lambda^{\text{P}})/\int I_{\text{F}}^{\text{P}}(\lambda') dt\}}{\{D_0^{\text{A}}(\lambda^{\text{A}})/\int I_{\text{F}}^{\text{A}}(\lambda') dt\}} \quad (5)$$

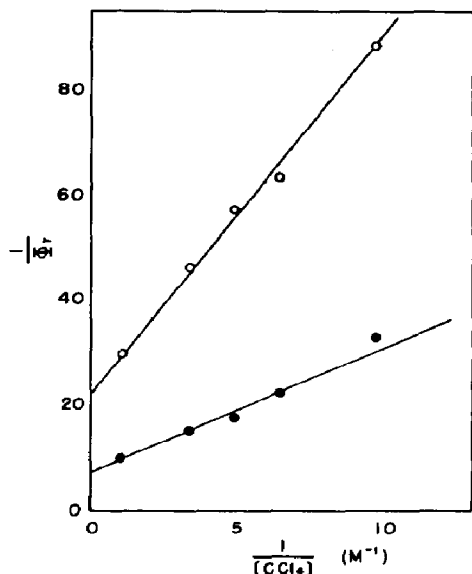


Fig. 5. Plots of  $1/\Phi_R$  vs.  $1/[\text{CCl}_4]$  for aerated (●) and deaerated (○) solutions.

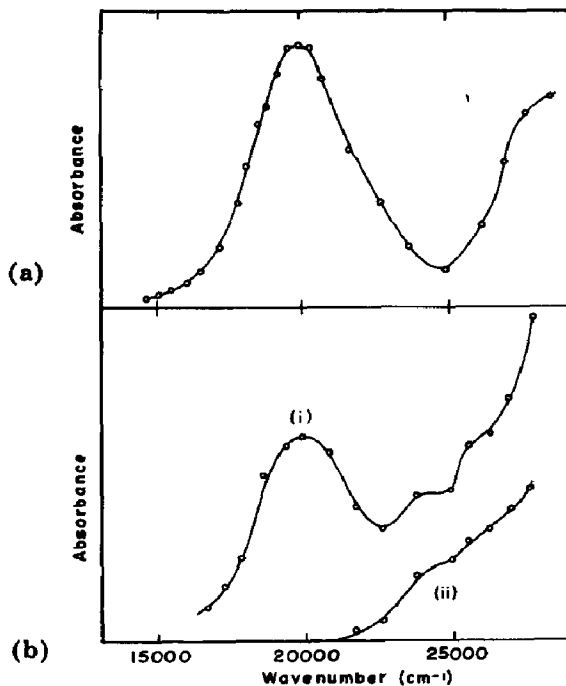


Fig. 6. (a) A T-T absorption spectrum in cyclohexane and (b) transient absorption spectra observed (i) 0.2 ms and (ii) 1 ms after flashing of a solution containing 0.45 M  $\text{CCl}_4$ .

where  $\alpha(\lambda')$  is a constant depending upon the experimental conditions,  $D_0(\lambda)$  is the absorbance of the T-T absorption at the end of the flash,  $\int I_F(\lambda') dt$  is the time-integrated fluorescence intensity during the flash excitation and the superscripts A and P denote anthracene (for reference) and PPO respectively. The results are listed in Table 1. With the assumption  $\Phi_{ST}^A = 1 - \Phi_F^A = 0.70$  ( $\Phi_F^A = 0.30$  in cyclohexane [4]),  $\Phi_{ST}^P = \Phi_{ST}^A$  was determined to be 0.12. Since the sum of  $\Phi_F^P$  and  $\Phi_{ST}^P$  is nearly equal to unity, internal conversion in the excited singlet state is negligible.

When  $\text{CCl}_4$  was added to the solution, a long-lived transient absorption as shown in Fig. 6(b) was observed in addition to the T-T absorption. The lifetime of this transient is longer than 1 s, but its decay is not fully reproducible. The observed decay rate of  $^3\text{PPO}$  increases with increasing  $\text{CCl}_4$  concentration as shown in Fig. 7:

$$k_{\text{obsd}}^C = k_{dt} + k_{qt}[\text{CCl}_4] \quad (6)$$

From the slope we obtain  $k_{qt} = 7.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

When ferrocene was added to the solution, the decay rate of  $^3\text{PPO}$  increased but no further transient absorption appeared. As shown in Fig. 8, the first order rate constants observed for  $^3\text{PPO}$  are linear with respect to ferrocene concentration:

TABLE 1

Ionization potentials IP and excitation energies  $E_s$ 

	IP (eV)	$E_s$ (eV)	IP - $E_s$ (eV)
Anthracene	7.29 <sup>a</sup>	3.29	4.00
PPO	7.99 <sup>b</sup>	3.72	4.27
9,10-Dichloroanthracene	7.84 <sup>a</sup>	3.08	4.76

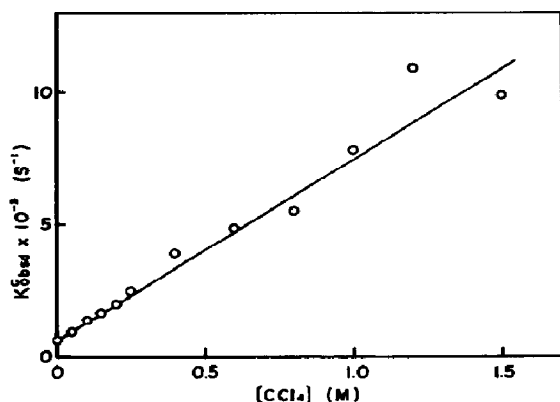
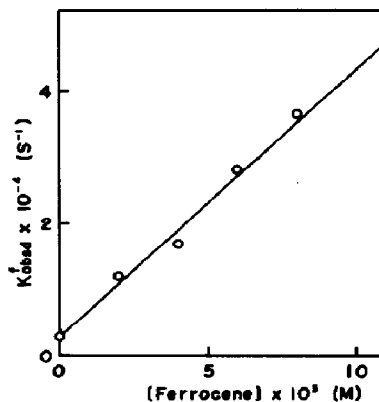
<sup>a</sup>Data taken from ref. 20.<sup>b</sup>Data taken from ref. 2.Fig. 7. The dependence of the triplet decay on  $\text{CCl}_4$  concentration.

Fig. 8. The dependence of the triplet decay on ferrocene concentration.

$$k_{\text{obs}}^t = k_{\text{dt}} + k'_{\text{qt}}[\text{ferrocene}] \quad (7)$$

We obtain  $k'_{\text{qt}} = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . When 0.1 mM ferrocene was added to the solution containing  $\text{CCl}_4$ , the T-T absorption disappeared but the long-lived transient remained observable.

It has been found [21 - 23] that an emission-absorption flash technique is one of the most excellent methods of investigating the fluorescence quenching mechanism. Since no fluorescence other than the prompt fluorescence appears with the addition of  $\text{CCl}_4$  and since the T-T absorption is observed even in the presence of  $\text{CCl}_4$ , whether or not the interaction between  $^1\text{PPO}^*$  and  $\text{CCl}_4$  causes the intersystem crossing enhancement can easily be confirmed using this technique. Figure 9 shows a plot of  $D_0(\lambda)/\int I_F(\lambda')dt$  versus  $[\text{CCl}_4]$ . Since the plot is linear and the slope is positive, it is concluded that the interaction enhances the intersystem crossing (see eqn. (12)). However, the enhanced intersystem crossing is not attributed to the heavy atom effect of  $\text{CCl}_4$ , because the fluorescence of PPO is not quenched by  $\text{CHCl}_3$  and  $\text{C}_2\text{H}_4\text{Cl}_2$ .

On the basis of these results, we summarize the reaction scheme in the deaerated solution as follows:

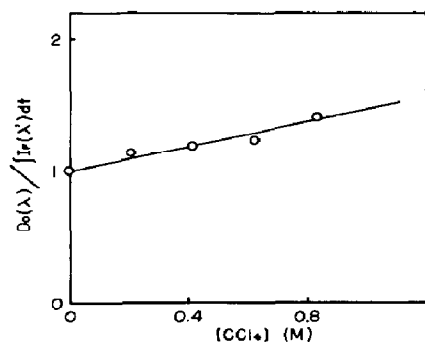
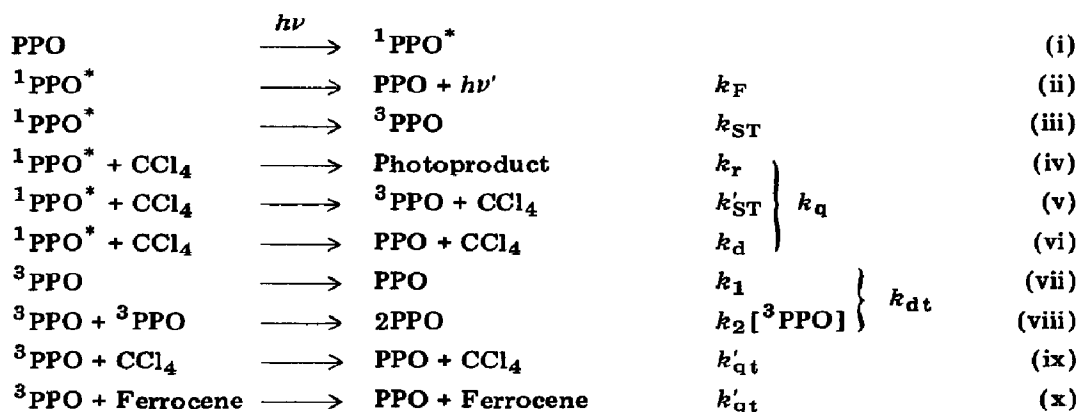


Fig. 9. A plot of  $D_0(\lambda)/\int I_F(\lambda')dt$  vs.  $[CCl_4]$ :  $\lambda = 500$  nm,  $\lambda' = 400$  nm.



Scheme 1.

In Scheme 1 exciplex formation between  $^1PPO^*$  and  $CCl_4$  was not taken into account, in contrast with previous work [11, 12], because no distinct evidence of complex formation in the ground and excited states was found. The contact exciplex, the formation of which is possible, was also not considered, because it cannot be distinguished from the encounter complex.

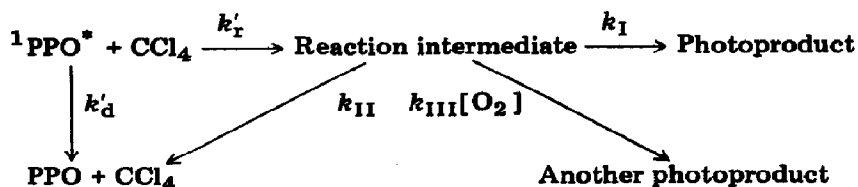
Using Scheme 1 the concentration effects of  $CCl_4$  on the quantum yields of photobleaching and intersystem crossing can be analysed. The yield of photobleaching is related to the  $CCl_4$  concentration as follows:

$$\frac{1}{\Phi_R} = \frac{k_q}{k_r} \left( 1 + \frac{1}{k_{qT_0}} \frac{1}{[CCl_4]} \right) \quad (8)$$

Therefore the ratio  $C_1/C_2$  of the intercept to the slope for the deaerated solution in Fig. 5 gives the quenching constant. The ratio is  $2.9 \text{ M}^{-1}$ , which agrees with  $K_Q = 2.6$  or  $3.0 \text{ M}^{-1}$  obtained from the fluorescence quenching. It is interesting that the ratio for the aerated solution ( $C_1/C_2 = 2.8 \text{ M}^{-1}$ ) also agrees with the quenching constant. This fact and the result that  $\Phi_R$  of the aerated solution is larger than that of the deaerated solution can be ex-



plained in terms of the detailed reaction mechanisms for processes (iv) and (vi) as given in Scheme 2.



Scheme 2.

A long-lived transient, shown in Fig. 6(b), can be assigned to the reaction intermediate, because the decay is faster in the aerated solution than in the deaerated solution. Then the rate constants of processes (iv) and (vi) are expressed as follows:

$$k_r = k'_r(k_I + k_{III}[\text{O}_2]) / (k_I + k_{II} + k_{III}[\text{O}_2]) \quad (9)$$

$$k_d = k'_d + k'_r k_{II} / (k_I + k_{II} + k_{III}[\text{O}_2]) \quad (10)$$

When  $k_I / (k_I + k_{II}) < (k_I + k_{III}[\text{O}_2]) / (k_I + k_{II} + k_{III}[\text{O}_2])$ , the effect of  $\text{O}_2$  on  $\Phi_R$  can be interpreted as follows: the reaction between  $\text{O}_2$  and the reaction intermediate suppresses the back reaction of the intermediate to reproduce PPO. From the intercept of the plot for the deaerated solution we obtain  $k_q/k_r = 22$ . As  $k_q = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_r$  is calculated to be  $9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .

The ratio of  $\Phi_{ST}$  to  $\Phi_F$  is related to the  $\text{CCl}_4$  concentration as follows:

$$\Phi_{ST}/\Phi_F = (k_{ST} + k'_{ST}[\text{CCl}_4]) / k_F \quad (11)$$

Hence we obtain the relation

$$\frac{D_0(\lambda)}{\int I_F(\lambda') dt} = \frac{\epsilon_T(\lambda)d}{\alpha(\lambda')k_F} (k_{ST} + k'_{ST}[\text{CCl}_4]) \quad (12)$$

From the intercept and slope of the plot in Fig. 9 we obtain

$$k_{ST}/k'_{ST} = 2.6 \text{ M}$$

Using  $\tau_0 = 1.3 \text{ ns}$  and  $\Phi_{ST}^0 = 0.12$ , we obtain  $k_{ST} = 8.5 \times 10^7 \text{ s}^{-1}$  and hence  $k'_{ST} = 3.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .  $k_d (= k_q - k_r - k'_{ST})$  is calculated to be  $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Consequently the relative rates of the fluorescence quenching pathways are as follows:

$$k_r : k'_{ST} : k_d = 1 : 0.4 : 21$$

Compared with the fluorescence quenching of anthracene derivatives by  $\text{CCl}_4$  [5], (1) the reaction efficiency  $k_r/k_q$  is smaller except for 9,10-dichloroanthracene (DCA), (2) the efficiency  $k'_{ST}/k_q$  of intersystem crossing is much smaller and (3) the efficiency  $k_d/k_q$  of trivial deactivation is much larger. It has been suggested [4] that the fluorescence quenching of anthracene derivatives by  $\text{CCl}_4$  occurs through donor-acceptor exciplex formation where the derivatives act as electron donors and  $\text{CCl}_4$  acts as the acceptor. The

ionization potentials (IP) and the excitation energies  $E_s$  of the first excited singlet states of anthracene, PPO and DCA are listed in Table 1. Since the fluorescence of DCA is not effectively quenched by  $\text{CCl}_4$  but that of anthracene is [12, 24] and  $\text{IP} - E_s$  of DCA is larger than that of anthracene, the mechanism proposed seems to be valid. Therefore, the fluorescence quenching of PPO by  $\text{CCl}_4$  can be attributed to charge transfer interaction. However, it should be noted that  $k_q$  of PPO ( $2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) is much larger than that of anthracene ( $2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  [12]). Since the value of  $\text{IP} - E_s$  for anthracene is smaller than that for PPO, charge transfer interaction alone cannot explain the experimental results.

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