

## THE FLUORESCENCE QUENCHING OF 1,4-BIS[2-(5-PHENYLOXAZOLYL)]-BENZENE BY BROMOMETHANES

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### Summary

The interaction between the ground and excited states of 1,4-bis[2-(5-phenyloxazolyl)]-benzene and bromomethanes such as CBr<sub>4</sub>, CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> were investigated in benzene. Distinct complex formation was not observed either in the ground state or in the excited states. The excited singlet and triplet states are deactivated by these bromomethanes. The triplet yield is increased on the addition of CHBr<sub>3</sub> or CH<sub>2</sub>Br<sub>2</sub>, whereas it is decreased on the addition of CBr<sub>4</sub>. The fluorescence quenching rate constants  $k_q$  at 23 °C were determined to be  $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,  $3.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $2.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for CBr<sub>4</sub>, CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> respectively. The rate constants  $k_{ST}'$  of the enhanced intersystem crossing associated with the fluorescence quenching were evaluated from emission-absorption flash photolysis experiments as  $3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $5.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for CBr<sub>4</sub>, CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> respectively.  $k_{ST}'$  increases with increasing number of bromine atoms contained in the quencher, so that the enhanced intersystem crossing is due to the external heavy-atom effect of the quencher. The apparent triplet yield for the quenching system depends not only on  $k_{ST}'$  but also on the rates of the other non-radiative processes. This is the reason why the apparent triplet yield does not necessarily increase on fluorescence quenching by bromomethanes.

### 1. Introduction

Alkyl halides are known to be efficient fluorescence quenchers for many fluorescent molecules [1 - 15]. The fluorescence quenching by alkyl halides has usually been explained in terms of a charge transfer interaction, although there is no convincing evidence of exciplex formation. The charge transfer interaction in the encounter complex or the exciplex may cause a

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photochemical reaction, an enhancement of the  $S_1 \rightarrow T_1$  intersystem crossing and other physical quenching; the first and third of these processes were found in many fluorescer-alkyl halide systems, whilst, in contrast, the second was not generally found because the resultant yield of the  $S_1 \rightarrow T_1$  intersystem crossing usually diminished with the quenching. A distinct enhancement in the  $S_1 \rightarrow T_1$  intersystem crossing yield was found for anthracene-alkyl iodide [4].

In a previous work [11], we studied the fluorescence quenching of 2,5-diphenyloxazole (PPO) by carbon tetrachloride ( $CCl_4$ ) using an emission-absorption flash technique and found that the quenching is caused by a photochemical reaction ( $k_r$ ), an enhanced intersystem crossing ( $k_{isc}'$ ) and a physical quenching ( $k_d$ ) with the relative rates  $k_r:k_{isc}':k_d = 1:0.4:21$ . The contribution of the enhanced intersystem crossing to the quenching is low in this case. However, if bromomethanes or iodomethanes are used as quenchers instead of  $CCl_4$ , the contribution of the enhanced intersystem crossing to the quenching is expected to increase enormously because the spin-orbit interaction in the encounter state or the exciplex is much larger for bromomethanes or iodomethanes than for  $CCl_4$ . Therefore a measurement of the rate of the enhanced intersystem crossing is necessary for a full understanding of the mechanism of the fluorescence quenching by alkyl halides, especially when the alkyl halides contain bromine or iodine atoms.

In the present work we have studied the fluorescence quenching of 1,4-bis[2-(5-phenyloxazolyl)]-benzene (POPOP) by dibromomethane ( $CH_2Br_2$ ), bromoform ( $CHBr_3$ ) and carbon tetrabromide ( $CBr_4$ ) using an emission-absorption flash technique to demonstrate how the heavy atoms included in the alkyl halides affect the fluorescence quenching mechanism. Benzene was used as the solvent instead of cyclohexane because in the latter POPOP was adsorbed onto the glass walls of the apparatus.

## 2. Experimental details

### 2.1. Materials

POPOP (Scintillation grade, Dojin) was used as received after checking its purity by thin-layer chromatography and by emission measurements.  $CH_2Br_2$  (Guaranteed Reagent grade, Nakarai) was treated with a 10%  $Na_2CO_3$  aqueous solution, washed with water, dried over  $CaCl_2$  and then distilled over  $P_2O_5$  in vacuum.  $CHBr_3$  (Extra Pure grade, Tokyo Kasei) was washed three times with an aqueous solution of  $CaCl_2$ , washed with water, dried over  $CaCl_2$  and distilled over molecular sieves (3A 1/16, Nakarai) in vacuum.  $CBr_4$  (Guaranteed Reagent grade, Tokyo Kasei) was recrystallized from ethanol and sublimed twice in vacuum. Benzene was purified by using standard methods.

### 2.2. Apparatus and procedure

Absorption spectra were recorded using a Hitachi 330 spectrophotometer. Fluorescence spectra were measured with a spectrophotometer built in

our laboratory. The spectral response was calibrated in units of relative number of quanta per wavenumber. The Stern–Volmer plots were obtained for an excitation wavelength of 380 nm where the bromomethanes employed do not absorb. Fluorescence lifetimes were measured using a phase fluorometer modulated at 10.7 MHz. A xenon flash lamp (130 J; full width at half-maximum (FWHM), 10  $\mu$ s) was used for the emission–absorption flash experiments. A combination of a Toshiba UVP bandpass filter with an L-39 cut-off filter was used for the excitation. The method for measuring the transient absorption and the time-integrated fluorescence intensity during a flash was essentially the same as reported previously [15]. The fluorescence yield was determined by using a 1 N H<sub>2</sub>SO<sub>4</sub> aqueous solution of quinine sulphate as a standard [16]. Busselle *et al.* [17] denied the necessity of a correction for the refractive index  $n$  whereas Ediger *et al.* [18] showed that a correction factor of  $1/n^2$  is appropriate for common experimental geometries. To check the validity of the  $1/n^2$  correction for our apparatus, we measured the fluorescence intensity  $\int I_F(\tilde{\nu}) d\tilde{\nu}$  of perylene in benzene and ethanol with and without a lens to collect the fluorescence.

Since the relative fluorescence intensity of these solutions does not change in the presence and absence of a lens and is in accord with the relative value of  $1/n^2$  for these solvents, the  $1/n^2$  correction is necessary under our experimental conditions.

Sample solutions were degassed by means of freeze–pump–thaw cycles. The measurements were made at 23 °C unless otherwise noted.

### 3. Results and discussion

#### 3.1. Photophysical properties of excited POPOP in benzene

The absorption and fluorescence spectra of POPOP are shown in Fig. 1. The molar extinction coefficient of the absorption maximum at 27 550

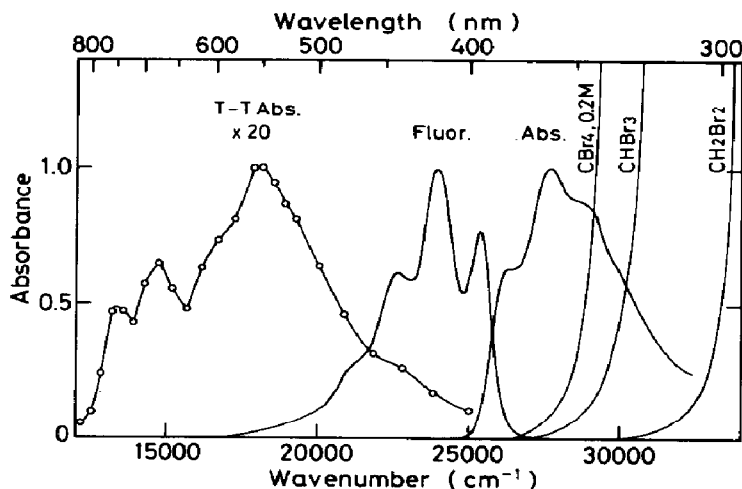


Fig. 1. Absorption, fluorescence and T–T absorption spectra of POPOP in benzene.

$\text{cm}^{-1}$  was  $49\,300\text{ M}^{-1}\text{ cm}^{-1}$ . The quantum yield  $\Phi_{\text{F}}^0$  of fluorescence was determined as 0.94, which is slightly larger than the value of 0.86 reported by Birks and Dyson [19]. The fluorescence lifetime  $\tau_{\text{F}}^0$  was measured to be 1.0 ns, which is slightly smaller than the values of 1.26 ns and 1.3 ns reported by Berlman [20] and Birks and Dyson [19] respectively. Using  $\tau_{\text{F}}^0 = 1.0\text{ ns}$  and  $\Phi_{\text{F}}^0 = 0.94$ , the radiative rate constant  $k_{\text{F}}$  is calculated to be  $9.4 \times 10^8\text{ s}^{-1}$ .

Figure 1 also shows the transient absorption spectrum, which was assigned to triplet-triplet (T-T) absorption due to triplet energy transfer from POPOP to anthracene (triplet energy,  $14\,870\text{ cm}^{-1}$  [21]) and pyrene (triplet energy,  $16\,930\text{ cm}^{-1}$  [21]). The triplet energy of POPOP was determined as  $19\,400\text{ cm}^{-1}$  from the 0-0 band of the phosphorescence in an ethanol-methanol (1:1 by volume) mixture at 77 K. The triplet decay is first order with a rate constant  $k_{\text{at}}$  of  $5.7 \times 10^2\text{ s}^{-1}$ . The molar extinction coefficient  $\epsilon_{\text{T}}$  for the T-T absorption due to triplet energy transfer from POPOP to pyrene was determined as  $37\,600\text{ M}^{-1}\text{ cm}^{-1}$  at  $\lambda_{\text{max}} = 550\text{ nm}$ . The molar extinction coefficient for the T-T absorption of pyrene was reported to be  $20\,900\text{ M}^{-1}\text{ cm}^{-1}$  at  $420\text{ nm}$  [22].

The quantum yield  $\Phi_{\text{ST}}^0$  of intersystem crossing was determined using an emission-absorption flash technique. The equation

$$\frac{\Phi_{\text{ST}}^{\text{P}}}{\Phi_{\text{ST}}^{\text{A}}} \frac{\epsilon_{\text{T}}^{\text{P}}(\lambda^{\text{P}})}{\epsilon_{\text{T}}^{\text{A}}(\lambda^{\text{A}})} = \frac{\{\alpha(\lambda')\Phi_{\text{F}}\}^{\text{P}}}{\{\alpha(\lambda')\Phi_{\text{F}}\}^{\text{A}}} \frac{\{D^{\text{P}}(\lambda^{\text{P}})/\int I_{\text{F}}^{\text{P}}(\lambda')\text{ dt}\}}{\{D^{\text{A}}(\lambda^{\text{A}})/\int I_{\text{F}}^{\text{A}}(\lambda')\text{ dt}\}} \quad (1)$$

was used [23], where  $\alpha(\lambda')$  is a constant depending on the experimental conditions,  $D(\lambda)$  is the absorbance of the T-T absorption at the end of the flash,  $\int I_{\text{F}}(\lambda')\text{ dt}$  is the time-integrated fluorescence intensity at  $\lambda'$  during the flash excitation and the superscripts A and P denote 9,10-dichloroanthracene (the reference) and POPOP respectively. The molar extinction coefficient for the T-T absorption of 9,10-dichloroanthracene was reported to be  $37\,900\text{ M}^{-1}\text{ cm}^{-1}$  at  $\lambda_{\text{max}} = 425.5\text{ nm}$  [24]. The results are listed in Table 1. With the assumption  $\Phi_{\text{ST}}^{\text{A}} = 1 - \Phi_{\text{F}}^{\text{A}} = 0.36$  ( $\Phi_{\text{F}}^{\text{A}} = 0.64$  in benzene),  $\Phi_{\text{ST}}^{\text{P}} \equiv \Phi_{\text{ST}}^0$  was determined as 0.054. The sum of  $\Phi_{\text{F}}^0$  and  $\Phi_{\text{ST}}^0$  is very close to unity. Using

TABLE 1

Determination of  $\Phi_{\text{ST}}^{\text{P}}$ 

$\epsilon_{\text{T}}^{\text{P}}(550\text{ nm})$	$\{\alpha(\lambda')\Phi_{\text{F}}\}^{\text{P}}$	$D^{\text{P}}(550\text{ nm})/\int I_{\text{F}}^{\text{P}}(\lambda')\text{ dt}$	$\Phi_{\text{ST}}^{\text{P}}$	$\Phi_{\text{ST}}^{\text{P}}$
$\epsilon_{\text{T}}^{\text{A}}(425.5\text{ nm})$	$\{\alpha(\lambda')\Phi_{\text{F}}\}^{\text{A}}$	$D^{\text{A}}(425.5\text{ nm})/\int I_{\text{F}}^{\text{A}}(\lambda')\text{ dt}$	$\Phi_{\text{ST}}^{\text{A}}$	
	0.59 ( $\lambda' = 434\text{ nm}$ )	0.26 ( $\lambda' = 434\text{ nm}$ )	0.15	
0.99	2.13 ( $\lambda' = 422.5\text{ nm}$ )	0.072 ( $\lambda' = 422.5\text{ nm}$ )	0.15	0.054 <sup>a</sup>

<sup>a</sup> $\Phi_{\text{ST}}^{\text{A}} = 0.36$ .

$\tau_F^0 = 1.0$  ns and  $\Phi_{ST}^0 = 0.054$ , the rate constant  $k_{ST}$  of intersystem crossing is calculated to be  $5.4 \times 10^7$  s $^{-1}$ .

### 3.2. Fluorescence quenching

The absorption and fluorescence spectra of POPOP in benzene do not change on adding  $CBr_4$  up to a concentration of about 0.3 M. The absorption and fluorescence spectra in  $CHBr_3$  and  $CH_2Br_2$  are similar to those in benzene, but the absorption and fluorescence peaks are shifted from 27 550 and 23 920  $cm^{-1}$  in benzene to 27 100 and 23 360  $cm^{-1}$  in  $CHBr_3$  and to 27 320 and 23 470  $cm^{-1}$  in  $CH_2Br_2$ . These shifts are a consequence of the general solvent effect. In these spectroscopic studies complex formation of POPOP with the bromomethanes employed was detected in neither the ground nor the excited singlet states.

Figure 2(a) shows the Stern–Volmer plots for the fluorescence quenching by  $CBr_4$ . The plot for  $\Phi_F^0/\Phi_F$  is not linear and deviates upward at high  $CBr_4$  concentrations. The quenching was enhanced on increasing the temperature. Furthermore, the Arrhenius plot for the quenching constants obtained for a lower quencher concentration gave an activation energy of 2.6 kcal mol $^{-1}$  which agreed with the activation energy for the viscosity of benzene. Therefore, the quenching is considered to occur dynamically and the upward deviation is attributed to the non-stationary quenching by  $CBr_4$  molecules. In accordance with such considerations the plot for  $\tau_F^0/\tau_F$  is linear as shown in Fig. 2(a). From the slope we obtain  $k_q = 1.6 \times 10^{10}$  M $^{-1}$  s $^{-1}$  as the bimolecular quenching rate constant.

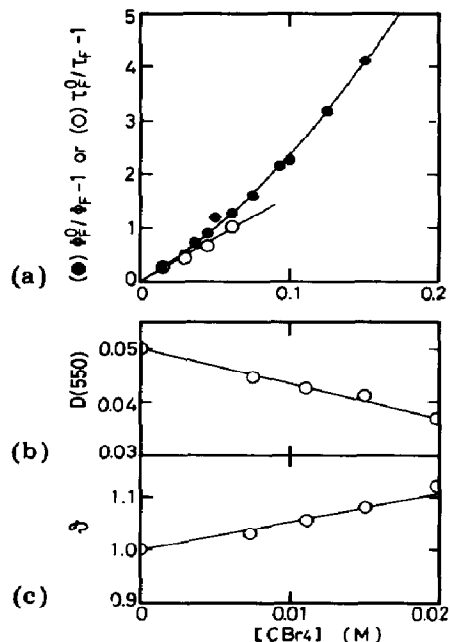


Fig. 2. Effects of  $CBr_4$  concentration on (a)  $\Phi_F^0/\Phi_F - 1$  and  $\tau_F^0/\tau_F - 1$ , (b)  $D(550$  nm) and (c)  $S$ .

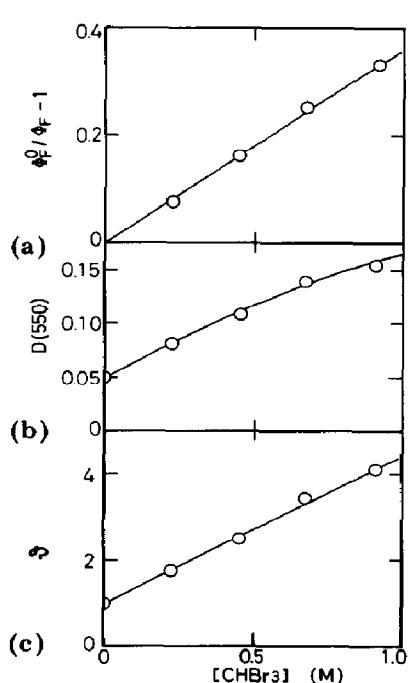


Fig. 3. Effects of  $\text{CHBr}_3$  concentration on (a)  $\Phi_F^0/\Phi_F - 1$ , (b)  $D(550\text{nm})$  and (c)  $\vartheta$ .

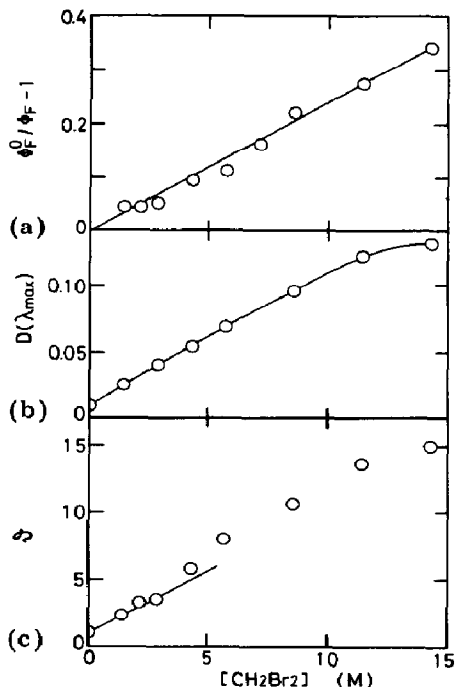


Fig. 4. Effects of  $\text{CH}_2\text{Br}_2$  concentration on (a)  $\Phi_F^0/\Phi_F - 1$ , (b)  $D(\lambda_{\text{max}})$  and (c)  $\vartheta$ .

When  $\text{CHBr}_3$  was used as the quencher, the Stern-Volmer plot for  $\Phi_F$  was linear with respect to the quencher concentration up to 1 M as shown in Fig. 3(a) and deviated gradually upward above 1 M. From the slope of the plot below 1 M we obtain a quenching rate constant  $k_q = 3.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . Since the quenching was enhanced on increasing the temperature and the activation energy of  $3.1 \text{ kcal mol}^{-1}$  for the quenching was close to that for the viscosity of benzene, the above rate constant is regarded as the dynamic one.

When  $\text{CH}_2\text{Br}_2$  was used as the quencher, the Stern-Volmer plot for  $\Phi_F$  was linear as shown in Fig. 4(a). Since the plot did not change in the temperature range 283 - 313 K and the absorption and fluorescence spectra showed progressive red shifts on increasing the quencher concentration, the quenching is attributed to the solvent effect and not to complex formation in the ground and/or the excited states. Direct evidence for quenching due to the solvent effect was obtained for the fluorescence quenching of fluoranthene with  $\text{CH}_2\text{Br}_2$  [25]. The values for  $\tau_F$  and  $\Phi_F$  in  $\text{CH}_2\text{Br}_2$  were determined as 0.8 ns and 0.70 respectively. For the quenching rate constant we obtained  $k_q = 2.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  from the slope of the Stern-Volmer plot.

### 3.3. Triplet quenching and apparent triplet yield

The absorbance of the T-T absorption at  $\lambda_{\text{max}}$  immediately after flashing decreased on the addition of  $\text{CBr}_4$  whereas it increased on the addition of

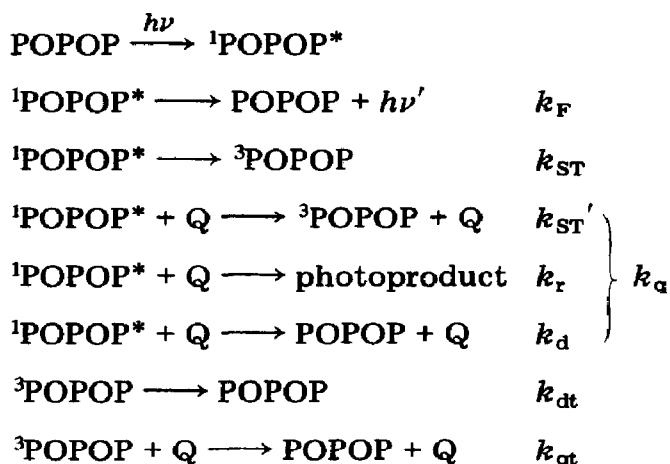
$\text{CHBr}_3$  or  $\text{CH}_2\text{Br}_2$  as shown in Figs. 2(b), 3(b) and 4(b). An enhancement in the intersystem crossing is evident for  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$ .

The observed decay rate  $k_{\text{obs}}$  of triplet POPOP increased linearly with increasing the quencher concentration  $[\text{Q}]$ . From the slope of the plot for  $k_{\text{obs}}$  versus  $[\text{Q}]$  we obtained  $k_{\text{qt}} = 4.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ,  $1.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $5.4 \times 10 \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{CBr}_4$ ,  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$  respectively, for the bimolecular rate constants for low concentrations of quencher.

The spectral shape of the T-T absorption was not changed by adding  $\text{CBr}_4$  or  $\text{CHBr}_3$ . However, a slight spectral change with a progressive red shift was observed in the case of  $\text{CH}_2\text{Br}_2$ :  $\lambda_{\text{max}} = 560 \text{ nm}$ .

### 3.4. Reaction scheme

On the basis of the results described in Sections 3.2 and 3.3, the following reaction scheme is proposed.



$\Phi_{\text{F}}$  and  $\Phi_{\text{ST}}$  are related to the quencher concentration by the equations

$$\Phi_{\text{F}} = \frac{k_{\text{F}}}{k_{\text{F}} + k_{\text{ST}} + k_{\text{d}} + k_{\text{q}}[\text{Q}]} \quad (2)$$

$$\Phi_{\text{ST}} = \frac{k_{\text{ST}} + k_{\text{ST}'}[\text{Q}]}{k_{\text{F}} + k_{\text{ST}} + k_{\text{d}} + k_{\text{q}}[\text{Q}]} \quad (3)$$

For an emission-absorption flash photolysis the following relation holds:

$$\frac{D(\lambda_{\text{max}})}{n^2 \iint I_{\text{F}}(t, \tilde{\nu}) dt d\tilde{\nu}} = \frac{\epsilon_{\text{T}}(\lambda_{\text{max}}) d}{\alpha} \frac{\Phi_{\text{ST}}}{\Phi_{\text{F}}} \quad (4)$$

where  $n^2 \iint I_{\text{F}}(t, \tilde{\nu}) dt d\tilde{\nu}$  is used instead of  $\int I_{\text{F}}(\lambda') dt$  in eqn. (1) to take into account the changes in the fluorescence spectrum and the refractive index  $n$

of the solvent. From eqns. (2) - (4) we obtain

$$\vartheta \equiv \left( \frac{n^0}{n} \right)^2 \frac{D(\lambda_{\max})/\iint I_F(t, \tilde{\nu}) dt d\tilde{\nu}}{D^0(\lambda_{\max})/\iint I_F^0(t, \tilde{\nu}) dt d\tilde{\nu}} = 1 + \frac{k_{ST}'}{k_{ST}} [Q] \quad (5)$$

where the zero superscript stands for a null quencher concentration. Equation (5) is valid if  $\epsilon_T(\lambda_{\max})$  and  $k_F$  do not change in the quencher concentration region employed. This assumption is valid for  $\text{CBr}_4$  and  $\text{CHBr}_3$ . The plots of  $\vartheta$  versus  $[Q]$  are shown in Figs. 2(c), 3(c) and 4(c). The plots for  $\text{CBr}_4$  and  $\text{CHBr}_3$  are linear. From the slopes of the plots we obtain  $k_{ST}'/k_{ST} = 5.5 \text{ M}^{-1}$  and  $3.4 \text{ M}^{-1}$  for  $\text{CBr}_4$  and  $\text{CHBr}_3$  respectively. The linearity of the plot for  $\text{CH}_2\text{Br}_2$  is not good. This might be attributed to a progressive increase in  $\epsilon_T(\lambda_{\max})$ , because the T-T absorption spectrum showed a progressive sharpening on the addition of  $\text{CH}_2\text{Br}_2$ . From the slope in the lower concentration region of  $\text{CH}_2\text{Br}_2$  we obtained  $k_{ST}'/k_{ST} = 0.94 \text{ M}^{-1}$ . Putting  $k_{ST} = 5.4 \times 10^7 \text{ s}^{-1}$ , the  $k_{ST}'$  are evaluated as  $3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $5.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{CBr}_4$ ,  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$  respectively. The  $k_{ST}'$  value is smaller than the  $k_q$  value for  $\text{CBr}_4$  and  $\text{CHBr}_3$ , so that the enhanced intersystem crossing and the other non-radiative deactivations participate in the fluorescence quenching, whereas the  $k_{ST}'$  value is somewhat larger than the  $k_q$  value for  $\text{CH}_2\text{Br}_2$ . This result seems strange, but it should be remembered that the  $k_{ST}'$  value for  $\text{CH}_2\text{Br}_2$  is only an apparent one. In any case, the fluorescence quenching by  $\text{CH}_2\text{Br}_2$  is mainly due to enhanced intersystem crossing.

The values for  $k_q$ ,  $k_{ST}'$  and  $k_r + k_d$  are summarized in Table 2. If the enhanced intersystem crossing is due to the external heavy-atom effect of the bromine atoms contained in the quencher, the  $k_{ST}'$  are expected to be related to the atomic spin-orbit coupling factor  $\xi$  of the bromine atom:

$$k_{ST}' \propto N^2 \xi^2 \quad (6)$$

where  $N$  is the number of bromine atoms contained in the quencher. Since the  $k_{ST}'$  value increases on increasing the number of bromine atoms contained in the quencher, the enhanced intersystem crossing is due to the external heavy-atom effect.

TABLE 2  
Summary of rate parameters

Quencher	$k_q$ ( $\text{M}^{-1} \text{ s}^{-1}$ )	$k_{ST}'$ ( $\text{M}^{-1} \text{ s}^{-1}$ )	$k_r + k_d$	$N^2 \xi^2$	$E_{1/2}^a$ (V(SCE))
$\text{CBr}_4$	$1.6 \times 10^{10}$	$3.0 \times 10^8$	$1.6 \times 10^{10}$	$16\xi^2$	-0.30
$\text{CHBr}_3$	$3.6 \times 10^8$	$1.9 \times 10^8$	$1.7 \times 10^8$	$9\xi^2$	-0.64
$\text{CH}_2\text{Br}_2$	$2.4 \times 10^7$	$5.1 \times 10^7$	—	$4\xi^2$	-1.48

SCE, standard calomel electrode.

<sup>a</sup>See ref. 26.



The quantum yields for the photoreaction of POPOP with  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$  and  $\text{CBr}_4$  were negligibly small and no transient absorption other than the T-T absorption was observed in the presence of these bromomethanes. Therefore we conclude from the results listed in Table 2 that (i) the fluorescence quenching by  $\text{CH}_2\text{Br}_2$  is mainly due to the enhanced intersystem crossing caused by the external heavy-atom effect, (ii) physical quenching is predominant in the case of  $\text{CBr}_4$  and (iii) physical quenching competes with the enhanced intersystem crossing in the case of  $\text{CHBr}_3$ . Since the  $k_d$  value decreases on lowering the reduction potential  $E_{1/2}$  of the quenchers, it seems that a charge transfer interaction plays an important role in the physical quenching. However, in order to prove that the physical quenching is due to a charge transfer interaction, it is necessary to study the dependence of  $k_d$  on the electron affinity or the reduction potential of the quenchers and on the solvent polarity for those cases for which  $k_d$  is below the diffusion-controlled limit. A study along these lines will be submitted for publication [25].

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