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# Diffusion processes involved in the exothermic triplet–triplet energy transfer in *n*-hexane at high pressure: evaluation of diffusion coefficients of benzophenone, triphenylene and naphthalene

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## Abstract

By using the exothermic energy transfer previously determined as a function of pressure, the rate constant for diffusion, $k_{\mathrm{diff}}$, was evaluated for benzophenone triplet ($^3$BZP*)/naphthalene (N), triphenylene triplet ($^3$TPH*)/N and triphenylene singlet ($^1$TPH*)/BZP, and the diffusion coefficients, $D_i$, for BZP, TPH and N were determined in *n*-hexane at pressures up to 400 MPa by assuming that $D_i$ for the excited states is equal to that for the ground state. The diffusion coefficients evaluated agreed well with the available data at 0.1 MPa. The quenching rate constants, $k_{\mathrm{q}}$, for $^1$TPH*/$O_2$ and $^1$TPH*/$CBr_4$ were also measured at pressures up to 400 MPa in this work. For these systems, the values of $k_{\mathrm{diff}}$ were also evaluated and compared with those calculated by coupling $D_i$ for TPH in this work with that for the quenchers determined by the dynamic fluorescence quenching in the previous works.

*Keywords:* Diffusion; Exothermic energy transfer; Benzophenone; Triphenylene; Naphthalene

## 1. Introduction

The exothermic excitation transfer from the lowest triplet state ($T_1$) of donor ($^3$D*) to the ground state acceptor (A), which is shown in Eq. (1), has been extensively studied and believed to be diffusion-controlled [1–3]:

$$^3\mathrm{D}^* + \mathrm{A} \xrightarrow{k_{\mathrm{q}}} \mathrm{D} + {}^3\mathrm{A}^* \qquad (1)$$

When the quenching of $^3$D* by A is fully diffusion-controlled, the rate constant for diffusion, $k_{\mathrm{diff}}$, is given by using the diffusion coefficient of $^3$D*, $D_{\mathrm{D}^*}$, and that of A, $D_{\mathrm{A}}$, as follows [4,5]:

$$k_{\mathrm{diff}}\ (\times 10^3) = 4\pi r_{\mathrm{D^*A}} D_{\mathrm{D^*A}} N_{\mathrm{A}} \qquad (2)$$

where $D_{\mathrm{D^*A}}$ is the sum of $D_{\mathrm{D}^*}$ and $D_{\mathrm{A}}$, and $r_{\mathrm{D^*A}}$ and $N_{\mathrm{A}}$ are the encounter distance ($=r_{\mathrm{D}^*} + r_{\mathrm{A}}$; the sum of the radius of $^3$D* and A) and Avogadro's number, respectively. However, the quenching rate constant, $k_{\mathrm{q}}$ is not equal to $k_{\mathrm{diff}}$ predicted by Eq. (2).

Recently, we examined the quenching of the $T_1$ states of benzophenone ($^3$BZP*) and triphenylene ($^3$TPH*) by naphthalene (N) and also fluorescence quenching of TPH by BZP as a function of pressure [6]. It was found that these quenching systems examined are not fully but nearly diffusion-controlled, and showed that $k_{\mathrm{q}}$ can be separated into $k_{\mathrm{diff}}$ and the bimolecular quenching rate constant, $k_{\mathrm{bim}}$, in the solvent cage [7,8]. More recently, the separation of $k_{\mathrm{q}}$ into $k_{\mathrm{diff}}$ and $k_{\mathrm{bim}}$ was modified by introducing the radial distribution function at contact with hard spheres and applied successfully to some fluorescence quenching systems [9–15]. The approach was also successfully applied to triplet–triplet annihilation in liquid solution [16]. Once one obtains the accurate $k_{\mathrm{diff}}$, the diffusion coefficient, $D_i$, for the solute molecule, *i*, in a given solvent may be calculated by Eq. (2) in the following cases: (i) $D_i$ is known for a reference molecule, either the donor or acceptor molecule and/or (ii) $k_{\mathrm{diff}}$ is measured for the systems more than three donor/acceptor pairs such as $^3$BZP*/N, $^3$TPH*/N and $^1$TPH*/BZP in the present work when $D_i$ for the excited state is assumed to be equal to that for the ground state. By the former approach, the relevant diffusion coefficients were successfully evaluated as a function of pressure from the fluorescence quenching of pyrene and 9,10-dimethylanthracence by oxygen and carbon tetrabromide [11,15] using the values of $D_i$ of benzo(a)pyrene as a reference fluorophore in *n*-hexane [17].

In this work, $k_{\mathrm{diff}}$ was determined for $^3$BZP*/N, $^3$TPH*/N and $^1$TPH*/BZP by using the data of $k_{\mathrm{q}}$ reported previously [6] and the diffusion coefficients for BZP, TPH and N were

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evaluated as a function of pressure according to Eq. (2). And also, the fluorescence quenching rate constant, $k_q$, of TPH by oxygen and $CBr_4$ was measured in order to evaluate $k_{diff}$ in *n*-hexane. The results were compared with $k_{diff}$ obtained from the diffusion coefficient for TPH together with that for the quenchers reported previously [11,15].

## 2. Experimental

Triphenylene (TPH) (guaranteed grade; Wako Pure Chemicals) was recrystallized from ethanol twice. Carbon tetrabromide ($CBr_4$) (Wako Pure Chemicals; guaranteed grade) was purified by sublimation twice under reduced pressure. *n*-Hexane of spectroscopic grade (Merck) was used without further purification.

Fluorescence decay curve measurements at high pressure were performed by using a 0.3 ns pulse from a PRA LN103 nitrogen laser for excitation (337.1 nm/less than 5 μJ per pulse by ND filters), which was operated with repetition of 10 Hz. The fluorescence intensities were measured by a Hamamatsu R1635-02 photomultiplier through a Ritsu MC-25NP monochromator and the resulting signal was digitized by using a LeCroy 9362 digitizing oscilloscope. The pulse width measured by using the system was less than 3 ns (HV for PMT = −1000 V). All data were analyzed by using a personal computer, which was interfaced to the digitizer. The details about the associated high pressure techniques have been described elsewhere [18].

The concentration of TPH for the fluorescence lifetime measurements was less than ca. $1 \times 10^{-4}$ M in order to minimize the reabsorption effects. The sample solution was deoxygenated by bubbling nitrogen gas under nitrogen atmosphere for 20 min. The change in the concentration of carbon tetrabromide by bubbling was corrected by weighing the sample solution. The concentration of dissolved oxygen in *n*-hexane was determined from the solubility data of oxygen [19,20]. The increase in the concentration due to the application of high pressure was corrected by using the compressibility of solvent [21–23].

Temperature was controlled at 25 ± 0.1 °C. Pressure was measured by a Minebea STD-5000 K strain gauge or a calibrated manganin wire.

## 3. Results and discussion

In this section, the experimental results of the fluorescence quenching of TPH by oxygen and carbon tetrabromide are first shown, and then the separation of $k_q$ into the rate constant of diffusion, $k_{diff}$, and the bimolecular rate constant in the solvent cage, $k_{bim}$, is accomplished.

### 3.1. Fluorescence quenching of TPH by $O_2$ and $CBr_4$

Table 1

Values of solvent viscosity, $\eta$, $\tau_f^0$ and $k_q$ for $^1TPH^*/O_2$ and $^1TPH^*/CBr_4$ in *n*-hexane and at 25 °C

| $P$ (MPa) | $\eta$ (cP) | $\tau_f^0$ (ns)[a] | $k_q$ ($\times 10^{10}$ M$^{-1}$ s$^{-1}$) | |
|---|---|---|---|---|
| | | | $^1TPH^*/O_2$[b] | $^1TPH^*/CBr_4$[c] |
| 0.1 | 0.294 | 36.3 | 3.49 ± 0.18 | 1.93 ± 0.02 |
| 50 | 0.472 | 36.4 | 2.75 ± 0.14 | 1.46 ± 0.02 |
| 100 | 0.650 | 36.8 | 2.27 ± 0.12 | 1.15 ± 0.02 |
| 150 | 0.849 | 36.6 | 1.84 ± 0.10 | 0.93 ± 0.02 |
| 200 | 1.063 | 37.0 | 1.57 ± 0.08 | 0.76 ± 0.02 |
| 250 | 1.310 | 36.6 | 1.33 ± 0.07 | 0.62 ± 0.02 |
| 300 | 1.610 | 36.4 | 1.15 ± 0.06 | 0.51 ± 0.02 |
| 350 | 1.948 | 36.3 | 0.98 ± 0.05 | 0.43 ± 0.02 |
| 400 | 2.368 | 36.0 | 0.83 ± 0.05 | 0.35 ± 0.02 |

[a] Errors were evaluated to be within 3%.

[b] Errors were evaluated from the values of $\tau_0$ and $\tau$.

[c] Errors were evaluated from the standard deviation of the plot of $1/\tau$ against $[CBr_4]$.

Fluorescence quenching was examined in the absence and presence of the quencher (Q: oxygen and $CBr_4$) in *n*-hexane at 25 °C. The decay curves were analyzed satisfactorily by a single exponential function in all the conditions examined. The values of the lifetime, $\tau_f^0$, in the absence of the quencher are listed in Table 1. The quenching rate constant, $k_q$, can be determined by

$$\frac{1}{\tau_f} - \frac{1}{\tau_f^0} = k_q[Q] \tag{3}$$

where $\tau_f$ represents the fluorescence lifetime in the presence of the quencher. For $^1TPH^*/O_2$, $k_q$ was determined from $\tau_f^0$ and $\tau_f$ in air-saturated *n*-hexane. For $^1TPH^*/CBr_4$, $k_q$ was evaluated from the least-squares plot of $1/\tau_f$ against the concentration of $CBr_4$, which is shown in Fig. 1. The values of $k_q$ for $^1TPH^*/O_2$ and $^1TPH^*/CBr_4$ are listed in Table 1. Fig. 2a shows the pressure dependence of $k_q$ for $^1TPH^*/O_2$ and $^1TPH^*/CBr_4$, together with that for $^3BZP^*/N$, $^3TPH^*/N$ and $^1TPH^*/BZP$ [6]. One can see in Fig. 2a that $k_q$ decreases significantly with increasing pressure for all the quenching systems. The apparent activation volume for $k_q$, $\Delta V^{\neq}_{app}$, evaluated by Eq. (4), is listed in Table 2:

$$RT\left(\frac{\partial \ln k_q}{\partial P}\right)_T = -\Delta V^{\neq}_{app} \tag{4}$$

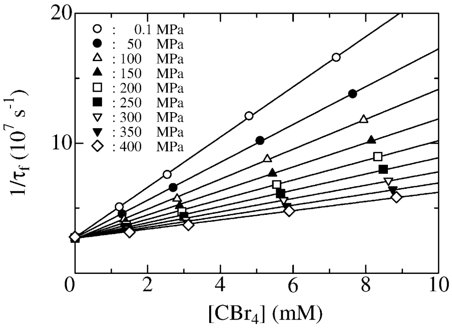

Fig. 1. Plots of $1/\tau_f$ against the concentration of $CBr_4$, $[CBr_4]$, in *n*-hexane at 25 °C and nine pressures.

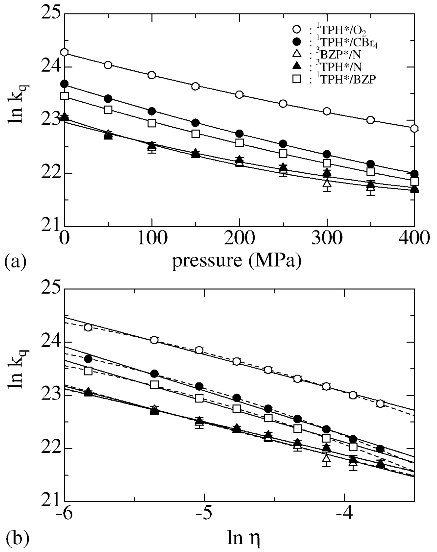

Fig. 2. Plots of $\ln k_q$ against pressure (a) and of $\ln k_q$ against $\ln\eta$ (b) in *n*-hexane at 25 °C. In (a), the solid lines were drawn by assuming that $\ln k_q = AP^2 + BP + C$. In (b), the solid and dotted lines were drawn by assuming that $\ln k_q = A(\ln\eta) + B$ and $\ln k_q = A(\ln\eta)^2 + B(\ln\eta) + C$, respectively.

It is noted in Table 2 that $\Delta V_q^{\neq}$ is approximately independent of the quenching systems, but significantly smaller than the activation volume, $\Delta V_\eta^{\neq}$, determined from the pressure dependence of the fluidity, $1/\eta$, where $\eta$ is the viscosity of the solvent [21–23]. The latter observation was often found for some quenching systems with a nearly diffusion-controlled rate [9–15].

A fractional power dependence of $k_q$ on $\eta$, that is, $k_q$ is proportional to $\eta^{-\beta}$, and also was examined for some systems in order to study the contribution of diffusion to the quenching where $0 < \beta \leq 1$ [24]. The plots of $\ln k_q$ against $\ln\eta$ are shown in Fig. 2b. The mean values of $\beta$ determined from the linear plot of $\ln k_q$ against $\ln\eta$ (the solid lines in Fig. 2b) are $0.70 \pm 0.03$ and $0.83 \pm 0.03$ for $^1TPH^*/O_2$ and $^1TPH^*/CBr_4$, respectively, and $0.68 \pm 0.03$, $0.62 \pm 0.02$ and $0.79 \pm 0.03$, for $^3BZP^*/N$, $^3TPH^*/N$ and $^1TPH^*/BZP$, respectively [6]; they indicate the difference between $\Delta V_q^{\neq}$ and $\Delta V_\eta^{\neq}$ (cm$^3$/mol) since $\Delta V_q^{\neq} = \beta\,\Delta V_\eta^{\neq}$ according to the fractional power dependence. Certainly, as seen in Fig. 2b for $^3BZP^*/N$ and $^3TPH^*/N$, the plots are approximately linear, whereas for $^1TPH^*/BZP$, $^1TPH^*/O_2$ and $^1TPH^*/CBr_4$ with larger $k_q$, they bend significantly downwards (the dotted lines in Fig. 2b). These results of the fractional power dependence are consistent with those observed for the nearly diffusion-controlled quenching previously reported [10–14]. As a result, the fluorescence quenching of TPH by oxygen and $CBr_4$ in this experimental study and the excitation transfer under consideration may occur kinetically via a similar mechanism.

Table 2
Values of $\Delta V_{app}^{\neq}$ (mol/cm$^3$) for some quenching systems at 0.1 MPa and 25 °C in *n*-hexane[a]

| | |
|---|---|
| $^1TPH^*/O_2$[b] | 10.9 ± 0.4 |
| $^1TPH^*/CBr_4$[b] | 12.6 ± 0.3 |
| $^3BZP^*/N$ [6] | 13.4 ± 1.2 |
| $^3TPH^*/N$ [6] | 10.9 ± 1.2 |
| $^1TPH^*/BZP$ [6] | 12.1 ± 0.4 |

[a] $\Delta V_{app}^{\neq}$ was evaluated by assuming that $\ln k_q = AP^2 + BP + C$. $\Delta V_\eta^{\neq}$ was evaluated to be 23.8 cm$^3$/mol from the pressure dependence of solvent viscosity, $\eta$, by assuming that $\ln\eta = AP^3 + BP^2 + CP + D$.

[b] From the data in this experiment.

### 3.2. Separation of $k_q$ into $k_{diff}$ and $k_{bim}$

The exothermic excitation transfer from $^3D^*$ to A may occur via encounter complex (DA)* as follows [3,9,25].

$$^3D^* + A \underset{k_{-diff}}{\overset{k_{diff}}{\rightleftarrows}} {}^3(DA)^* \xrightarrow{k_{et}} D + {}^3A^*$$

Scheme 1.

For the fluorescence quenching of some fluorophores by oxygen and heavy atom quenchers, a mechanism similar to Scheme 1 was used [9–16]. In Scheme 1, the observed quenching rate constant, $k_q$, is equal to $k_{diff}$ when $k_{et} \gg k_{-diff}$, and $k_q = k_{diff}k_{et}/k_{-diff}$ when $k_{-diff} \gg k_{et}$; for the former limiting case, the energy transfer occurs upon every encounter, whereas for the latter case the efficiency is less than unity.

In general, the diffusion coefficient, $D_i^{SE}$, by the Stokes–Einstein (SE) equation for the *i* species with a hard sphere radius, $r_i$, in a continuum medium of the viscosity, $\eta$, is given by

$$D_i^{SE} = \frac{k_B T}{f_i \pi r_i \eta} \tag{5}$$

where $f_i$ is 4 and 6 for the slip and stick boundary limits, respectively. When $r_i$ for the donor and acceptor molecules is approximately equal, the rate constant for diffusion, $k_{diff}$, derived from Eqs. (2) and (5) is given by the Debye equation:

$$k_{diff} = \frac{8RT}{\alpha\eta} \tag{6}$$

where $\alpha$ is 2000 and 3000 for slip and stick boundary limits, respectively. In the previous works [9–16], we have shown that $f_i$ (Eq. (5)) and $\alpha$ (Eq. (6)) are not predicted by the SE equation and the Debye equation, respectively, although the $1/\eta$ dependence of $k_{diff}$ holds, and also shown that $\alpha$ in Eq. (6) should be taken as a parameter ($\alpha^{ex}$) determined experimentally ($\alpha$ in Eq. (6) is replaced by $\alpha^{ex}$). On the basis of Scheme 1 together with Eq. (6), we can derive the following equation [9]:

$$\frac{\gamma}{k_q} = \frac{1}{k_{bim}^0} + \frac{\alpha^{ex}}{8RT}\gamma\eta \tag{7}$$

Table 3
Values of $\alpha^{ex}$ and $k^0_{bim}$ ($\times 10^{10}\,M^{-1}\,s^{-1}$) at 0.1 MPa and 25 °C in *n*-hexane

| | $^3$BZP*/N[a] | $^3$TPH*/N[a] | $^1$TPH*/BZP[a] | $^1$TPH*/$O_2$ | $^1$TPH*/$CBr_4$ |
|---|---|---|---|---|---|
| $\alpha^{ex}$ | 3090 ± 240 | 2890 ± 120 | 2620 ± 20 | 945 ± 20 | 2300 ± 10 |
| $k^0_{bim}$ | 1.1 ± 0.4 | 1.1 ± 0.2 | 3.4 ± 0.3 | 5.5 ± 0.6 | 6.3 ± 0.4 |

[a] Values of $\alpha^{ex}$ and $k^0_{bim}$ were recalculated according to Eq. (7) by using the data of Ref. [6].

where

$$k^0_{bim} = k_{et}\left(\frac{k_{diff}}{k_{-diff}}\right)_0 \tag{8}$$

In Eqs. (7) and (8), $\gamma$ is the ratio of the radial distribution function at contact of $^3D^*$ and A, $g(r_{D^*A})_P$, at $P$ (in MPa) to that at 0.1 MPa, $g(r_{D^*A})_P/g(r_{D^*A})_0$, and $(k_{diff}/k_{-diff})_0$ is $k_{diff}/k_{-diff}$ at 0.1 MPa [9]. Similar equation to Eq. (7) was successfully applied to the fluorescence quenching of some fluorophores by the quenchers including oxygen, $CBr_4$ and polybromoethanes although the definition of $k^0_{bim}$ (Eq. (8)) is modified [9].

The plots of $\gamma/k_q$ against $\gamma\eta$ for $^3$BZP*/N, $^3$TPH*/N and $^1$TPH*/BZP, where the values of $k_q$ reported previously are used [6], are shown in Fig. 3, together with those for $^1$TPH*/$O_2$ and $^1$TPH*/$CBr_4$ in this experimental work. The plots shown in Fig. 3 are approximately linear with a positive intercept for a given system, see Appendix A, indicating that the quenching competes with diffusion, and also, $k^0_{bim}$ is approximately independent of $\gamma\eta$, that is, pressure. These observations are consistent with those found for the fluorescence quenching systems studied previously [9–16]. The values of $\alpha^{ex}$ and the bimolecular rate constant, $k^0_{bim}$, were determined from the least-squares slope and intercept of the plots (Fig. 3), respectively, and are summarized in Table 3.[1] The values of $\alpha^{ex}$ (and $k^0_{bim}/10^{10}\,M^{-1}\,s^{-1}$) are 940 ± 20 (5.4 ± 0.8) [10], 945 ± 20 (5.5 ± 0.6) [11] and 980 ± 20 (6.9 ± 1.2) [13] for the fluorescence quenching of benzo(a)pyrene, 9,10-dimethylanthracene and pyrene by oxygen, and 1980±20 (7.0±0.5) [10], 1820±30 (5.5±0.9) [11] and 2280 ± 20 (69 ± 96) [14] for that by $CBr_4$, respectively; they are in good agreement with the present results for $^1$TPH*/$O_2$ and $^1$TPH*/$CBr_4$ although the error of $k^0_{bim}$ is very large for pyrene/$CBr_4$.

### 3.3. *Rate constant for diffusion, $k_{diff}$, and diffusion coefficient, $D_i$*

As mentioned in the previous paragraph, the values of $\alpha^{ex}$ were evaluated, and hence, one may determine the accurate $k_{diff}$ for $^3$BZP*/N, $^3$TPH*/N, $^1$TPH*/BZP, $^1$TPH*/$O_2$ and $^1$TPH*/$CBr_4$, by using $\alpha^{ex}$ and the solvent viscosity, $\eta$, as a function of pressure according to Eq. (6) where $\alpha$ is replaced by $\alpha^{ex}$. Table 4 shows the values of $k_{diff}$ as a function of pressure for three quenching pairs. The values of the sum of the diffusion coefficients, $D_{D^*} + D_A$, determined according to Eq. (2) by using $k_{diff}$ and $r_{D^*A}$ are also included in Table 4. The values of $k_{diff}$ are about twice as large as $k_q$ at 0.1 MPa [6], and approach $k_q$ as pressure increases, indicating that the quenching is nearly diffusion-controlled in the lower pressure region. From the values of $D_{D^*} + D_A$ listed in Table 4, the diffusion coefficient, $D_i$ ($i$ = BZP, TPH and N) was calculated by assuming that $D_i$ for the excited states is equal to that of the ground state. Table 5 shows the values of $D_i$ ($i$ = BZP, TPH and N) thus estimated. Previously, we reported the values of $D_i$ for $O_2$ and $CBr_4$ by coupling $k_{diff}$ for the fluorescence quenching of benzo(a)pyrene (BZ(a)PY)/$O_2$ and BZ(a)PY/$CBr_4$ [10] with $D_i$ for BZ(a)PY that was measured as a function of pressure by Dymond and Woolf [17]. The results are also listed in Table 5. The values of $f_i$ in Eq. (5) determined from the plot of $D_i$ against $1/\eta$ are 5.56 ± 0.01, 4.92 ± 0.03 and 6.93 ± 0.01 for BZP, TPH and N, respectively; they are approximately in the range of 4–6 as predicted by the SE equation, but clearly depend on the compounds examined.

There are few reliable data of diffusion coefficient at 0.1 MPa as well as at high pressure to the author's knowledge. The values of $D_i$ observed for BZP and N in *n*-hexane are $(2.86\text{–}2.91) \times 10^{-9}$ [28] and $3.6 \times 10^{-9}\,m^2\,s^{-1}$ [17,29], respectively, at 25 °C and 0.1 MPa. One may evaluate the values of $D_i$ empirically or semi-empirically; they are $2.4 \times 10^{-9}$, $2.7 \times 10^{-9}$ and $3.3 \times 10^{-9}\,m^2\,s^{-1}$ by the Wilke–Chang equation [30], and $(2.6\text{–}3.1) \times 10^{-9}$, $(2.9\text{–}3.4) \times 10^{-9}$ and $(3.3\text{–}4.2) \times 10^{-9}\,m^2\,s^{-1}$ by the Spernol–Wirtz equation [31,32] for TPH, BZP and N,

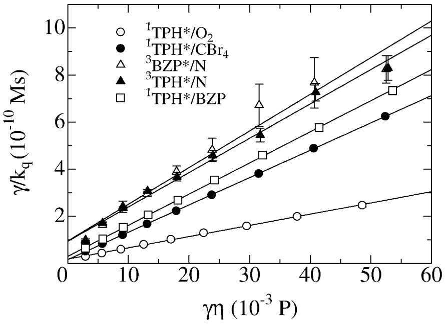

Fig. 3. Plots of $\gamma/k_q$ against $\gamma\eta$ in *n*-hexane at 25 °C.

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[1] In the previous work [6], we assumed to be $\gamma = 1$ in Eq. (6). The values of $\alpha^{ex}$ (and $k^0_{bim}/10^{10}\,M^{-1}\,s^{-1}$) obtained from the plots of $1/k_q$ and $\eta$ are: 2840 ± 190 (1.4 ± 0.3), 2580 ± 100 (1.3 ± 0.2) and 2510 ± 20 (3.9 ± 0.2) for $^3$BZP*/N, $^3$TPH*/N and $^1$TPH*/BZP, respectively; they are slightly smaller and larger than those in $\alpha^{ex}$ and in $k^0_{bim}$, respectively, as seen in Table 3.

Table 4
Values of $k_{\mathrm{diff}}$ ($\times 10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) and $D_{\mathrm{D}^*} + D_{\mathrm{A}}$ ($\times 10^{-9}\,\mathrm{m}^2\,\mathrm{s}^{-1}$) for $^3$BZP*/N, $^3$TPH*/N and $^1$TPH*/BZP in *n*-hexane at 25 °C[a]

| *P* (MPa) | $^3$BZP*/N | | $^3$TPH*/N | | $^1$TPH*/BZP | |
|---|---|---|---|---|---|---|
| | $k_{\mathrm{diff}}$ | $D_{\mathrm{D}^*} + D_{\mathrm{A}}$ | $k_{\mathrm{diff}}$ | $D_{\mathrm{D}^*} + D_{\mathrm{A}}$ | $k_{\mathrm{diff}}$ | $D_{\mathrm{D}^*} + D_{\mathrm{A}}$ |
| 0.1 | 2.18 ± 0.17 | 4.42 ± 0.34 | 2.33 ± 0.09 | 4.59 ± 0.18 | 2.58 ± 0.02 | 4.82 ± 0.03 |
| 50 | 1.36 ± 0.11 | 2.76 ± 0.21 | 1.45 ± 0.06 | 2.85 ± 0.12 | 1.61 ± 0.01 | 3.01 ± 0.02 |
| 100 | 0.99 ± 0.08 | 2.00 ± 0.15 | 1.05 ± 0.05 | 2.07 ± 0.09 | 1.17 ± 0.01 | 2.19 ± 0.02 |
| 150 | 0.76 ± 0.06 | 1.53 ± 0.12 | 0.81 ± 0.04 | 1.59 ± 0.07 | 0.89 ± 0.01 | 1.67 ± 0.01 |
| 200 | 0.60 ± 0.05 | 1.22 ± 0.10 | 0.64 ± 0.03 | 1.27 ± 0.05 | 0.71 ± 0.01 | 1.33 ± 0.01 |
| 250 | 0.48 ± 0.04 | 0.99 ± 0.08 | 0.52 ± 0.03 | 1.03 ± 0.05 | 0.58 ± 0.01 | 1.08 ± 0.01 |
| 300 | 0.40 ± 0.03 | 0.81 ± 0.07 | 0.43 ± 0.02 | 0.84 ± 0.04 | 0.47 ± 0.01 | 0.88 ± 0.01 |
| 350 | 0.33 ± 0.03 | 0.67 ± 0.06 | 0.35 ± 0.02 | 0.69 ± 0.03 | 0.39 ± 0.01 | 0.73 ± 0.01 |
| 400 | 0.27 ± 0.03 | 0.55 ± 0.05 | 0.29 ± 0.02 | 0.57 ± 0.03 | 0.32 ± 0.01 | 0.60 ± 0.01 |

[a] The radius, $r_i$, for BZP, TPH, N and *n*-hexane was estimated to be 0.345, 0.365, 0.309 and 3.01 nm, respectively, according to the method of Bondi [27].

respectively. These values are comparable with those evaluated at 0.1 MPa in this work.

The values of $k_{\mathrm{diff}}$ for $^1$TPH*/$O_2$ and $^1$TPH*/$CBr_4$ can be determined by using $\alpha^{\mathrm{ex}}$ (Table 3) and $\eta$ (Table 1) according to Eq. (6) ($k_{\mathrm{diff}}$ (obs)), and also by using $D_i$ for TPH, $O_2$ and $CBr_4$ (Table 4) according to Eq. (2) ($k_{\mathrm{diff}}$ (cal)). Fig. 4 compares the pressure dependence of $k_{\mathrm{diff}}$ (obs) with that of $k_{\mathrm{diff}}$ (cal). As seen in Fig. 4, $k_{\mathrm{diff}}$ (obs) is equal to $k_{\mathrm{diff}}$ (cal) for $^1$TPH*/$O_2$ and $^1$TPH*/$CBr_4$ within the experimental errors, indicating that $D_i$ for TPH evaluated in this work gives a good estimation. Unfortunately, such a check of $D_i$ for N and BZP was not made because N cannot be excited by the nitrogen laser used in this work and BZP is apparently nonfluorescent.

Finally, we refer to the similarity in the diffusion coefficient between the excited and ground states for relatively bulky molecules. Meyer and Nickel [33] measured the diffusion coefficient, $D_i$ of the lowest triplet state of some aromatic hydrocarbons and found that $D_i$ is estimated to be at most 10% smaller than that of molecules in the ground state. The evidence may support the assumption in this work that $D_i$ for the excited state molecule is approximately equal to that for the ground state one.

Table 5
Values of $D_i$ ($\times 10^{-9}\,\mathrm{m}^2\,\mathrm{s}^{-1}$) for BZP, TPH, N, $O_2$ and $CBr_4$ in *n*-hexane and 25 °C

| *P* (MPa) | BZP (this work) | TPH (this work) | N (this work) | $O_2$[a] | $CBr_4$ [10] |
|---|---|---|---|---|---|
| 0.1 | 2.33 ± 0.28 | 2.49 ± 0.28 | 2.09 ± 0.62 | 15.6 | 4.41 |
| 50 | 1.46 ± 0.17 | 1.55 ± 0.17 | 1.30 ± 0.39 | 9.50 | 2.54 |
| 100 | 1.06 ± 0.13 | 1.13 ± 0.13 | 0.94 ± 0.28 | 6.88 | 1.83 |
| 150 | 0.81 ± 0.10 | 0.86 ± 0.10 | 0.73 ± 0.22 | 5.25 | 1.38 |
| 200 | 0.64 ± 0.08 | 0.69 ± 0.08 | 0.58 ± 0.17 | 4.18 | 1.09 |
| 250 | 0.52 ± 0.07 | 0.56 ± 0.07 | 0.47 ± 0.14 | 3.40 | 0.89 |
| 300 | 0.43 ± 0.05 | 0.46 ± 0.05 | 0.38 ± 0.12 | 2.79 | 0.75 |
| 350 | 0.35 ± 0.05 | 0.38 ± 0.05 | 0.32 ± 0.10 | 2.32 | 0.63 |
| 400 | 0.29 ± 0.04 | 0.31 ± 0.04 | 0.26 ± 0.08 | | |

[a] Mean values determined from the fluorescence quenching for benzo(a)pyrene/$O_2$ [10], 9,10-dimethylanthracene/$O_2$ [14] and pyrene/$O_2$ [14].

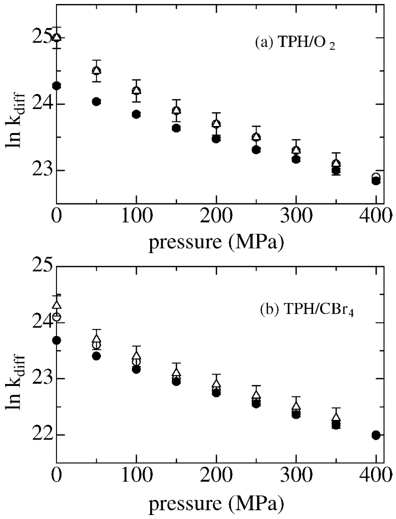

Fig. 4. Pressure dependence of $k_{\mathrm{diff}}$ (obs) (○), $k_{\mathrm{diff}}$ (cal) (△) and $k_{\mathrm{q}}$ (obs) (●) for $^1$TPH*/$O_2$ (a) and $^1$TPH*/$CBr_4$ (b) in *n*-hexane at 25 °C.

## Appendix A

The radial distribution function at the closest approach distance, $r_{\mathrm{M^*Q}}$ ($= r_{\mathrm{M^*}} + r_{\mathrm{Q}}$) with hard spheres, $g(r_{\mathrm{M^*Q}})$, is given by [26]

$$g(r_{\mathrm{M^*Q}}) = \frac{1}{1-y} + \frac{3y}{(1-y)^2}\left(\frac{r_{\mathrm{red}}}{r_{\mathrm{S}}}\right) + \frac{2y^2}{(1-y)^3}\left(\frac{r_{\mathrm{red}}}{r_{\mathrm{S}}}\right)^2 \tag{A.1}$$

where $r_{\mathrm{red}} = r_{\mathrm{M^*}} r_{\mathrm{Q}} / r_{\mathrm{M^*Q}}$, and $y$ is the packing fraction, given in terms of the molar volume of solvent, $V_{\mathrm{S}}$, and the radius of hard sphere solvent, $r_{\mathrm{S}}$, by

$$y = \frac{4N_{\mathrm{A}}\pi r_{\mathrm{S}}^3}{3V_{\mathrm{S}}} \tag{A.2}$$

The values of $r_{\mathrm{M^*}}$, $r_{\mathrm{Q}}$, and $r_{\mathrm{S}}$ were estimated by the method of Bondi [27]; the radius, $r_i$, for BZP, TPH, N and *n*-hexane was 0.345, 0.365, 0.309 and 3.01 nm, respectively. The values of $g(r_{M^*Q})$ were calculated by Eq. (A.1) by using $r_i$ together with the data of the solvent density [21–23].

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