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Fluorescence quenching of benzo(a)pyrene by oxygen and carbon tetrabromide in *n*-hexane under high pressure: estimation of the diffusion coefficient of quencher

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Abstract

The contribution of diffusion to the fluorescence quenching by oxygen and carbon tetrabromide (CBr_4) of benzo(a)pyrene (BZPY) in *n*-hexane at pressures up to 400 MPa was investigated. For both BZPY/O_2 and BZPY/CBr_4, the fluorescence quenching rate constant, k_q, decreased significantly with increasing pressure. The apparent activation volume for k_q, $\Delta V_q^{\neq}$, was 10.1 ± 0.1 and $13.2 \pm 1.0\,cm^3/mol$ for BZPY/O_2 and BZPY/CBr_4, respectively. It was also found that the plot of $\ln k_q$ against $\ln \eta$, where η is the solvent viscosity, showed significant downward curvature. From these results, it was concluded that the quenching competes with diffusion for both of the systems at the lower-pressure region. The contribution of diffusion to the quenching was analyzed on the basis of a kinetic model with solvent cage in which the quenching occurs, and the observed k_q was separated into the contributions of the bimolecular rate constant in the solvent cage, k_{bim}, and the rate constant for diffusion, k_{diff}. By using the values of k_{diff} thus separated, together with those of the diffusion coefficient of BZPY that was measured by other workers, the diffusion coefficients for O_2 and CBr_4 were estimated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fluorescence quenching; Benzo(a)pyrene; Diffusion coefficient

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1. Introduction

It is well known that the fluorescence of some aromatic molecules is quenched by oxygen and carbon tetrabromide with a nearly diffusion-controlled rate in liquid solution [1–8]. In fact, the quenching rate constant, k_q, is about the order of $10^{10}\,M^{-1}\,s^{-1}$ in non-viscous solvents, which is close to the rate constant for diffusion, k_{diff}, calculated by the Debye equation in a continuum medium with viscosity, η (in Poise), given by

$$k_{diff} = \frac{8RT}{\alpha\eta} \quad (1)$$

where $\alpha = 2000$ and 3000 for the slip and stick boundary limits, respectively [9,10].

Recently, the fluorescence quenching by poly-bromoethanes and CBr_4 of pyrene [11] and also by oxygen and CBr_4 of 9,10-dimethylanthracene [12] at high pressure was examined, and concluded that the quenching competes with diffusion. The contribution of diffusion to the quenching was satisfactorily interpreted by a kinetic scheme via an encounter complex, followed by the formation of an exciplex in the solvent cage, and the quenching rate constant, k_q, was separated into the contributions of the rate constant for the bimolecular reaction in the solvent cage, k_{bim}, and the rate constant for diffusion, k_{diff}.

The present work is focussed on the pressure and the pressure-induced solvent viscosity dependence of the fluorescence quenching by oxygen and CBr_4 of benzo(a)pyrene (BZPY) in order to obtain further insight into the rapid reactions in liquid solution. We chose BZPY as a fluorophore since the diffusion coefficient of BZPY, D_{BZPY}, is known at high pressure [13]. Thus, we measured the rate constant of the fluorescence quenching, k_q, for BZPY/O_2 and BZPY/CBr_4 at pressures up to 400 MPa in *n*-hexane, for whose systems the quenching is expected to be nearly diffusion-controlled on the basis of the results of the fluorescence quenching of 9,10-dimethylanthracene [8,12]. From the pressure-induced solvent viscosity dependence of k_q, the contribution of diffusion to the quenching was analyzed, and k_q was separated into k_{bim} and k_{diff} by the method reported previously [11]. By using the values of k_{diff}, together with those of D_{BZPY} [13], the diffusion coefficient of oxygen and CBr_4 was evaluated.

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2. Experimental

Benzo(a)pyrene (BZPY) (Tokyo Kasei Chemical) was used as received. Carbon tetrabromide (CBr_4) (Wako Pure Chemicals) of guaranteed grade was purified by sublimation twice under reduced pressure. Spectroscopic grade of *n*-hexane (Merk) 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/<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 about 3 ns (HV for PMT $= -700$ V). All data were analyzed by using an NEC 9801 microcomputer, which was interfaced to the digitizers. The details about the associated high-pressure techniques have been described elsewhere [14].

The concentration of BZPY for the fluorescence lifetime measurements was <0.1 in absorbance (1 cm cell) at maximum absorption wavelength 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 [15,16]. The increase in the concentration due to the application of high pressure was corrected by using the compressibility of solvent [17–19]. Temperature was controlled at 25 ± 0.2°C. Pressure was measured by a Minebea STD-5000K strain gauge or a calibrated manganin wire.

Table 1
Solvent viscosity, η, and fluorescence lifetime, $\tau_f{}^0$, of BZPY in the absence of quencher, and quenching rate constant, k_q, for BZPY/O_2 and BZPY/CBr_4 in *n*-hexane at 25°C

P (MPa)	η (cP)	$\tau_f{}^0$ (ns)[a]	k_q ($10^{10}\,M^{-1}\,s^{-1}$)	
			BZPY/O_2	BZPY/CBr_4
0.1	0.294	54.2	3.67 ± 0.11	2.30 ± 0.04
50	0.472	49.2	3.00 ± 0.09	1.63 ± 0.01
100	0.650	46.1	2.44 ± 0.07	1.33 ± 0.03
150	0.849	43.8	2.05 ± 0.06	1.01 ± 0.01
200	1.063	41.1	1.71 ± 0.05	0.88 ± 0.02
250	1.310	39.1	1.43 ± 0.04	0.74 ± 0.02
300	1.610	37.6	1.21 ± 0.04	0.60 ± 0.01
350	1.948	35.7	1.02 ± 0.03	0.52 ± 0.02
400	2.368	34.4	0.88 ± 0.03	0.43 ± 0.01

[a] Error was estimated to be ±2%.

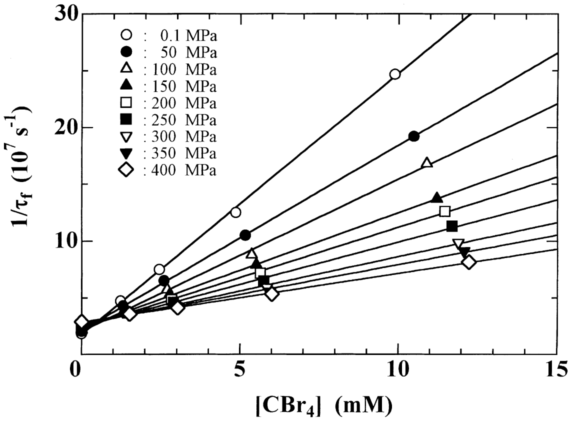


Fig. 1. Plots of $1/\tau_f$ against the concentration of carbon tetrabromide, [CBr_4], in *n*-hexane at 25°C.

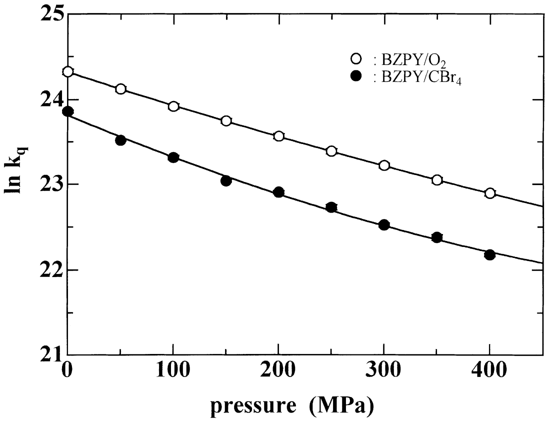


Fig. 2. Pressure dependence of k_q for BZPY/O_2 and BZPY/CBr_4 in *n*-hexane at 25°C. The solid lines were drawn by assuming that $\ln k_q = A + BP + CP^2$.

3. Results

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 satisfactorily analyzed 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, was determined by

$$\frac{1}{\tau_f} - \frac{1}{\tau_f{}^0} = k_q[Q] \qquad (2)$$

where τ_f represents the fluorescence lifetime in the presence of the quencher. The plot of $1/\tau_f$ against the concentration of CBr_4 is shown in Fig. 1. The values of k_q were determined from the least-squares slope of the plot according to Eq. (2) and are listed in Table 1. Fig. 2 shows the pressure dependence of k_q. One can see in Fig. 2 that k_q decreases significantly with increasing pressure for both the quenching systems. The apparent activation volume for k_q, $\Delta V_q{}^{\neq}$, evaluated by Eq. (3), is listed in Table 2.

$$RT\left(\frac{\partial \ln k_q}{\partial P}\right)_T = -\Delta V_q{}^{\neq} \qquad (3)$$

Table 2
Activation volumes (cm^3/mol) for BZPY/O_2 and BZPY/CBr_4 in *n*-hexane at 25°C[a]

BZPY/O_2	BZPY/CBr_4
10.1 ± 0.1	13.2 ± 1.0

[a] Activation volume of viscosity for *n*-hexane, $\Delta V_\eta^{\neq}$, was $23 \pm 1\,cm^3/mol$.

It is noted in Table 2 that $\Delta V_q^{\neq}$ for BZPY/O_2 is slightly smaller than that for BZPY/CBr_4, and $\Delta V_q^{\neq}$ for both the systems is significantly smaller than the activation volume, $\Delta V_\eta^{\neq}$, determined from the pressure dependence of the solvent viscosity [13,17–19].

For the fluorescence quenching with a nearly diffusion-controlled rate, a fractional power dependence of k_q on η, i.e., k_q is proportional to $\eta^{-\beta}$, has often been shown (Ref. [7] and references cited therein). The plots of $\ln k_q$ against $\ln \eta$, which is shown in Fig. 3, bend significantly downward. The mean values of β are 0.71 ± 0.04 and 0.81 ± 0.02 at the whole pressure range examined, and 0.81 ± 0.02 and 0.89 ± 0.08 at pressures above 300 MPa for BZPY/O_2 and BZPY/CBr_4, respectively, indicating that β approaches unity as pressure increases. These observations are consistent with those that are concluded to be nearly diffusion-controlled as described previously [7,11,12,20].

4. Discussion

4.1. Rate constant for diffusion, k_{diff}

When the transient terms can be neglected, the rate constant, k_{diff}, for the bimolecular diffusion-controlled reaction between the fluorescence state of M, $^1M^*$, and quencher, Q, is given by Eq. (4) in a solvent with the relative diffusion coefficient, D_{M^*Q} ($= D_{M^*} + D_Q$) [9,10];

$$k_{diff} = \frac{4\pi r_{M^*Q} D_{M^*Q} N_A}{10^3} \tag{4}$$

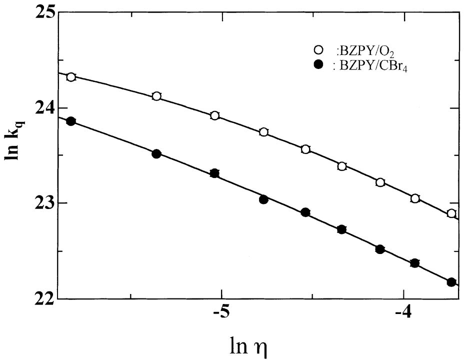


Fig. 3. Plots of $\ln k_q$ against $\ln \eta$ for BZPY/O_2 and BZPY/CBr_4 in *n*-hexane at 25°C. The solid lines were drawn by assuming that $\ln k_q = A + B \ln \eta + C (\ln \eta)^2$.

where r_{M^*Q} and N_A are the encounter distance and Avogadro's number, respectively.

The relationship between D_i (i = M* or Q) and ζ_i, the friction coefficient, for the solute molecule, i, in a given solvent is expressed by the Einstein equation, $D_i = k_B T/\zeta_i$, where k_B is the Boltzmann constant. Since the hydrodynamic friction, $\zeta_i{}^H$, for the solute molecule of the spherical radius, r_i, in a continuum medium with viscosity, η, is given by $\zeta_i{}^H = f_i \pi r_i \eta$ (Stokes' law), one can obtain the Stokes–Einstein (SE) equation,

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

where $f_i = 4$ and 6 for the slip and stick boundary limits, respectively. However, the SE equation has been often observed to break down for diffusion in liquid [9,21,22].

In the previous publication [11,12,20,23], the solvent–viscosity dependence of k_{diff} induced by pressure was successfully described for several quenching systems on the basis of an empirical equation proposed by Spernol and Wirtz [2,24,25]. According to their approach, the diffusion coefficient, $D_i{}^{SW}$, is expressed by

$$D_i{}^{SW} = \frac{k_B T}{6\pi f_i{}^{SW} r_i \eta} \tag{6}$$

where $f_i{}^{SW}$ represents a microfriction factor and is given by

$$f_i{}^{SW} = \left(\frac{0.16 + 0.4 r_i}{r_S}\right)(0.9 + 0.4 T_S{}^r - 0.25 T_i{}^r) \tag{7}$$

In Eq. (7), the first parenthetical quantity depends only on the solute-to-solvent size ratio, (r_i/r_S), which can be calculated using the van der Waals radii of the solute and solvent molecules [13,26] listed in Table 3. The second parenthetical quantity involves the reduced temperatures, $T_S{}^r$ and $T_i{}^r$, of solvent and solute, respectively, which can be calculated by using the melting point, T_{mp}, and boiling point, T_{bp}, of the solvent or solute at the experimental temperature, T, according to

$$T^r_{i(S)} = \frac{T - T_{mp(S)}}{T_{bp(S)} - T_{mp(S)}} \tag{8}$$

The values of $f_i{}^{SW}$ (full) and $f_i{}^{SW}$ (trunc) can be evaluated by Eq. (7) and by neglecting the second parenthetical quantity in Eq. (7), respectively [2], and are listed in

Table 3
van der Waals radii, r_W, $f_i{}^{SW}$ (trunc) and $f_i{}^{SW}$ (full) of solute and solvent molecules

	r_W (nm)	$f_i{}^{SW}$ (trunc)	$f_i{}^{SW}$ (full)
BZPY	0.348[a]	0.652	0.858
Oxygen	0.173[a]	0.405	−0.213
CBr_4	0.289[a]	0.569	0.779
n-Hexane	0.283[b]	0.560	0.566

[a] Estimated by the method of Bondi [26].
[b] Ref. [13].

Table 4
Values of α^{SW}, α^{ex} and $k_{\mathrm{bim}}{}^{0}$ for BZPY/O$_2$ and BZPY/CBr$_4$ in *n*-hexane at 25°C

	α^{SW}[a]	α^{ex}	$k_{\mathrm{bim}}{}^{0}$ (10^{10} M^{-1} s^{-1})
BZPY/O$_2$	1232 (−966)	900 ± 20	7.2 ± 0.1
BZPY/CBr$_4$	1795 (2420)	1980 ± 200	7.0 ± 0.5

[a] α^{SW} (trunc)/α^{SW} (full) (see the text).

Table 3. In Table 3, one can see that $f_{\mathrm{i}}{}^{\mathrm{SW}}$ (full) is negative. This may arise as a result of the small difference between the melting and boiling points (see Eqs. (7) and (8)) for oxygen, indicating that the estimation of $f_{\mathrm{i}}{}^{\mathrm{SW}}$ (full) is invalid. However, $f_{\mathrm{i}}{}^{\mathrm{SW}}$ (trunc) for oxygen was successfully applied to the system for 9,10-dimethylanthracene/O$_2$ [12].

From the approximation by Spernol and Wirtz, Eq. (9) can be derived.

$$k_{\mathrm{diff}} = \frac{2RTr_{\mathrm{M^*Q}}}{3000\eta}\left(\frac{1}{f_{\mathrm{M^*}}{}^{\mathrm{SW}}r_{\mathrm{M^*}}} + \frac{1}{f_{\mathrm{Q}}{}^{\mathrm{SW}}r_{\mathrm{Q}}}\right) \tag{9}$$

By comparing with Eq. (1), α^{SW} is given by

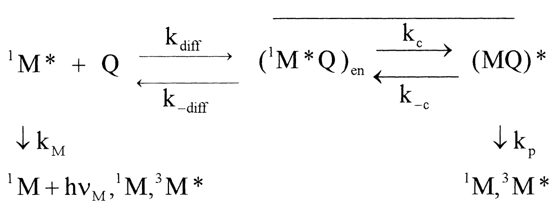
$$\alpha^{\mathrm{SW}} = \frac{1.2\times 10^{4}}{r_{\mathrm{M^*Q}}}\left(\frac{1}{f_{\mathrm{M^*}}{}^{\mathrm{SW}}r_{\mathrm{M^*}}} + \frac{1}{f_{\mathrm{Q}}{}^{\mathrm{SW}}r_{\mathrm{Q}}}\right)^{-1} \tag{10}$$

The values of α^{SW} (full) and α^{SW} (trunc) thus estimated by Eq. (10) for the quenching systems studied in this work are shown in Table 4. It is noted in Table 4 that α^{SW} (trunc) and α^{SW} (full) are close to the value for the slip boundary limit ($\alpha = 2000$) for BZPY/CBr$_4$. However, for BZPY/O$_2$, α^{SW} (trunc) is significantly smaller than the value for the slip boundary limit. This may be attributed to the large difference in the size of O$_2$ and solvent as predicted by the first parenthetical quantity of Eq. (7).

4.2. Contribution of diffusion to the quenching

For the fluorescence quenching by heavy-quencher (Q) of pyrene (^{1}M*) in liquid solution, the quenching occurs via an exciplex (^{1}MQ)* which is formed from an encounter complex (M*Q)$_{\mathrm{en}}$ between M* and Q in the solvent cage as shown in Scheme 1 [11]; where the bar indicates the solvent cage. Scheme 1 was also successfully applied to the fluorescence quenching by oxygen and CBr$_4$ of 9,10-dimethylanthracene in liquid and supercritical carbon dioxide and *n*-alkanes (C$_4$–C$_7$) [12]. Based on Scheme 1, the observed rate constant, k_{q}, is given by

$$k_{\mathrm{q}} = \frac{k_{\mathrm{diff}}}{1 + k_{-\mathrm{diff}}((k_{\mathrm{p}} + k_{-\mathrm{c}})/k_{\mathrm{c}}k_{\mathrm{p}})} \tag{11}$$



Scheme 1.

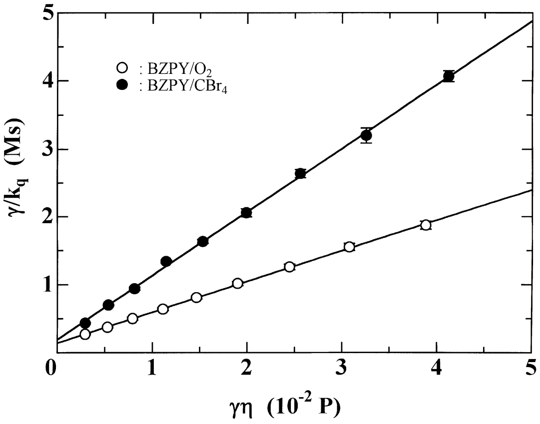


Fig. 4. Plots of γ/k_{q} against $\gamma\eta$ for BZPY/O$_2$ and BZPY/CBr$_4$ in *n*-hexane at 25°C.

When the rate constant for diffusion, k_{diff}, is expressed by Eq. (1) (α is replaced by α^{ex}), one may derive Eq. (12) from Eqs. (1) and (11).

$$\frac{1}{k_{\mathrm{q}}} = \left(\frac{k_{\mathrm{p}} + k_{-\mathrm{c}}}{k_{\mathrm{c}}k_{\mathrm{p}}}\right)\left(\frac{k_{-\mathrm{diff}}}{k_{\mathrm{diff}}}\right) + \frac{\alpha^{\mathrm{ex}}}{8RT}\eta \tag{12}$$

In Eq. (12), the pressure dependence of $k_{\mathrm{diff}}/k_{-\mathrm{diff}}$ is given by that of the radial distribution function, $g(r_{\mathrm{M^*Q}})$, at the closest approach distance (the encounter distance), $r_{\mathrm{M^*Q}}$ ($= r_{\mathrm{M^*}} + r_{\mathrm{Q}}$) with hard spheres [11]. By using this relation, Eq. (13) is derived.

$$\frac{\gamma}{k_{\mathrm{q}}} = \left(\frac{k_{\mathrm{p}} + k_{-\mathrm{c}}}{k_{\mathrm{c}}k_{\mathrm{p}}}\right)\left(\frac{k_{-\mathrm{diff}}}{k_{\mathrm{diff}}}\right)_0 + \frac{\alpha^{\mathrm{ex}}}{8RT}\gamma\eta \tag{13}$$

where γ is the ratio of $g(r_{\mathrm{M^*Q}})$ at P MPa to that at 0.1 MPa, $g(r_{\mathrm{M^*Q}})/g(r_{\mathrm{M^*Q}})_0$, and $(k_{-\mathrm{diff}}/k_{\mathrm{diff}})_0$ is $k_{-\mathrm{diff}}/k_{\mathrm{diff}}$ at 0.1 MPa.[1] According to Eq. (13), the plot of γ/k_{q} against $\gamma\eta$ should be linear when $(k_{\mathrm{p}} + k_{-\mathrm{c}})/k_{\mathrm{c}}k_{\mathrm{p}}$ is independent of pressure.

The plot of γ/k_{q} against $\gamma\eta$ for BZPY/O$_2$ and BZPY/CBr$_4$ is shown in Fig. 4. The plots are approximately linear with

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[1] The radial distribution function at the closest approach distance, $r_{\mathrm{M^*Q}}$ ($= r_{\mathrm{M^*}} + r_{\mathrm{Q}}$) with the hard sphere assumption, $g(r_{\mathrm{M^*Q}})$ is given by [27]

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

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_{S}, by

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

By using the values of r_{S}, $r_{\mathrm{M^*}}$ and r_{Q} listed in Table 1, together with the data of the solvent density [17–19], $g(r_{\mathrm{M^*Q}})$ was calculated by (A.1).

positive intercepts, indicating that the quenching competes with diffusion, and hence $(k_p + k_{-c})/k_c k_p$ is approximately independent of $\eta\gamma$, i.e., pressure. These observations are consistent with those found for the fluorescence quenching by polybromomethanes of pyrene [11], and by CBr_4 and O_2 of 9,10-dimethylanthracene [12]. The values of α^{ex} and the bimolecular rate constant, ${k_{bim}}^0$, defined by

$$ {k_{bim}}^0 = \left(\frac{k_c k_p}{k_p + k_{-c}}\right)\left(\frac{k_{diff}}{k_{-diff}}\right)_0 \quad (14)$$

were determined from the least-squares intercept and slope of the plots (Fig. 4), and are summarized in Table 4. For BZPY/O_2 and BZPY/CBr_4, α^{ex} is nearly equal to α^{SW} (trunc). The values of α^{ex} and ${k_{bim}}^0$ are approximately equal to those for the fluorescence quenching by O_2 and CBr_4 of 9,10-dimethylanthracene in *n*-hexane [12].

The values of k_{bim} can be calculated by $k_{bim} = {k_{bim}}^0\gamma$, and those of k_{diff} also reproduced using α^{ex} (Table 4) and the solvent viscosity, η, according to Eq. (1). By using the values of k_{bim} and k_{diff}, k_q(cal) was calculated by Eq. (15) (see Eq. (12)).

$$ k_q(\text{cal}) = \frac{k_{bim} k_{diff}}{k_{bim} + k_{diff}} \quad (15)$$

The pressure dependence of k_{bim}, k_{diff}, k_q and k_q(cal) thus calculated is shown in Fig. 5a and b for BZPY/O_2 and BZPY/CBr_4, respectively. For BZPY/O_2 (Fig. 5a), k_{diff} is nearly equal to k_{bim}, whereas for BZPY/CBr_4 it is considerably smaller than k_{bim} at 0.1 MPa. Therefore, the contribution of diffusion to the quenching is more significant for BZPY/CBr_4 than for BZPY/O_2 at 0.1 MPa. This leads to larger slope in the plot of $\ln k_q$ against $\ln \eta$ for BZPY/CBr_4 compared to that for BZPY/O_2 (Fig. 3). As a result, for both of the systems, the quenching approaches a diffusion-controlled rate at the higher-pressure region since k_{diff} decreases whereas k_{bim} increases with increasing pressure.

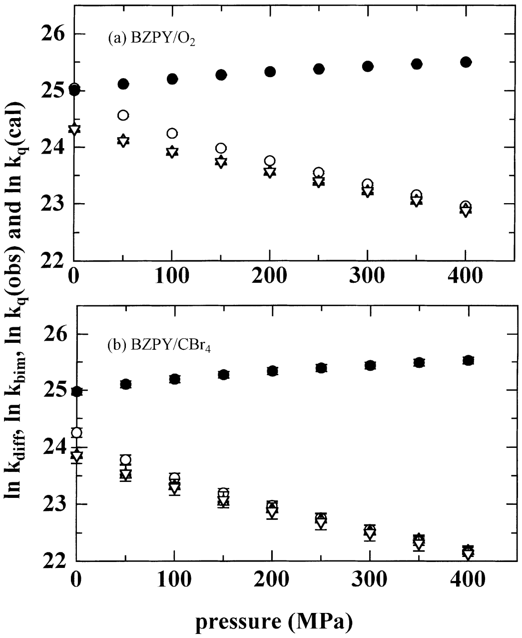

Fig. 5. Pressure dependence of (○) k_{diff}, (●) k_{bim}, (△) k_q and (▽) k_q(cal) for (a) BZPY/O_2 and (b) BZPY/CBr_4 in *n*-hexane at 25°C.

4.3. Estimation of the diffusion coefficient of the quencher

We successfully separated k_q into the contributions of k_{bim} and k_{diff} as described in the previous section. In Table 5, the values of the diffusion coefficient of BZPY, D_{BZPY}, measured by Dymond and Woolf [13] are listed, together with those of ${f_i}^{SW}$ calculated by Eq. (6) using D_{BZPY} [13]. The values of k_{diff} for BZPY/O_2 are also included in Table 5, and those for BZPY/CBr_4 are listed in Table 6.

By using the values of k_{diff}, we can evaluate the relative diffusion coefficients, D_{M^*Q} $(= D_{M^*} + D_Q)$ according to Eq. (4), and also, the values of D_Q and ${f_Q}^{SW}$ for O_2 and CBr_4 can be evaluated if we assume that $D_{M^*} = D_M$ for BZPY since the diffusion coefficient for BZPY in *n*-hexane is known at high pressures [13]. The values of $D_{BZPY^*} + D_Q$, D_Q and ${f_Q}^{SW}$ thus obtained are listed in Tables 5 and 6 for BZPY/O_2 and BZPY/CBr_4, respectively.

Experimental diffusion coefficient data for O_2 and CBr_4 in *n*-hexane are not available in literature to our knowledge. Although there are a few data of diffusion coefficient for oxygen in some liquid solutions at 0.1 MPa, they are very scattered; for example, they are 9.0×10^{-9} and 6.7×10^{-9} in acetone [3,28], 5.7×10^{-9} and 3.5×10^{-9} in benzene [3,28], and 3.9×10^{-9}, 1.6×10^{-9} and 2.6×10^{-9} $m^2\,s^{-1}$ in ethanol [3,29,30].

As seen in Tables 5 and 6, for oxygen the value of ${f_Q}^{SW}$ at 0.1 MPa is about 50% smaller than that of ${f_Q}^{SW}$ (trunc) (Table 3), whereas for CBr_4 it is very close to ${f_Q}^{SW}$ (trunc). We can also see for both of the quenchers that ${f_Q}^{SW}$ is approximately independent of pressure, indicating that the $1/\eta$ dependence of D_Q holds when the solvent viscosity is changed by pressure. The $1/\eta$ dependence has been found in the measurements of self-diffusion coefficients for a number of liquids at high pressure [31–33] as well as for D_i for BZPY [13].

Evans et al. [21,22] measured the diffusion coefficients of spherical solutes with different molecular sizes by using Taylor dispersion technique in some liquid solutions at 0.1 MPa at 25°C, and found that $D_i\eta/T$ increases rapidly with decreasing size of solute, r_W. The plot of D_i (i = tetradodecyltin/Dd$_4$Sn to Ar) against ${r_W}^{-1}$ in *n*-hexane using their data is shown in Fig. 6, in which the solid line was approximated by a polynomial with the fourth order, together with the values of D_Q estimated for O_2 and CBr_4 in this work. In Fig. 6, the values of ${f_i}^{SW}$ decrease from 1.0 (Dd$_4$Sn) to 0.46 (Ar) with decreasing the size of solute. The values of D_{BZPY} [13] and D_Q for CBr_4 evaluated in this work are close to the solid line, but the values of D_Q for O_2 at 0.1 MPa (16×10^{-9} $m^2\,s^{-1}$, Table 5) seem to be slightly larger judging from the experimental values in other

Table 5
Diffusion coefficients, D_i, and f_i^{SW} for BZPY, and rate constants for diffusion, k_{diff}, and the parameters for diffusion associated with the fluorescence quenching for BZPY/O_2 in *n*-hexane at 25°C

P (MPa)	D_{BZPY} $(10^{-9}\,m^2\,s^{-1})$[a]	$f_{BZPY}^{SW b}$	k_{diff} $(10^{10}\,M^{-1}\,s^{-1})$	$D_{BZPY^*} + D_Q$ $(10^{-9}\,m^2\,s^{-1})$[c]	D_Q $(10^{-9}\,m^2\,s^{-1})$[d]	$f_Q^{SW e}$
0.1	2.68	0.80	7.51 ± 0.16	19.1	16.4	0.26
50	1.88	0.71	4.68 ± 0.10	11.9	10.0	0.27
100	1.38	0.70	3.40 ± 0.07	8.65	7.27	0.27
150	1.08	0.69	2.60 ± 0.06	6.62	5.54	0.27
200	0.87	0.68	2.08 ± 0.05	5.29	4.42	0.27
250	0.70	0.69	1.68 ± 0.04	4.29	3.59	0.27
300	0.55	0.71	1.37 ± 0.03	3.49	2.94	0.27
350	0.44	0.73	1.13 ± 0.03	2.89	2.45	0.27
400			0.93 ± 0.02	2.37		

[a] Values interpolated from the data by Dymond and Woolf [13].
[b] Values calculated from Eq. (6) using D_{BZPY}.
[c] Error was evaluated to be ±8%.
[d] Error was evaluated to be ±11%.
[e] Values calculated from Eq. (6) using estimated D_Q.

Table 6
Rate constants for diffusion, k_{diff}, and the parameters for diffusion associated with the fluorescence quenching for BZPY/CBr_4 in *n*-hexane at 25°C

P (MPa)	k_{diff} $(10^{10}\,M^{-1}\,s^{-1})$	$D_{BZPY^*} + D_Q$ $(10^{-9}\,m^2\,s^{-1})$[a]	D_Q $(10^{-9}\,m^2\,s^{-1})$[b]	$f_Q^{SW c}$
0.1	3.40 ± 0.27	7.09	4.41	0.58
50	2.12 ± 0.17	4.42	2.54	0.63
100	1.54 ± 0.13	3.21	1.83	0.64
150	1.18 ± 0.10	2.46	1.38	0.65
200	0.94 ± 0.08	1.96	1.09	0.65
250	0.76 ± 0.07	1.59	0.89	0.65
300	0.62 ± 0.05	1.30	0.75	0.63
350	0.51 ± 0.05	1.07	0.63	0.62
400	0.42 ± 0.04	0.88		

[a] Error was evaluated to be ±15%.
[b] Error was evaluated to be ±18%.
[c] Values calculated from Eq. (6) using estimated D_Q.

solvents described above. However, the value of D_Q for O_2 seems to be close to that extrapolated r_W^{-1} (5.78 nm^{-1}) for O_2; the value extrapolated by the solid line in Fig. 6 was estimated to be $14 \times 10^{-9}\,m^2\,s^{-1}$, which is close to D_Q $(10 \times 10^{-9}\,m^2\,s^{-1})$ calculated using f_i^{SW} (trunc) for O_2 (see Table 3).

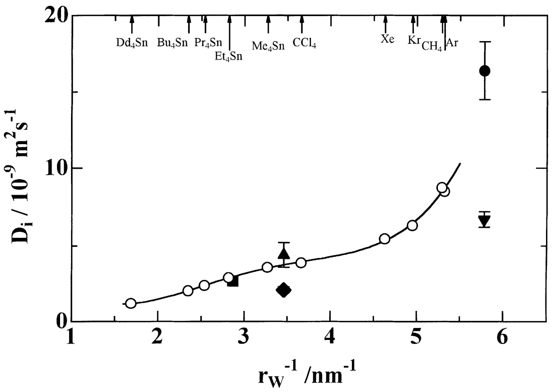

Fig. 6. Plots of D_i against the inverse of van der Waals radius, r_W^{-1}, in *n*-hexane at 25°C and 0.1 MPa. Data were taken from Refs. [21,22] (○). The value of D_{BZPY} (■) [13]. The values of D_Q estimated for O_2 (●) and CBr_4 (▲) in this work (see text), and for O_2 (▼) and CBr_4 (◆) by assuming that the observed k_q is equal to k_{diff} in this work.

Finally, the values of D_Q for O_2 and CBr_4 at 0.1 MPa estimated by assuming that the observed k_q (Table 1) is equal to k_{diff}, i.e., the fluorescence quenching by O_2 and CBr_4 of BZPY is fully diffusion-controlled, are also shown in Fig. 6. It can be clearly seen that the values of D_Q for O_2 and CBr_4 thus estimated are significantly far from those expected by the solid line in Fig. 6. This also suggests that the quenching examined in this work is not fully diffusion-controlled.

5. Summary

It has been shown that the fluorescence quenching by oxygen and carbon tetrabromide (CBr_4) of benzo(a)pyrene (BZPY) is not fully diffusion-controlled, but competes with diffusion. The contribution of diffusion to the quenching was successfully analyzed by Eq. (13), and the observed k_q was separated into the contributions of the bimolecular rate constant in the solvent cage, k_{bim}, and the rate constant for diffusion, k_{diff}. By using the values of k_{diff} thus separated, together with those of the diffusion coefficient, D_{BZPY}, for

BZPY that was determined experimentally [13], the values of D_Q for O_2 and CBr_4 were evaluated at pressures up to 350 MPa according to Eq. (4). It was also shown that D_Q for O_2 and CBr_4 is approximately inversely proportional to the pressure-induced solvent viscosity.

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