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Effect of Pressure on the Intersystem Crossing between the Encounter Complex Pairs Involved in Triplet−Triplet Annihilation of 2-Acetonaphthone in Liquid Solution

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The bimolecular rate constant, k_{TT}, for triplet−triplet annihilation (TTA) of 2-acetonaphthone (ACN) in methylcyclohexane (MCH) and *n*-hexane at pressures up to 400 MPa at 25 °C has been measured. It was found that k_{TT} decreases significantly with increasing pressure, and the activation volumes for k_{TT}, $\Delta V_{TT}^{\ddagger}$, were determined to be 18 and 11 cm^3/mol, whereas those for the solvent viscosity, $\Delta V_{\eta}^{\ddagger}$, were 24 and 23 cm^3/mol in MCH and *n*-hexane, respectively. The significant difference between $\Delta V_{TT}^{\ddagger}$ and $\Delta V_{\eta}^{\ddagger}$ was attributed to the competition of the quenching with diffusion. From the analysis on the basis of the pressure dependence of the solvent viscosity, η, on the quenching, the observed rate constant, k_{TT}, was separated into the contributions of the rate constant for diffusion, k_{diff}, and the bimolecular rate constant for quenching, k_{bim}, in the solvent cage. By using the values of k_{diff} thus determined, $2k_{TT}/k_{diff}$ was found to be about 4/9 at 0.1 MPa and to approach unity with increasing pressure. The results were interpreted by a kinetic model that involves the encounter complex pairs, ${}^i(M^*M^*)_{en}$ ($i = 1, 3, 5$), with singlet, triplet, and quintet spin multiplicities. It was concluded that the rate constant for the dissociation, k_{-diff}, decreases more significantly than that for the intersystem crossing, k^{en}isc(i), between the encounter complex pairs with increasing pressure (Scheme 4).

Introduction

The decay processes for the lowest triplet state (T$_1$), ${}^3M^*$, generated after the excitation of ${}^1M$ may be described as in Scheme 1. Triplet−triplet annihilation (TTA) represented by the third step, which often leads to monomer and excimer delayed fluorescence for some compounds, is an important triplet decay pathway.[1−3] Studies on varying solvent[4] and temperature[5,6] have revealed that the TTA process is diffusion-controlled in nature and also involves encounter complexes pairs, ${}^i(M^*M^*)$ ($i = 1, 3,$ or 5), formed between the T$_1$ states that have three different spin multiplicities.[3] Therefore, the quenching has often been investigated by evaluating the ratio of the rate constant for TTA (k_{TT}) to that for diffusion.[3,6] However, it is very difficult to evaluate accurately the rate constant for diffusion in liquid solution. We reported in the previous publication[7] the quenching by oxygen of the T$_1$ state of 9-acetylanthracene having the same requirement of spin statistics as the present system. The ratio of the quenching rate constant for the T$_1$ state of 9-acetylanthracene to that for the fluorescence of 9,10-dimethylanthracene, for which the quenching is assumed to be fully diffusion-controlled, was found to increase with increasing pressure, and it was concluded that the intersystem crossing between the encounter complex pairs, ${}^i(M^*O_2)$ ($i = 1, 3,$ or 5), is enhanced by pressure.

The rate constant for diffusion, k_{diff}, in a continuum medium with viscosity η is described by the Debye equation derived on the basis of the Stokes−Einstein equation as follows:

$$k_{diff} = 8RT/\alpha\eta \qquad (1)$$

where α is 2000 and 3000 for the slip and stick boundary limits, respectively.[8,9] However, the expression of eq 1 has often failed.[10,11] This may be mainly attributed to the neglect of the difference in size of the solute and solvent molecules; it may also be due to the deviation from the continuum model that arises as a result of short-range interactions between the solute and solvent molecules such as translational and rotational coupling. An empirical equation developed by Spernol and Wirtzs,[12,13] for which α in eq 1 is replaced by α^{SW} that depends on the properties of the solvent and solute molecules, has been applied successfully to diffusion-controlled radical self-termination reactions,[14] exothermic triplet excitation transfer,[13,15,16] and exciplex formation reactions.[17] Recently, we examined the fluorescence quenching of pyrene by heavy-atom quenchers with wide quenching abilities in liquid solution at high pressure, and the observed quenching rate constant was separated into k_{diff} and the bimolecular rate constant for quenching, k_{bim}, in the solvent cage by introducing the radial distribution function at the closest approach distance between the solutes with hard spheres.[18] The same analysis for the separation into k_{diff} and k_{bim} was successfully applied to the fluorescence quenching of bezo(*a*)pyrene[19] and 9,10-dimethylanthracene[20] by oxygen and carbon tetrabromide and showed that the value of α^{ex} thus estimated is in good agreement with those of α^{SW}.

SCHEME 1

$$
\begin{gathered}
{}^1M \xrightarrow{h\nu} {}^1M^* \xrightarrow{k_{ISC}} {}^3M^* \\
{}^3M^* \xrightarrow{k_1} {}^1M \\
2\ {}^3M^* \xrightarrow{k_{TT}} {}^1M
\end{gathered}
$$

In this work, TTA of 2-actonaphthone (ACN), which is virtually nonfluorescent, the quantum yield of the T$_1$ state at 0.1 MPa is 0.94 and 0.89 in methylcyclohexane and *n*-hexane, respectively, by the time-resolved thermal lensing,[21] was investigated to obtain further insight into the effect of pressure on the intersystem crossing between the encounter complex pairs, ${}^i(M^*M^*)$ ($i = 1, 3,$ or 5). For this purpose, we measured the bimolecular rate constant, k_{TT}, as a function pressure up to

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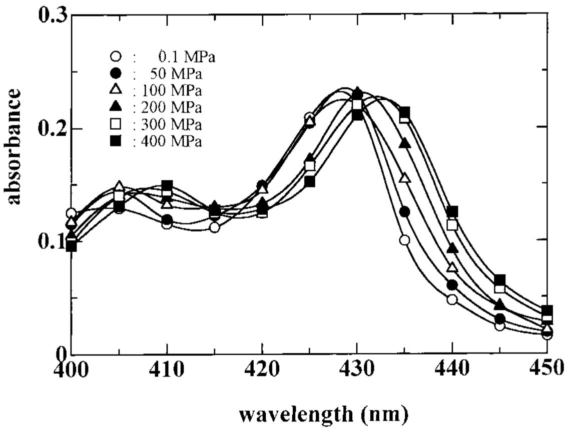


Figure 1. Transient absorption spectra of ACN in MCH observed at 120 ns after the laser pulse excitation.

400 MPa in methylcyclohexane and *n*-hexane at 25 °C. The observed rate constant for TTA, k_{TT}, was separated into the contributions of k_{diff} and k_{bim}, and the pressure dependence of the efficiency of the quenching, $2k_{TT}/k_{diff}$, was determined.

Experimental Section

2-Acetonaphthone (ACN, Tokyo Kasei Kogyo Co., Ltd.) of guaranteed grade was recrystalized from ethanol twice. 9-Acetylanthracene (Aldrich Chemical Co.) was chromatographed twice on silica gel, developed and eluted with *n*-pentane, and followed by recrystalization from ethanol twice. Methylcyclohexane (MCH, Dojin Pure Chemicals Co.) and *n*-hexane (Merk) of spectroscopic grade were used as received.

Transient absorption measurements at high pressure were performed by using an 8-ns pulse from a nitrogen laser (337.1 nm/ 5mJ per pulse) for excitation and a xenon analyzing flash lamp positioned at right angles to the direction of the excitation pulse. The analyzing light intensities were monitored by a Hamamatsu R928 photomultiplier through a Ritsu MC-25N monochromator. The signal was accumulated 3−6 times, averaged and digitized by using a Hewlett-Packard 54510A digitizing oscilloscope. All data were analyzed by using a NEC 9801 microcomputer, which was interfaced to the digitizer. The associated high-pressure techniques have been described in detail elsewhere.[22]

The concentration of ACN for the decay measurements was changed from 0.5 to 1.5 in absorbance (1-cm cell) at 337.1 nm. In the measurements of T−T′ absorption spectra as a function of pressure, the higher concentration of ACN and 9-acetylanthracene (ca. 1.6) was chosen in order to minimize the concentration dependence on the number of absorbed photons. The sample solution was deoxygenated by bubbling nitrogen gas under nitrogen atmosphere.

Temperature was controlled at 25 ± 0.2 °C. Pressure was measured by a Minebea STD-5000K strain gauge.

Results and Discussion

Figure 1 shows the transient absorption spectra of the lowest triplet state (T_1) of ACN, ^{3}ACN*, in MCH at 120 ns after the laser pulse. It is noted in Figure 1 that the intensity is approximately independent of pressure, although a small spectral shift induced by pressure is observed, indicating that the quantum yield of ^{3}ACN* is independent of pressure provided that the pressure dependence of the molar extinction coefficient is not significant. In the previous work, similar observations were found for measurements of the triplet−triplet absorption spectra of 9-acetylanthracene.[7] The molar extinction coefficient of the T_1 state of 9-acetylanthracene at the maximum wavelength (422 nm) at 0.1 MPa and 25 °C in MCH was evaluated to be 2.5 x 10^4 $M^{-1}cm^{-1}$ by the singlet depletion method.[23] By comparing the absorbance of ^{3}ACN* with that of the T_1 state of 9-acetylanthracene in the photolysis for optically identical samples, the molar extinction coefficient, ϵ_T, of ^{3}ACN* at 430 nm, at the wavelength which the decay curves were measured throughout in this work, was evaluated to be 1.5 x 10^4 $M^{-1}cm^{-1}$, which is in good agreement with that (1.05 x 10^4 M^{-1} cm^{-1}) in benzene reported by other workers.[24] In the present work, the value of ϵ_T in *n*-hexane at 430 nm is assumed to be 1.5 x 10^4 M^{-1} cm^{-1}.

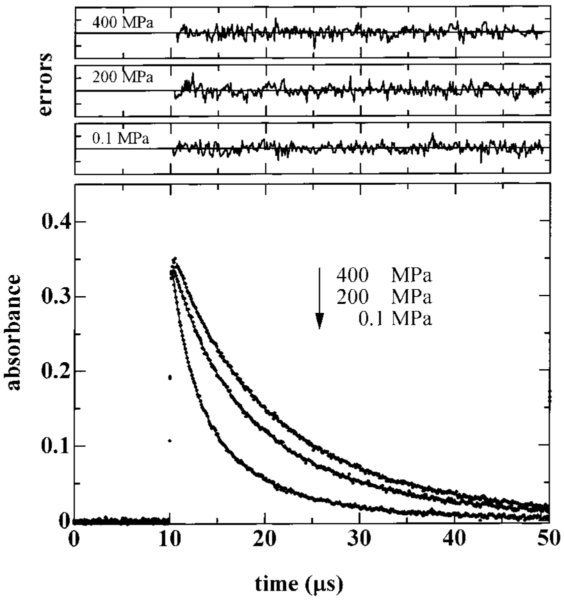


Figure 2. Decay curves of ^{3}ACN* observed at 430 nm in MCH. The absorbance of the sample solution was 0.50 at 337.1 nm and 0.1 MPa. The solid lines are the best fit curves according to eq 2.

On the basis of Scheme 1, the change in absorbance (path length, *l*; $l = 0.5$ cm in this work) of ^{3}ACN* with time, *t*, *A*(*t*), may be expressed by eq 2

$$A(t) = \frac{k_1A(0)}{\{(k_1 + k_2A(0)\}\ \exp(k_1t) - k_2A(0)} \qquad (2)$$

where

$$k_2 = k_{TT}/\epsilon_T l \qquad (3)$$

The decay curves were measured for the samples with absorbances of 0.5, 1.0, and 1.5 at 337.1 nm (1-cm path length). Figure 2 shows the decay curves in MCH at three pressures. The values of k_1 and k_2 were evaluated by an iterative nonlinear least-squares method according to eq 2. Typical examples of the analysis are shown by the solid lines in Figure 2. The errors of the recovered values of k_1 and k_2 thus obtained were estimated to be approximately ±5% where no significant concentration dependence was observed. The value of k_1^{-1} was approximately 12 μs in MCH at 0.1 MPa and slightly increased with increasing pressure; the short lifetime of k_1^{-1} may be due to the quenching by residual oxygen in the sample solution. The values of k_2^{-1} increased significantly from 1.5 to 11 μs in MCH at 25 °C on going from 0.1 to 400 MPa.

The pressure dependence of k_{TT}, determined using eq 3 and the value of ϵ_T (=1.5 x 10^4 M^{-1} cm^{-1}), is shown in Figure 3. The value of k_{TT} is 5.0 x 10^9 and 8.4 x 10^9 M^{-1} s^{-1} in MCH

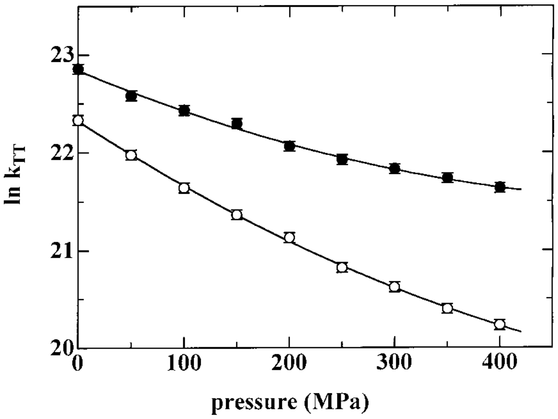
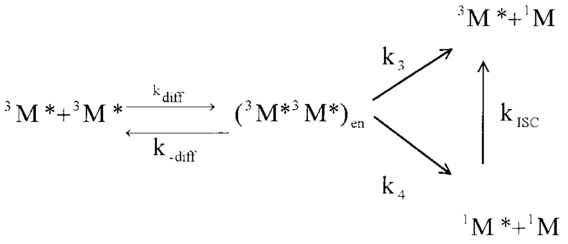


Figure 3. Pressure dependence of k_{TT} in MCH (○) and *n*-hexane (●). The solid lines were drawn by assuming that $\ln k_{TT} = A + BP + CP^2$.

TABLE 1: Activation Volume (cm³/mol) for the Solvent Viscosity, *η*, and k_{TT} at 25 °C and 0.1 MPa

	$\Delta V_\eta^\ddagger$	$\Delta V_{TT}^\ddagger$
MCH	24	18 ± 1
n-hexane	23	11 ± 1

SCHEME 2



and *n*-hexane at 0.1 MPa, respectively, and decreases significantly with increasing pressure, suggesting that TTA is qualitatively diffusion-controlled as concluded by many workers.[3−6] The apparent activation volumes for k_{TT} , $\Delta V_{TT}^\ddagger$, evaluated by eq 4, are listed in Table 1, together with those, $\Delta V_\eta^\ddagger$, determined from the pressure dependence of the solvent viscosity, *η*. [25−28]

$$RT\left(\frac{\partial \ln k_{TT}}{\partial P}\right)_T = -\Delta V_{TT}^\ddagger \tag{4}$$

The value of $\Delta V_{TT}^\ddagger$ is significantly smaller compared to that of $\Delta V_\eta^\ddagger$. It is also noted in Table 1 that $\Delta V_{TT}^\ddagger$ in MCH is significantly larger than that in *n*-hexane, whereas $\Delta V_\eta^\ddagger$ is nearly equal in both of the solvents. These results suggest that TTA is not fully diffusion-controlled.[16−20] An additional test for the reactions with a nearly diffusion-controlled rate is given by the fractional power dependence of *η* on k_{TT}; k_{TT} is proportional to $\eta^{-\beta}$ where $0 < \beta \leq 1$.[29] It was found that the plot of ln k_{TT} against ln *η* is approximately linear and the value of *β* was estimated to be 0.72 ± 0.01 and 0.60 ± 0.02 in MCH and *n*-hexane, respectively. However, the approximately linear plot of logarithms of the quenching rate constant against ln *η* has been observed for some systems for which the quenching competes with diffusion.[16−20] From these results, it was inferred that TTA is nearly, but not fully, diffusion-controlled.

The decay of ^{3}ACN* may occur via the encounter complex, $(^3M^{*3}M^*)_{en}$, as given by Scheme 2.[3,6] On the basis of Scheme 2, the observed bimolecular rate constant, k_{TT}, may be given by

$$\frac{1}{2k_{TT}} = \frac{1}{k_3 + (2 - \phi_{ISC})k_4}\left(\frac{k_{-diff}}{k_{diff}}\right) + \frac{k_3 + k_4}{k_3 + (2 - \phi_{ISC})k_4}\left(\frac{1}{k_{diff}}\right) \tag{5}$$

where ϕ_{ISC} is the quantum yield for the intersystem crossing. As mentioned above, ϕ_{ISC} is 0.94 and 0.89 in MCH and *n*-hexane at 0.1 MPa, respectively,[21] and approximately independent of pressure. Here, we assume that $k_3 + (2 - \phi_{ISC})k_4$ is approximately equal to $k_3 + k_4$ since the ratio is insensitive to the large variation in k_3/k_4 and approximately equal to unity.

Since the pressure dependence of k_{diff}/k_{-diff} is given by that of the radial distribution function, $g(r_{M^*M^*})$, at the closest approach distance, $r_{M^*M^*}$, between two triplet molecules with hard spheres,[30] one may obtain eq 6 from eqs 1 and 5.

$$\frac{\gamma}{2k_{TT}} = \frac{1}{k_3 + (2 - \phi_{ISC})k_4}\left(\frac{k_{-diff}}{k_{diff}}\right)_0 + \frac{\alpha^{ex}}{8RT}\gamma\eta \tag{6}$$

Where *γ* is the ratio of $g(r_{M^*M^*})$ at *P* MPa to that at 0.1 MPa, $g(r_{M^*M^*})/\ g(r_{M^*M^*})_0$, and $(k_{-diff}\ /k_{diff})_0$ is $k_{-diff}\ /k_{diff}$ at 0.1 MPa.[31] In Table 2, the van der Waals radii of solvent and solute,[32] which are needed to calculate the value of $g(r_{M^*M^*})$, are listed. The similar equation to eq 6 taking *γ* into account was successfully applied to the fluorescence quenching by the heavy-atom quenchers and oxygen in liquid solution[18,19] and supercritical carbon dioxide.[20] According to eq 6, the plot of $\gamma/2k_{TT}$ against $\gamma\eta$ should be linear when $\{k_3 + (2 - \phi_{ISC})k_4\}^{-1}$ is independent of pressure.

Figure 4 shows the plot of $\gamma/2k_{TT}$ against $\gamma\eta$ in MCH and *n*-hexane. The plots shown in Figure 4 are approximately linear with positive intercepts, indicating that the quenching rate constant is comparable with that for diffusion.[18−20] The linear plot also indicates that $\{k_3 + (2 - \phi_{ISC})k_4\}^{-1}$ is approximately independent of $\gamma\eta$, that is, pressure. The values of α^{ex} and the bimolecular rate constant, $k_{bim}0$, defined by eq 7

$$k_{bim}{}^0 = \{k_3 + (2 - \phi_{ISC})k_4\}\left(\frac{k_{diff}}{k_{-diff}}\right)_0 \tag{7}$$

were determined from the least-squares intercept and slope (Figure 4), respectively, and are listed in Table 2.

In the previous publications,[16−20] we showed that the values of α^{ex} estimated from the pressure induced-solvent viscosity dependence of the quenching constant for several quenching systems with a nearly diffusion rate are approximately equal to those of α^{SW} calculated by the method of Spernol and Wirts[3,12,13,15] using the values of the van der Waals radii of solvent and solute. The values of α^{SW}(trunc) and α^{SW}(full) obtained are also listed in Table 2.[33] It can be seen in Table 2 that the values of α^{ex} obtained in this work agree fairly well with those of α^{SW}(trunc) that are smaller than the value for the slip boundary limit ($\alpha = 2000$) in eq 1.

The values of k_{diff} reproduced by using α^{ex} (Table 2) and the solvent viscosity, *η*, according to eq 1 were evaluated to be 2.0 x 10^{10} and 3.9 x 10^{10} M^{-1} s^{-1} in MCH and *n*-hexane at 0.1 MPa, respectively. They are in good agreement with those estimated for the fluorescence quenching by carbon tetrabromide of pyrene (1.7 x 10^{10} M^{-1} s^{-1})[17,18] and benzanthracene (1.6 x 10^{10} M^{-1} s^{-1})[17] in MCH and also by carbon tetrabromide of benzo[*a*]pyrene (3.4 x 10^{10} M^{-1} s^{-1})[19] and 9,10-dimethylanthracene (3.7 x 10^{10} M^{-1} s^{-1})[20] in *n*-hexane at 0.1 MPa and 25 °C. The values of $k_{bim}{}^0$ defined by eq 7, which are shown in Table 2, are approximately equal to those for the systems with a nearly diffusion-controlled rate.[16−20]

TABLE 2: Values of k_{bim}^0, α^{ex}, r_W, and α^{SW} Evaluated by the Empirical Equation of Spernol and Wirts

	r_w/nm[a]	$k_{bim}^0/10^{10}$ M^{-1} s^{-1}	α^{ex}	α^{SW} (full)	α^{SW} (trunc)
MCH	0.304	1.2 ± 0.3	1500 ± 100	2170	1810
n-hexane	0.301	2.0 ± 0.4	1700 ± 100	2230	1830

[a] The van der Waals radii, r_w, estimated by the method of Bondi.[32] The value of r_w for ACN was estimated to be 0.338 nm.[32]

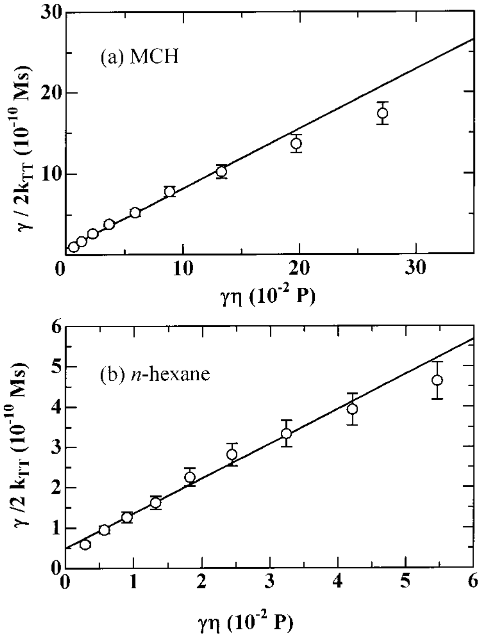


Figure 4. Plots of $\gamma/2k_{TT}$ against $\gamma\eta$ in MCH (a) and *n*-hexane (b).

Since the values of k_{bim} is calculated by $k_{bim} = \gamma k_{bim}0$, $2k_{TT}$ can be evaluated by eq 8 using k_{diff} and k_{bim}.

$$2k_{TT}(\text{cal}) = \frac{k_{bim}k_{diff}}{k_{bim} + k_{diff}} \qquad (8)$$

The pressure dependence of k_{bim}, k_{diff}, and $2k_{TT}$(cal) thus obtained is shown in Figure 5, together with that of the observed rate constant, k_{TT}. As seen in Figure 5, k_{bim} is close to k_{diff} at the lower pressure range, indicating that the quenching competes with diffusion. However, when pressure increases further, the difference between k_{bim} and k_{diff} increases and the quenching approaches diffusion-controlled.

The decay process of ^{3}ACN* by TTA process has often been explained by Scheme 3.[3] In Scheme 3, the encounter complex pair with quintet spin multiplicity, ^{5}(M*M*)$_{en}$, does not have the triplet decay pathway. When the decay process via the encounter complex pairs, ^{i}(M*M*)$_{en}$ (i = 1, 3) are fully diffusion-controlled and that via ^{5}(M*M*)$_{en}$ is fully dissociative, $2k_{TT}/k_{diff}$ is expected to be 4/9. In fact, as seen in Figure 6, which shows the plot of $2k_{TT}/k_{diff}$ against k_{diff} in MCH and *n*-hexane, the value of $2k_{TT}/k_{diff}$ is close to 4/9 at 0.1 MPa. The results obtained in this work at 0.1 MPa may indicate this case.

As seen in Figure 6, the value of $2k_{TT}/k_{diff}$ increases and gradually approaches unity with decreasing k_{diff}, that is, increasing pressure, indicating that the participation of the additional decay processes of the triplet may be involved in the quenching with increasing pressure. Unfortunately, however, there is no experimental evidence about TTA of ^{3}ACN* at 0.1 MPa as well as at high pressure to the authors' knowledge. In the previous paper,[7] we examined the quenching by oxygen of the T$_1$ state

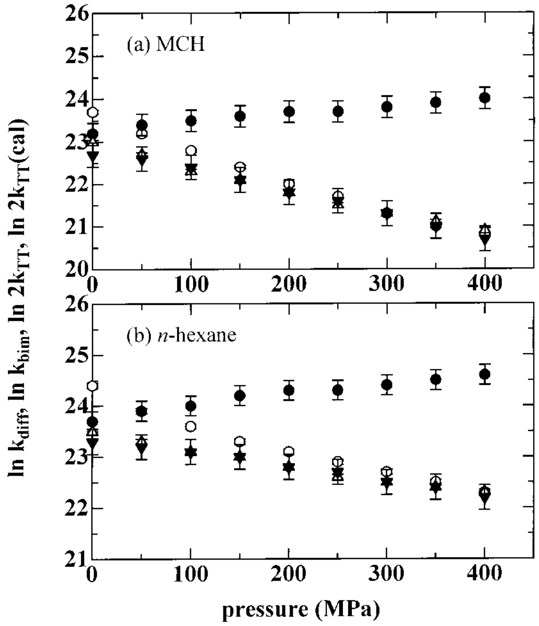


Figure 5. Pressure dependence of k_{diff} (○), k_{bim} (●), $2k_{TT}$ (△), and $2k_{TT}$(cal) (▼) in MCH (a) and *n*-hexane (b).

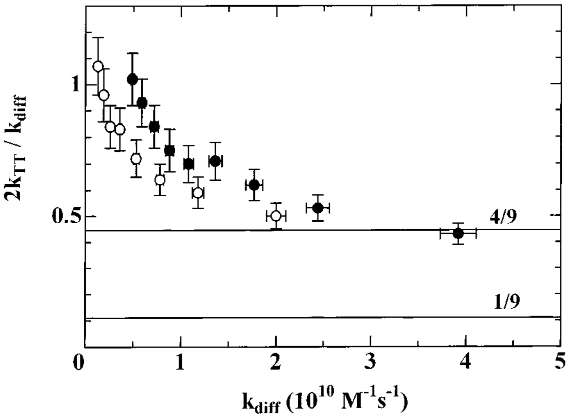
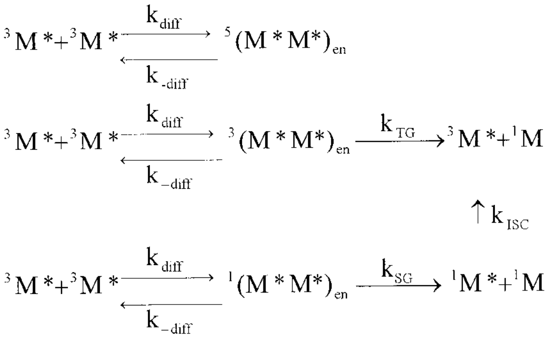


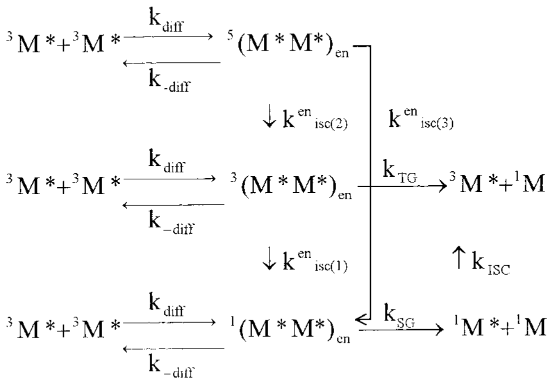
Figure 6. Plots of $2k_{TT}/k_{diff}$ against k_{diff} in MCH (○) and n-*h*exane (●).

SCHEME 3



of 9-acetylanthracene whose system has the same spin statistical requirement as the present one. The ratio, k_q^T/k_q^S, of the oxygen quenching rate constant for the T$_1$ state of 9-acetylanthracene, k_q^T, to that for the fluorescence quenching of 9,10-dimethylanthracene, k_q^S, that is assumed to be diffusion-controlled was found to increase over $^1/_9$ with increasing pressure. From the results, together with the findings that the quantum yield for the formation of singlet oxygen ($^1\Delta$g) sensitized by the T$_1$ state of 9-acethylanthracene is unity and independent of pressure, the increase in the ratio, k_q^T/k_q^S, was interpreted by the increased

SCHEME 4



intersystem crossing between the encounter complex pairs $^i(M^*O_2)$ (i = 1, 3, or 5) by pressure. This may be applied to the present system when the quintet state, $^5(M^*M^*)$, of the encounter complex pairs is still dissociative at high pressure. In this case, the decay processes may be described by Scheme 4. As a result, it may be concluded that the increase in $2k_{TT}/k_{diff}$ for the system examined in this work is attributed to the increase in $k^{en}{}_{isc(i)}$ (see Scheme 4) compared to k_{-diff} with increasing pressure.

Saltiel et al.[3,6] have measured the rate constant for TTA of the T_1 state of anthracene in toluene and benzene at 0.1 MPa and found that $2k_{TT}/k_{diff}$ is 0.57, independent of temperature. They have interpreted their results by Scheme 3 in which $^5(M^*M^*)_{en}$ is fully dissociative.[3]

For TTA of benzophenone, k_{TT} has been reported to be 0.81 x 10^{10} to 1.1 x 10^{10} M^{-1} s^{-1} in benzene at 0.1 MPa.[34,35] Since the values of α^{SW}(trunc) and α^{SW}(full) can be evaluated by the method of Spernol and Wirts as described above, k_{diff} at 25 °C and 0.1 MPa is calculated:[36] α^{SW}(trunc) = 2020, k_{diff} = 1.6 x 10^{10} M^{-1} s^{-1}; α^{SW}(full) = 2080, k_{diff} =1.5 x 10^{10} M^{-1} s^{-1}. Thus, by using these values, $2k_{TT}/k_{diff}$ was estimated to be nearly unity, implying that the intersystem crossing between the encounter complex pairs is fully open when $^5(M^*M^*)_{en}$ is fully dissociative (Scheme 4). Unfortunately, there is no experimental evidence in liquid solution that would allow to discuss further in the literature to our knowledge. However, it has been shown that $2k_{TT}/k_{diff}$ is $^5/_9$ for TTA of benzophenone in supercritical carbon dioxide.[37] In this system, TTA may be interpreted by Scheme 3 where $2k_{TT}/k_{diff} = {}^4/_9$. This implies that the difference between TTA in liquid and supercritical carbon dioxide is significant.

Finally, for TTA of ACN as mentioned above, $2k_{TT}/k_{diff}$ increased significantly with increase in solvent viscosity by the application of pressure at 298 K. However, for TTA for anthracene, $2k_{TT}/k_{diff}$ is independent of temperature (258.2−318.2 K) at 0.1 MPa.[3,6] The pressure dependence of $2k_{TT}/k_{diff}$ is attributed to the larger decrease in k_{-diff} compared to $k^{en}{}_{isc(i)}$, which may arise as a result of the decrease in the excluded volume with increasing pressure.

Summary

Triplet−triplet annihilation (TTA) of 2-acetonaphthone (ACN) in methylcyclohexane (MCH) and *n*-hexane at pressures up to 400 MPa has been examined. From the pressure dependence of solvent viscosity on the rate constant for TTA, k_{TT}, together with that of the radial distribution function at the closet approach distance between the triplets with hard spheres, the rate constant for diffusion, k_{diff}, involved in TTA was evaluated by eq 6. It was found that the ratio $2k_{TT}/k_{diff}$ is about $^4/_9$ at 0.1 MPa and approaches unity with increasing pressure in both of the solvents examined in this work. The results are interpreted by a kinetic model that involves the encounter complex pairs, $^i(M^*M^*)_{en}$ (i = 1, 3, 5), with singlet, triplet, and quintet spin multiplicities (Schemes 3 and 4). The pressure dependence of $2k_{TT}/k_{diff}$ is attributed to the larger decrease in the rate constant for the dissociation, k_{-diff}, compared to that for the intersystem crossing, $k^{en}_{isc(i)}$, between the encounter complex pairs with increasing pressure (Scheme 4).

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(31) The radial distribution function at the closest approach distance, $2r_{M^*}$ with the hard sphere assumption, $g(r_{M^*M^*})$ is given by[30] $g(r_{M^*M^*}) = [1/(1-y)] + \{[3y/(1-y)^2](r_{red}/r_S)\} + [2y^2/(1-y)^3(r_{red}/r_S)^2]$ (A1), where r_S is the radius of solvent and $r_{red} = r_{M^*}/2$, and y is the packing fraction, given in terms of the molar volume of solvent, V_S, by $y = 4N_A\pi r_S/3V_S$ (A2). By using the values of r_S and r_{M^*} listed in Table 2, together with the data of the solvent density,[25−28] $g(r_{M^*M^*})$ was calculated by (A1).

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