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Effect of high pressure on the quenching by hexamethylbenzene of singlet oxygen in liquid solution

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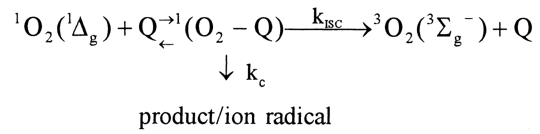
Abstract

The quenching mechanism by hexamethylbenzene (HMB) of singlet oxygen ($^1O_2$ ($^1\Delta_g$)) was investigated as a function of pressure up to 400 MPa by measurements of the phosphorescence decay. The quenching rate constant, k_{obs}, increases significantly with increasing pressure in the solvents examined, and the activation volume for k_{obs}, $\Delta V^{\neq}_{obs}$ falls in the range from −29.7 to −25.8 cm^3/mol, depending on the solvent. It was found that $\Delta V^{\neq}_{obs}$ is almost independent of the solvent polarity parameter, $q_P(=\partial[\{(\varepsilon - 1)/(2\varepsilon + 1)\}/\partial P]_T)$, where ε is the dielectric constant of the solvent. However, k_{obs} is correlated linearly to $q(=(\varepsilon - 1)/(2\varepsilon + 1))$ at a given pressure, up to 400 MPa. These observations were interpreted by assuming that quenching occurs through a nonpolar encounter complex between $^1O_2$ and HMB, and the singlet, ^1E, and triplet, ^3E, exciplexes. The volumetric analysis on the basis of this scheme revealed that the activation volume for the observed rate constant, k_{ISC}, of the intersystem crossing from ^1E to ^3E decreases with increasing solvent polarity. The solvent–polarity dependence of k_{ISC} is discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Quenching; Hexamethylbenzene (HMB); Singlet oxygen

1. Introduction

Singlet oxygen ($^1O_2$ ($^1\Delta_g$)), the lowest excited singlet state of oxygen, is quenched effectively by many compounds (Q) with low ionization potentials, such as amines [1–4], furans [5–7], phenols [8,9] and hydrazines [10] as well as solvent molecules [11,12], we have:



$$\begin{array}{c} {}^1O_2({}^1\Delta_g) + Q \rightleftarrows {}^1(O_2 - Q) \xrightarrow{k_{ISC}} {}^3O_2({}^3\Sigma_g^-) + Q \\ \downarrow k_c \\ \text{product/ion radical} \end{array}$$

For these systems, the charge-transfer character of an initially formed complex of singlet spin multiplicity between singlet oxygen and quencher has been commonly taken into account, and it has been proposed that the quenching involves an exciplex [1–10]. In many cases, the physical quenching that occurs via intersystem crossing competes with chemical processes leading to products (chemical quenching) [13].

In the previous publication [14], we measured the pressure effect on the lifetime of singlet oxygen in benzene, toluene, *o*-, *m*, *p*-xylenes and mesitylene, and found that the activation volume for the quenching rate constant decreases significantly as ionization potential of solvent decreases. On the basis of the facts, together with the findings from the analysis by the hard-sphere model, it has been shown that the quenching involves exciplexes of the singlet and triplet spin multiplicities.

In the present work, the quenching of singlet oxygen by hexamethylbenzene (HMB), that has a lower ionization potential (7.85 eV) [15] than that of aromatic molecules used as solvent in the previous study [14], was investigated. Generally, the rate processes associated with the formation and dissociation processes of exciplex are affected significantly upon applying high pressure [16] as well as changing polarity of solvent. For theses systems, both the effects of solvent and pressure on the rate processes are important to obtain the information about the reaction mechanism in solution. Studies along this line have been demonstrated for the singlet oxygen/amines (σ-donors) systems [17,18]. The present work is focused on the quenching mechanism by HMB of π-donor of singlet oxygen in order to compare with the results of the singlet oxygen/amines systems. For this purpose, the quenching rate constants were measured in five solvents at pressures of up to 400 MPa.

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2. Experimental section

9-Acetylanthracene (ACA) (Aldrich) was chromatographed twice on silica gel, developed and eluted with *n*-pentane, and followed by recrystallization from ethanol twice. Hexamethylbenzene (HMB, Nakarai Chemicals) of guaranteed grade was recrystallized from ethanol three times. Methylcyclohexane (MCH, Dojin Pure Chemicals), acetonitrile (Dojin Pure Chemicals), *n*-pentane (Merck), toluene (Dojin Pure Chemicals) of spectroscopic grade were used without further purification. Chlorobenzene (Wako) of guaranteed grade was used as received.

The phosphorescence decay curves of singlet oxygen at 1270 nm were measured as a function of pressure by a method similar to that described previously [14]. In the present work, the element used in the near-IR detection system was replaced by an InGaAs sensor (1 mm diameter, Hamamatsu G5832-01) which was biased reversely at 5 V since the time response is much better (the total rise time was ca. 0.4 μs). Phosphorescence generated by excitation of a sensitizer (ACA) using an 8-ns pulse from a nitrogen laser (337.1 nm) were monitored by the InGaAs sensor, and the resulting signal was averaged and digitized on a Hewlett–Packard 54510A digitizing oscilloscope. The concentrations of ACA used as the sensitizer were adjusted to give ca. 0.5 in absorbance at 337.1 nm (1-cm cell). The increase in the concentration of HMB by applying high pressure was corrected by using the compressibility of solvent [19–23].

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

3. Results

The phosphorescence of singlet oxygen showed a single exponential decay in all the experimental conditions examined. The quenching rate constant, k_{obs}, was determined from the dependence of the concentration of hexamethylbenzene, [HMB], according to Eq. (1):

$$1/\tau_{\Delta} - 1/\tau_{\Delta}^{0} = k_{\mathrm{obs}}[\mathrm{HMB}] \qquad (1)$$

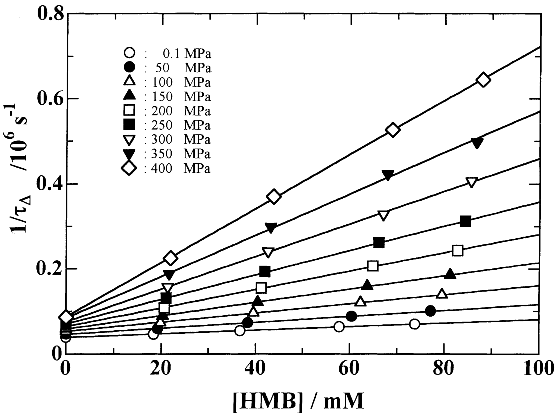


Fig. 1. Plots of $1/\tau_{\Delta}$ against the concentration of HMB, [HMB] in methylcyclohexane (MCH).

where τ_{Δ} and τ_{Δ}^{0} represent the lifetimes of singlet oxygen in the presence and absence of HMB, respectively. Fig. 1 shows typical examples of the plots of $1/\tau_{\Delta}$ against [HMB] in MCH. It is observed that the intercepts of the plots shown in Fig. 1 increase with increasing pressure. This increase in $1/\tau_{\Delta}^{0}$ by the application of pressure is consistent with the results reported previously [24,25]. The values of k_{obs} at 0.1 MPa are listed in Table 1, together with those of the dielectric constant, ε, of the solvent.

The pressure dependence of k_{obs} in five solvents is shown in Fig. 2. It can be seen in Fig. 2 that k_{obs} increases significantly with increasing pressure in all the solvents examined. The activation volume for k_{obs}, $\Delta V^{\neq}_{\mathrm{obs}}$, is given by

$$RT\left(\frac{\partial \ln k_{\mathrm{obs}}}{\partial P}\right)_T = -\Delta V^{\neq}_{\mathrm{obs}} - RT\kappa \qquad (2)$$

where κ is the isothermal compressibility of solvent [19–23]. The values of $\Delta V^{\neq}_{\mathrm{obs}}$ are summarized in Table 2.

4. Discussion

The quenching of singlet oxygen by the molecules with low ionization potential is generally expressed by the following scheme [14,17,18]:

Table 1
Solvent properties and the observed quenching rate constant, k_{obs}, at 0.1 MPa in five solvents

	ε[a]	q[b]	q_P[c]/(10^{-10} Pa^{-1})	RTκ[d]/(cm^3 mol^{-1})	k_{obs}/(10^5 M^{-1} s^{-1})
Acetonitrile	37.70	0.480	0.234	2.3	71.8 ± 0.8
Chlorobenzene	5.55	0.376	0.937	1.5	33.6 ± 0.5
Toluene	2.28	0.240	1.611	2.0	19.9 ± 0.2
Methylcyclohexane	2.01	0.201	1.847	2.2	4.16 ± 0.06
n-Pentane	1.83	0.178	2.600	3.9	2.75 ± 0.03

[a] Dielectric constant of solvent.

[b] The solvent-polarity parameter defined by Kirkwood, $q=(\varepsilon-1)/(2\varepsilon+1)$.

[c] $q_P = (\partial q/\partial P)_T$, Refs. [21–23,27–29].

[d] κ is the isothermal compressibility of the solvent.

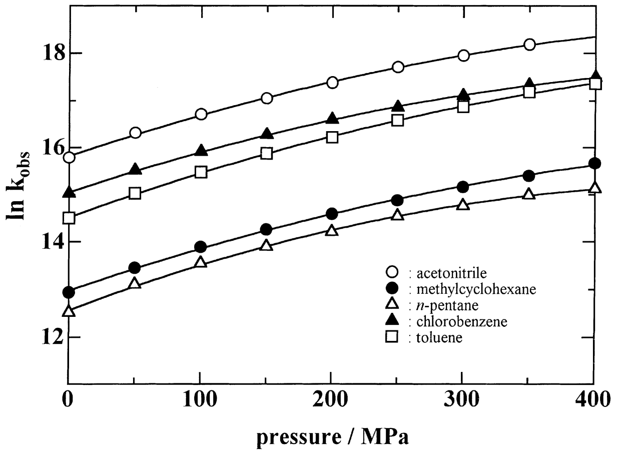
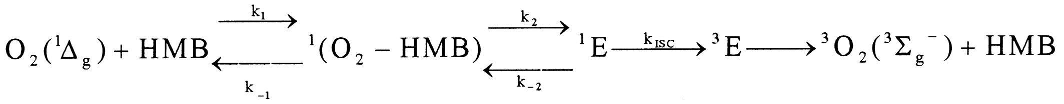


Fig. 2. Pressure dependence of k_{obs} in five solvents. The solid lines were drawn by assuming that ln k_{obs} = A + BP + CP^2.



$$O_2(^1\Delta_g) + HMB \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^1(O_2-HMB) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} {}^1E \xrightarrow{k_{ISC}} {}^3E \longrightarrow {}^3O_2(^3\Sigma_g^-) + HMB$$

Scheme 1.

where ^{1}(O$_2$-HMB) is an encounter complex, and ^1E and ^3E represent exciplexes with the singlet and triplet spin multiplicities, respectively. In Scheme 1, the rate determining step may be assumed for the step of k_{ISC} with the spin-forbidden rate. Thus, the pre-equilibrium condition is probably established since the experimentally observed rate constant, k_{obs}, is much smaller than the diffusion-controlled rate constant expected for the steps of k_1 and k_2. In the pre-equilibrium limit, k_{obs} is given by

$$k_{obs} = K_1 K_2 k_{ISC} \qquad (3)$$

where $K_1(=k_1/k_{-1})$ and $K_2(=k_2/k_{-2})$ are the equilibrium constants. From Eq. (3), the observed activation volume, $\Delta V^{\neq}_{obs}$, is given by

$$\Delta V^{\neq}_{obs} = \Delta V_1 + \Delta V_2 + \Delta V^{\neq}_{ISC} \qquad (4)$$

where ΔV_1 and ΔV_2 are the volume changes for K_1 and K_2, respectively, and $\Delta V^{\neq}_{ISC}$ is the activation volume for k_{ISC}. By analyzing the individual term in Eq. (4), the quenching mechanism is discussed below.

In general, when the polar intermediates and/or the polar transition states are involved in the reactions, the solvent effect on the reaction rate has been often interpreted by the dielectric model developed by Kirkwood [26]. As seen in Table 1, the values of k_{obs} at 0.1 MPa increases with the dielectric constant, ε, or with the solvent-polarity parameter defined by Kirkwood, $q(=(\varepsilon-1)/(2\varepsilon+1))$ [21–23,27–29], which are listed in Table 1, predicting clearly the dielectric model. When this model is applied for the equilibrium between the nonpolar encounter complex, (^{1}O$_2$-HMB), and the polar exciplex, ^1E, the solvent effect on the equilibrium constant, K_2, is expressed by

$$\ln K_2 = \ln K_2^0 + \frac{2N_A}{\pi\varepsilon_0 RT}\left(\frac{\mu_E^2}{d_E^3} - \frac{\mu_{en}^2}{d_{en}^3}\right)q \qquad (5)$$

where μ_E is the dipole moment of the exciplex with diameter d_E and μ_{en} the dipole moment of the encounter complex with diameter d_{en}, and K_2^0 refers to K_2 in a solvent $q = 0$. From Eqs. (3) and (5), the observed quenching constant, k_{obs} is given by

$$\ln k_{obs} = \ln k^0_{obs} + \frac{2N_A}{\pi\varepsilon_0 RT}\left(\frac{\mu_E^2}{d_E^3} - \frac{\mu_{en}^2}{d_{en}^3}\right)q \qquad (6)$$

where

$$k^0_{obs} = K_1 K_2^0 k_{ISC} \qquad (7)$$

When μ_i and d_i (i = E or en) are independent of pressure, the observed activation volume, $\Delta V^{\neq}_{obs}$, is expressed by

$$\Delta V^{\neq}_{obs} = \Delta V^{0\neq}_{obs} + \frac{2N_A}{\pi\varepsilon_0}\left(\frac{\mu_E^2}{d_E^3} - \frac{\mu_{en}^2}{d_{en}^3}\right)q_P \qquad (8)$$

where $q_P=(\partial q/\partial P)_T$. Generally, the contribution to the activation volume consists of the structural and solvation terms. $\Delta V^{0\neq}_{obs}$ in Eq. (8) is due to the former contribution, and given by

$$\Delta V^{0\neq}_{obs} = \Delta V_1 + \Delta V_2^0 + \Delta V^{\neq}_{ISC} \qquad (9)$$

Table 2

Activation volume for k_{obs}, and the volumetric parameters associated with the quenching by HMB of singlet oxygen in five solvents[a]

	$\Delta V^{\neq}_{obs}$	$\Delta V_1^{(HS)}$	$\Delta V^{\neq}_{CT}$	ΔV_{solv}	$\Delta V_2^0 + \Delta V^{\neq}_{ISC}$
Acetonitrile	−25.9 ± 0.7	−6.8 ± 0.3	−19.1 ± 1.0	−0.7 ± 0.1	−18.4 ± 1.1
Chlorobenzene	−24.7 ± 0.3	−5.8 ± 0.2	−18.9 ± 0.5	−2.6 ± 0.2	−16.3 ± 0.7
Toluene	−27.0 ± 0.5	−7.1 ± 0.3	−19.9 ± 0.8	−4.5 ± 0.3	−15.4 ± 1.1
Methylcyclohexane	−25.8 ± 0.7	−8.0 ± 0.3	−17.8 ± 1.0	−5.1 ± 0.3	−12.7 ± 1.3
n-Pentane	−29.7 ± 0.7	−11.5 ± 0.4	−18.2 ± 1.1	−7.2 ± 0.4	−11.0 ± 1.5

[a] cm^3/mol.

According to Eq. (8), the plot of $\Delta V^{\neq}_{\mathrm{obs}}$ against q_{P} should be linear with a negative slope if $\Delta V^{0\neq}_{\mathrm{obs}}$ is independent of the solvent, but the data listed in Tables 1 and 2 showed a bell-shaped curve.

The pressure dependence of the lifetime of singlet oxygen in simple liquid solution with no CT interaction has been successfully explained in terms of ΔV_1 alone, as estimated by the application of the hard-sphere theory [24,25]. In a hard-sphere solution, consisting of a hard-sphere oxygen molecule with diameter of d_{O} and a hard-sphere HMB molecule with diameter of d_{D} in a hard-sphere solvent molecule with diameter of d_{S}, the volume change, $\Delta V_1^{(\mathrm{HS})}$, for the encounter complex formation is given by [30]

$$\Delta V_1^{(\mathrm{HS})} = -RT\left[\frac{\partial \ln g(d_{\mathrm{OD}})}{\partial P}\right]_T - RT\kappa \qquad (10)$$

$$g(d_{\mathrm{OD}}) = \frac{1}{1-y} + \frac{3y}{2(1-y)^2}\left(\frac{d_{\mathrm{O}}d_{\mathrm{D}}}{d_{\mathrm{OD}}d_{\mathrm{S}}}\right) + \frac{y^2}{2(1-y)^3}\left(\frac{d_{\mathrm{O}}d_{D}}{d_{\mathrm{OD}}d_{\mathrm{S}}}\right)^2 \qquad (11)$$

where $g(d_{\mathrm{OD}})$ is the radial distribution function at the closest approach distance, $d_{\mathrm{OD}}(=(d_{\mathrm{O}} + d_{\mathrm{D}})/2)$, and κ the isothermal compressibility of the solvent. In Eq. (11), y is the packing fraction, given in terms of the molar volume of solvent, V_{S}, by

$$y = \frac{N_{\mathrm{A}}\pi d_{\mathrm{S}}^3}{6V_{\mathrm{S}}} \qquad (12)$$

The isothermal compressibility of the hard-sphere liquid, $\kappa^{(\mathrm{HS})}$, is expressed by [30]

$$\kappa^{(\mathrm{HS})} = \frac{V_{\mathrm{S}}(1-y)^4}{RT(1+4y+4y^2-4y^3+y^4)} \qquad (13)$$

The packing fraction, y, was estimated by equating $\kappa^{(\mathrm{HS})}$ to the observed isothermal compressibility, κ, for a given solvent (see Table 1) [25], and the diameters of the solvent molecules were evaluated by Eq. (12); the values of d_{S} were 0.402, 0.550, 0.548, 0.584 and 0.536 nm for acetonitrile, chlorobenzene, toluene, methylcyclohexane and *n*-pentane, respectively. The diameters d_{O} and d_{D} for the solute molecules were calculated to be 0.346 and 0.716 nm, respectively, according to the method of Bondi [31]. The values of $\Delta V_1^{(\mathrm{HS})}$ evaluated using these values are listed in Table 2.

From Eqs. (8) and (9), $\Delta V^{\neq}_{\mathrm{CT}}(= \Delta V^{\neq}_{\mathrm{obs}} - \Delta V_1^{(\mathrm{HS})})$ is expressed by

$$\Delta V^{\neq}_{\mathrm{CT}} = \Delta V^0_2 + \Delta V^{\neq}_{\mathrm{ISC}} + \Delta V_{\mathrm{solv}} \qquad (14)$$

where ΔV_{solv} is the volume change for solvation of the polar ^1E exciplex formation, given by

$$\Delta V_{\mathrm{solv}} = -\frac{2N_{\mathrm{A}}}{\pi\varepsilon_0}\left(\frac{\mu_{\mathrm{E}}^2}{d_{\mathrm{E}}^3} - \frac{\mu_{\mathrm{en}}^2}{d_{\mathrm{en}}^3}\right)q_{\mathrm{P}} \qquad (15)$$

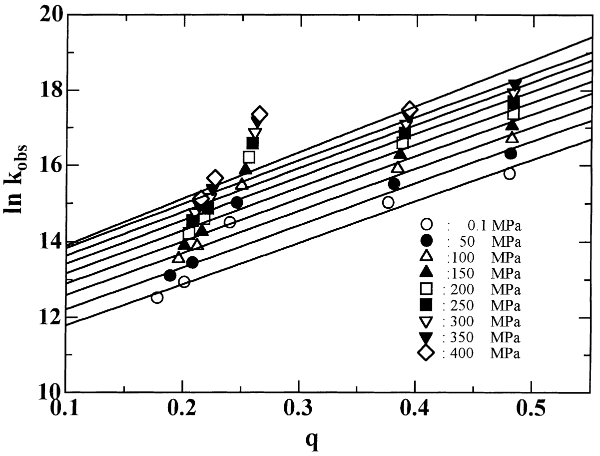


Fig. 3. Plots of $\ln k_{\mathrm{obs}}$ against q $(=(\varepsilon-1)/(2\varepsilon+1))$ at nine different pressures.

The values of $\Delta V^{\neq}_{\mathrm{CT}}$ are also listed in Table 2. Although the plot of $\Delta V^{\neq}_{\mathrm{CT}}$ against q_{P} should be linear with a negative slope according to Eqs. (14) and (15), the data in Tables 1 and 2 show that $\Delta V^{\neq}_{\mathrm{CT}}$ is nearly independent of q_{P}, implying the breakdown of the dielectric model. However, the plots of $\ln k_{\mathrm{obs}}$ against q (see Eq. (6)), which are shown in Fig. 3, are linear at a given pressure up to 400 MPa, except for the data on toluene. The deviation from the linear plots in toluene might be due to the CT interaction between singlet oxygen and the solvent as described previously [14]. Thus, the dielectric model may be still valid for the present system. The solvation term of the polar ^1E exciplex formation, ΔV_{solv}, were estimated by Eq. (15) from this slope in the plots of $\ln k_{\mathrm{obs}}$ against q (Fig. 3). The values of ΔV_{solv} are listed in Table 2, together with those of $\Delta V^0_2 + \Delta V^{\neq}_{\mathrm{ISC}}$ (see Eq. (14)). It is noted in Table 2 that $\Delta V^0_2 + \Delta V^{\neq}_{\mathrm{ISC}}$ decreases significantly, from −11 to −18 cm^3/mol, with increasing solvent polarity. This decrease in $\Delta V^0_2 + \Delta V^{\neq}_{\mathrm{ISC}}$ may be mainly attributed to the solvent-polarity dependence of $\Delta V^{\neq}_{\mathrm{ISC}}$ since ΔV^0_2, which is the structural term for the formation of ^1E (see Eq. (9)), is expected to be independent of the solvent.

The activation volume for the intersystem crossing, $\Delta V^{\neq}_{\mathrm{ISC}}$, is often assumed to be zero for the quenching of singlet oxygen by amines and aromatic solvent, being independent of solvent molecules [14,17,18]. However, the present results shows that $\Delta V^{\neq}_{\mathrm{ISC}}$ clearly depends on the solvent polarity. In the previous publication [16], we reported that the activation volume for the unimolecular decay constant of the exciplex for the fluorescence quenching of pyrene by *p*-dicyanobenzene decreases from zero (toluene) to −7 cm^3/mol (1,2-dichloroethane, $\varepsilon = 10.36$ at 0.1 MPa). The negative activation volume is not discussed, but is probably related to the increase in the contribution of ionic photodissociation of the exciplex with increasing solvent polarity [32]. In order to check the formation of ionic species in the present system, transient absorption spectra were measured in an aerated acetonitrile solution of HMB (18 mM), but no transients except for the absorption due to the triplet state of ACA were observed. By analogy with the pyrene/*p*-dicyanobenzene system, however, the solvent-polarity dependence of $\Delta V_2^0 + \Delta V_{\mathrm{ISC}}^{\neq}$ seems to suggest still the participation of photodissociation (rate constant, k_{C}) from ${}^1E$ as well as the intersystem crossing (rate constant, k_{ISC}^0) that is probably independent of pressure and solvent:

$${}^1\mathrm{E} \xrightarrow{k_{\mathrm{ISC}}^0} \mathrm{E} \rightarrow {}^3\mathrm{O}_2\left({}^3\sum\nolimits_g^-\right) + \mathrm{HMB}$$

$${}^1\mathrm{E} \xrightarrow{k_{\mathrm{C}}} \text{ion radical}$$

In this case, the observed k_{ISC} is rewritten as the sum of the rate constants, $k_{\mathrm{ISC}} = k_{\mathrm{C}} + k_{\mathrm{ISC}}^0$. Since the ion pair and/or free ion formation processes are generally accelerated by the application of pressure [33], the activation volume for the observed k_{ISC} is negative. One-electron transfer mechanism, in fact, has been postulated for many reactions between singlet oxygen and donors in solution [13].

An alternative explanation may be given by a CT-mediated coupling mechanism. Ogilby et al. [34,35] have found that the quenching constant by naphthalene of singlet oxygen is larger in acetonitrile than in cylohexane, and also found that the quenching constant by 1-methylnaphthalene with lower oxidation potential has larger value in acetonitrile, whereas it is almost constant in cyclohexane. They concluded that the enhanced quenching in acetonitrile occurs by the mixing of the (${}^3\mathrm{O}_2({}^3\sum_g^-)$-organic molecule) state with the (${}^1\mathrm{O}_2({}^1\Delta_{\mathrm{g}})$)-organic molecule) state which depends on the extent of CT character between them. The activation volume expected for this mechanism might be negative since the polar exciplex ${}^1E$ is stabilized further with increasing pressure.

As a result, in the argument presented above, it is important that two mechanisms of the observed k_{ISC} have the same trend for the pressure and the solvent polarity dependence. However, in nonpolar solvent, the contribution to the observed k_{ISC} of ionic photodissociation (k_{c}) is not significant, and also the mixing with the CT state that facilitates the intersystem crossing is not significant. Thus, the volume change, ΔV_2^0, for the structural term of ${}^1E$ formation from the encounter complex may be estimated to be ca. -11 cm^3/mol, since the rate constant for the intersystem crossing in nonpolar solvent is expected to be independent of pressure ($\Delta V_{\mathrm{ISC}}^{\neq} = 0$). Taking into account the value of -11 cm^3/mol for ΔV_2^0, the bond distance between ${}^1\mathrm{O}_2$ and HMB for ${}^1E$ can be estimated to be 0.25 nm by using the values of d_{O} (0.346 nm) and d_{D} (0.716 nm) according to the method by Bondi [31], and then the dipole moment of ${}^1E$ may be evaluated to be ca. 5*D* together with the slopes in the plots of ln k_{obs} against q (Fig. 3 and Eq. (6)). The dipole moment of ${}^1E$ in the present system is compared with the results for the amines systems studied by Brauer et al. [18].

It is worth summarizing the difference in the pressure dependence of the quenching between amines (σ-donors) [17,18] and HMB (π-donor) as quenchers, although the reasons are still unresolved. For the quenching by amines of singlet oxygen, the mechanism is also expressed by Scheme 1, and the solvent-polarity dependence of $\Delta V_{\mathrm{CT}}^{\neq}$ is satisfactorily described by Eqs. (14) and (15); the plot of $\Delta V_{\mathrm{CT}}^{\neq}$ against q_{P} is linear, and the intercept gives $\Delta V_2^0 + \Delta V_{\mathrm{ISC}}^{\neq}$. The values of ΔV_2^0 estimated by assuming that $\Delta V_{\mathrm{ISC}}^{\neq} = 0$ varies in the range from -2.2 to -12.4 cm^3/mol, depending on amines. In sharp contrast to the amines system, $\Delta V_{\mathrm{ISC}}^{\neq}$ for the quenching by HMB in the present study (Table 2) decreased significantly with increasing the solvent polarity, leading to $\Delta V_{\mathrm{CT}}^{\neq}$ that is almost independent of q_{P}. Finally, the value of ΔV_2^0 (~ -11 cm^3/mol) estimated in the present work is comparable to that for the quenching by piperazine (-12.4 cm^3/mol) for which the dipole moment of ^{1}E is evaluated to be 5.7 D [18].

Acknowledgements

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