Lifetime of Singlet Oxygen ($^1\Delta_g$) in Liquid and Supercritical Carbon Dioxide

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The lifetime of singlet oxygen, $^1O_2$ ($^1\Delta_g$), in liquid and supercritical carbon dioxide (SCF CO_2) was determined by a time-resolved phosphorescence method. In both the systems, the lifetime decreased significantly with increasing pressure. The pressure dependence of the lifetime in SCF CO_2 was satisfactorily interpreted by the quenching mechanism in liquid phase that involves solvent cage.

Singlet oxygen, $^1O_2$ ($^1\Delta_g$), the lowest electronically excited singlet state, is quenched by the solvent molecules. The lifetime depends strongly on the nature and structure of the solvent molecule, and varies in the time range from microseconds to milliseconds.[1–5] It has been established that the radiationless deactivation process occurs by the collisional energy transfer from $^1O_2$ to the vibrational levels of the solvent molecules.[4–7] We found that the lifetime of $^1O_2$ in liquid solvents decreases significantly by the application of high pressure,[8] and interpreted in terms of the radial distribution function with hard sphere assumption at the closest approach distance between the solvent and solute molecules. Similar interpretation of the pressure dependence of the lifetime was also made by other workers.[9] Supercritical fluid (SCF), which can dissolve many substances, is an interesting solvent because the physical properties change dramatically with a small change of temperature or pressure. In the present work, we measured the lifetime of singlet oxygen in supercritical carbon dioxide (SCF CO_2) as well as in liquid CO_2 in order to obtain further insight into the quenching mechanism by the solvent molecules and also to characterize SCF CO_2 by using $^1O_2$ as a probe.

The phosphorescence decay curves of singlet oxygen at 1270 nm were measured as a function of pressure by a similar method described previously.[10,11] Phosphorescence generated by excitation of 9-acetylanthracene using an 8-ns pulse from a nitrogen laser (337.1 nm) was monitored by an InGaAs sensor (1 mm ϕ, Hamamatsu G5832-01) operated at room temperature, and the signal was accumulated 256 times and averaged on a Hewlett Packard 54510A digitizing oscilloscope.

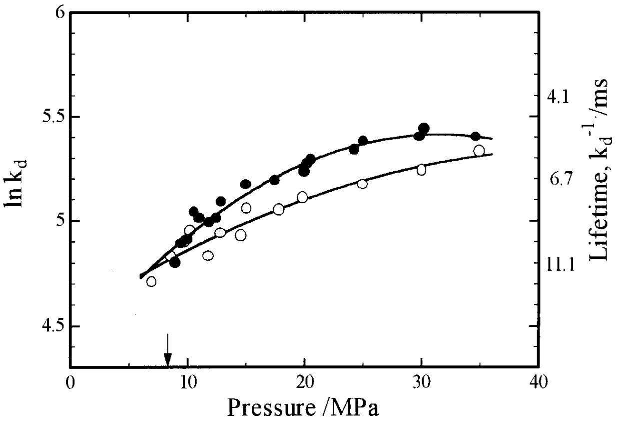

Figure 1. Plots of ln k_d against pressure in liquid CO_2 at 25 °C (○) and SCF CO_2 at 35 °C (●). The solid lines were drawn by assuming that ln $k_d = A + BP + CP^2$. The arrow indicates the pressure corresponding to the critical density at 35 °C.

The intensity of phosphorescence of singlet oxygen in liquid and SCF CO_2 was very weak, but the decay curves obtained were analyzed satisfactorily by a single exponential function in all the experimental conditions examined. Figure 1 shows the plots of logarithm of the decay constant, k_d, against pressure in liquid CO_2 at 25 °C and SCF CO_2 at 35 °C. The difference of the pressure dependence of k_d between liquid and SCF CO_2 was clearly observed although the data were slightly scattered. The lifetime, k_d^{-1}, changes by about two times on going from 7.0 and 35 MPa in both the systems, indicating that the pressure dependence of k_d^{-1} is significantly larger than that in liquid organic solvents such as *n*-alkanes (C_5 to C_8 and C_{12}) [11] in which k_d^{-1} changes about two times on going from 0.1 to 400 MPa. Since the rate constant for the radiative process is assumed to be very small compared to k_d,[6,7] the bimolecular quenching constant, k_D, was determined by

$$k_D = k_d/[S] \qquad (1)$$

where [S] is the molar concentration of the solvent. The pressure dependence of k_D is shown in Figure 2. The activation

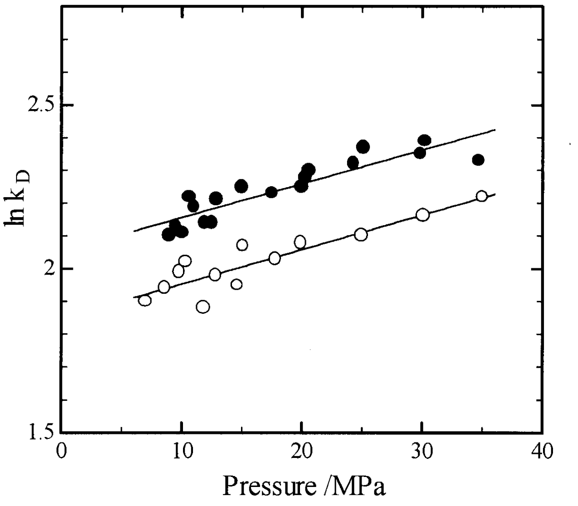

Figure 2. Plots of ln k_D against pressure in liquid CO_2 at 25 °C (○) and SCF CO_2 at 35 °C (●). The solid lines were drawn by assuming that ln $k_D = A + BP$.

volume for k_D, $\Delta V_D^{\ddagger}$, was determined by eq 2 where κ is the isothermal compressibility of the solvent.

$$RT(\partial \ln k_D/\partial P)_T = -\Delta V_D^{\neq} - RT\kappa \qquad (2)$$

The results are listed in Table 1, together with those in *n*-hexane for comparison.[11] The values of $\Delta V_D^{\ddagger}$ are significantly larger in liquid CO_2 as well as in SCF CO_2, compared with those in liquid organic solvents.[8–11]

Table 1. Activation volumes and the isothermal compressibility, κ_{obs}, of liquid CO_2 at 25 °C and SCF CO_2 at 35 °C.

	RTκ	$\Delta V_D^{\neq}$	$\Delta V^{\neq(HS)}$
liquid CO_2[a]	140±15	-170±20	-190±20
SCF CO_2[b]	340±70	-360±80	-360±60
n-hexane[c]	3.4	-9.8	-8.6

[a]Values at 7.0 MPa at 25 °C. [b]Values at 9.0 MPa at 35 °C. [c]Reference 11.

In liquid solution, the collisional decay processes of $^1O_2$ have been described kinetically by assuming an encounter complex, $^1(O_2–S)_{en}$ with singlet spin multiplicity where the intersystem crossing (rate constant, k_{ISC}) occurs in the solvent cage.[9–11]

$$^1O_2(^1\Delta_g) + S \underset{k_{-diff}}{\overset{k_{diff}}{\rightleftarrows}} {}^1(O_2 - S)_{en} \xrightarrow{k_{ISC}} {}^3O_2(^3\Sigma_g^-) + S \qquad (3)$$

Based on eq 3, the observed rate constant, k_D, is given by

$$k_D = k_{ISC}(k_{diff}/k_{-diff}) \qquad (4)$$

Since $k_{diff}/k_{–diff}$ is proportional to the radial distribution function, $g(r_{OS})$, at the closest approach distance, r_{OS}, which is the sum of the radius of the solute (r_O) and solvent (r_S) molecules with hard spheres,[12] the pressure dependence of k_D is equal to that of $g(r_{OS})$ when k_{ISC} is independent of pressure. In liquid organic solvents, the activation volume for k_{ISC}, $\Delta V_{ISC}^{\ddagger}$, is approximately zero.[8–11]

The value of $g(r_{OS})$ was calculated by using r_O (0.173 nm)[13] and r_S (0.200 nm)[13], together with the density data of liquid CO_2 and SCF CO_2,[14–17] and the activation volume for $g(r_{OS})$, $\Delta V^{\ddagger(HS)}$, was evaluated. The results are listed in Table 1, together with those in *n*-hexane.[11] One can see in Table 1 that $\Delta V_D^{\ddagger}$ is nearly equal to $\Delta V^{\ddagger(HS)}$ in *n*-hexane as described previously.[11,18] One can also find that $\Delta V_D^{\ddagger}$ is approximately equal to $\Delta V^{\ddagger(HS)}$ in SCF CO_2 as well as in liquid CO_2, indicating that k_{ISC} is independent of pressure, that is, $\Delta V_{ISC}^{\ddagger}$ ~0, in both the systems. In liquid CO_2, the increase in k_D can be understood as a result of the increase in $k_{diff}/k_{–diff}$ due to the decrease in the excluded volume with increasing pressure as described previously.[8–11] The result in SCF CO_2 also can be interpreted in the same frame work as the quenching in liquid phase, indicating the existence of the solvent cage. The interpretation by the radial distribution function mentioned above is consistent with that by the isolated binary collision model (IBC model).[19–21]

Finally, very fast bimolecular reactions with a nearly diffusion rate have been examined in SCF and the contribution of the clustering of the solutes to the reactions at the near critical density has been discussed.[22] In order to obtain further insight into the quenching of $^1O_2$ by the solvent molecules, the lifetime measurements in other SCF are needed.

References

1 F. Wilkinson and J. B. Brumer, *J. Phys. Chem., Ref. Data*, **10**, 809 (1981).
2 A. A. Gorman, *Adv. Photochem.*, **17**, 217 (1992).
3 A. A. Gorman and M. A. J. Rodgers, *J. Photochem. Photobiol., B, Biol.*, **14**, 159 (1992).
4 J. B. Hurst and G. B. Schuster, *J. Am. Chem. Soc.*, **105**, 5756 (1983).
5 M. A. J. Rodgers, *J. Am. Chem. Soc.*, **105**, 6201 (1983).
6 R. Schmidt and H.-D. Brauer, *J. Am. Chem. Soc.*, **109**, 6976 (1987).
7 R. Schmidt, *J. Am. Chem. Soc.*, **111**, 6983 (1989).
8 M. Okamoto, F. Tanaka and H. Teranishi, *J. Phys. Chem.*, **94**, 669 (1990).
9 R. Schmidt, K. Seikel, and H-D. Brauer, *Ber. Bunsen-Ges. Phys. Chem.*, **94**, 1100 (1990).
10 M. Okamoto and F. Tanaka, *J. Phys. Chem.*, **97**, 177 (1993).
11 M. Okamoto and F. Tanaka, submitted for the publication to *Phys. Chem. Chem. Phys.*
12 Y. Yoshimura and M. Nakahara, *J. Chem. Phys.*, **81**, 4080 (1984).
13 A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
14 W. Herreman, W. Grevendonk, and A. De Bock, *J. Chem. Phys.*, **53**, 19 (1970).
15 H. Iwasaki and M. Takahashi, *J. Chem. Phys.*, **74**, 1930 (1981).
16 D. E. Diller and M. J. Ball, *Inter. J. Thermophys.*, **6**, 619 (1985).
17 P. S. van der Gulik, R. Mostert, and H. R. van den Berg, *High-Temp. High-Press.*, **23**, 87 (1991).
18 For the lifetimes in liquid organic solvents including *n*-hexane at high pressure, see also References 8–10.
19 T. A. Litovitz, *J. Chem. Phys.*, **26**, 469 (1957).
20 D. Schwarzer, J. Troe, M. Votsmeier, and M. Zerezke, *J. Chem. Phys.*, **105**, 3121 (1996).
21 T. Yamaguchi, Y. Kimura, and N. Hirota, *J. Chem. Phys.*, **111**, 4169 (1999).
22 As a review article: O. Kajimoto, *Chem. Rev.*, **99**, 355 (1999).