Lifetime of Singlet Oxygen and Quenching by NaN_3 in Mixed Solvents

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Singlet oxygen was generated by the photosensitization of erythrosine. The lifetime of singlet oxygen and the quenching rate constant for singlet oxygen by NaN_3 were measured by a thermal lensing method in MeOH–H_2O mixed solvents. The reciprocal of the lifetime increased linearly with the increase of the H_2O mole fraction. Semi-log plot of the quenching constant against the reciprocal of the solvent polarity exhibited a linear relation. The quenching of the singlet oxygen by NaN_3 may proceed through a partial charge-transfer intermediate. The activation energy for the quenching reaction of $N_3^- + {}^1O_2 \rightarrow [N_3 \cdots {}^1O_2^-]$ increased with the increase of the solvent polarity. The lifetime was also measured in MeOH-ethyleneglycol mixed solvents, and its relation with viscosity was obtained.

Introduction

Singlet oxygen takes part in various chemical and biological photooxidation reactions; *e.g.*, photodynamic action [1], carcinogenesis [2] and photomedical treatment [3]. The lifetime of singlet oxygen is an important factor to clarify the reaction mechanism of the photooxidation, and it has been studied by many workers (Long *et al.* [4]; Young *et al.* [5]; Linding and Rodgers [6]) with laser flash photolysis. However, the lifetime was indirectly estimated. Recently, Fuke *et al.* [7, 8] developed a thermal lensing technique for the direct measurement of the lifetime by detecting the heat generated in the non-radiative deactivation process of singlet oxygen.

In the present investigation, we measured the lifetime of singlet oxygen and the quenching rate constant by NaN_3 in MeOH–H_2O mixed solvents by the thermal lensing method, and the effects of solvent polarity and viscosity on them were investigated. The temperature dependence of the quenching rate constant was also examined.

Materials and Methods

Ery (Wako-junyaku Co.), MeOH, NaN_3, EG and distilled water (Nakarai Chemicals LTD.) were guaranteed or of special grade for analytical use. The dielectric constant of MeOH–H_2O mixed solvents was obtained from the data in ref. 9. Singlet oxygen was generated by the Ery-photosensitization in O_2-bubbled MeOH–H_2O mixed solvents. The sample was maintained at the constant temperature within ± 0.5 °C by water-refluxing from a water bath.

The deactivation of singlet oxygen was measured with a thermal lensing apparatus consisting of an exciting pulse laser (Molectron UV-12 and DL-14), a monitoring He–Ne laser and a detecting system. The detailed description about the apparatus was made in the previous paper [8]. The thermal lensing signals through a photomultiplier were recorded on a Tektronix 465 osilloscope. The dye in the exciting pulse laser (a nitrogen laser pumped dye laser) was C-485 (Exciton Chemical Company, Inc.).

Results and Discussion

Singlet oxygen was generated by Ery-photosensitization. The singlet energy is mainly converted into heat through the non-radiative deactivation from the singlet to the ground state, resulting in the elevation of the local temperature around the oxygen molecule (formation of a thermal lens). The quantum yield for the emission from singlet oxygen is very small ($\sim 10^{-8}$). The temperature rise leads to a change in the refractive index. This enables us to study the lifetime of singlet oxygen in solution by the thermal lensing technique. The effect of thermal diffusion ($\sim$10 ms) can be neglected, since the lifetime of singlet oxygen about 2–20 μs. The signal intensity [S(t)] of thermal lensing at the time t after the laser pulse passed through the sample is

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Abbreviations: Ery, erythrosine; EG, ethyleneglycol.

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represented approximately by the following equation.

$$S(t) = -\sum_i C_i[1-\exp(-k_i t)], \quad (1)$$

where k_i is the rate constant of each decay process i and C_i the time-independent constant. Assuming $C_i = C$ and $k_i = k$,

$$\Delta S = S(m) - S(t) = C\exp(-kt), \quad (2)$$

where S(m) is the signal intensity when the thermal lens becomes a maximum (complete decay of singlet oxygens). Eq. (2) is simplified as follows.

$$\ln \Delta S = \ln NC - kt, \quad (3)$$

where N is the number of singlet oxygen concerned with the lens. The semi-log plot of ΔS against t gives a stright line, and we can obtain the k value from the slope of the curve. k is expressed as follows,

$$k = \begin{cases} k_d \text{ in the absence of quencher Q,} & (4) \\ k_q[Q] + k_d \text{ in the presence of Q,} & (5) \end{cases}$$

where k_q and k_d are the quenching and physical decay (reciprocal of the lifetime) rate constants, respectively.

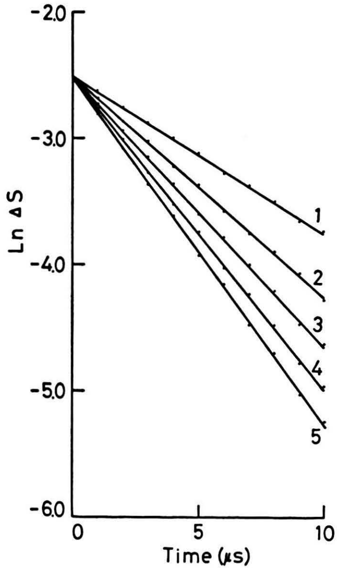

Fig. 1. Decay of ΔS at various mole fractions of H_2O in MeOH–H_2O mixed solvents. Mole fractions of H_2O in Curves 1, 2, 3, 4 and 5, 0, 0.20, 0.35, 0.50, 0.60, respectively; concentration of Ery, $3.6 \cdot 10^{-5}$ M; temperature, 30 °C; excitation, 520 nm dye laser light. As for ΔS see text.

Fig. 1 shows the decay of ΔS at various mole fractions of H_2O in MeOH–H_2O mixed solvents. The $\ln \Delta S$ was linear against the time as expected from eq. (3). The slope of the curve gives the $k(=k_d)$ value (eq. (4)).

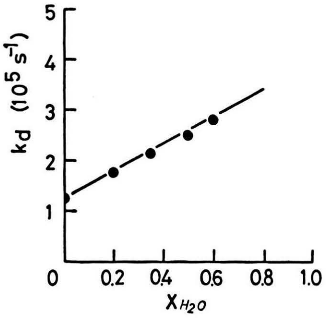

Fig. 2. Physical decay rate constant (k_d) of singlet oxygen in MeOH–H_2O mixed solvents. k_d = reciprocal of lifetime (τ^1O_2) of singlet oxygen; X_{H_2O}, mole fraction of H_2O; concentration of Ery, $3.6 \cdot 10^{-5}$ M; temperature, 30 °C; excitation, 520 nm dye laser light.

The k_d value obtained is plotted against the mole fraction of H_2O in Fig. 2. Merkel and Kearns [10] obtained the lifetime (τ^1O_2) of singlet oxygen in a solvent from the optical densities at 7880 (OD_{7880}) and 6280 cm^{-1} (OD_{6280}) (0–0 and 0-1 components in the $^1O_2(^1\Delta)$–$^3O_2(^3\Sigma)$ transition), using the following relation.

$$\tau^1O_2^{-1}\,(\mu s^{-1}) = k_d \times 10^{-6} \simeq 0.5\,(OD_{7880}) + 0.05\,(OD_{6280}) + \text{higher terms} \quad (6)$$
$$\equiv D$$

Usui *et al.* [11] assumed that the physical decay rate constant $k_d(1,2)$ of singlet oxygen in mixed solvents was expressed as follows;

$$k_d(1,2) \times 10^{-6} \simeq X_1 D_1 + X_2 D_2, \quad (7)$$

where D_1 and D_2 are the D values in eq. (6) in solvents 1 and 2, respectively. X_1 and X_2 are the mole fractions of solvents 1 and 2, respectively. As shown in Fig. 2, the k_d value in MeOH–H_2O mixed solvents was linear against the mole fraction of H_2O obeying eq. (7). The lifetime ($1/k_d$) was about 8 μs in MeOH from the intercept of the curve with the ordinate. The signal intensity in low MeOH concentration range ($X_{MeOH} < 40\%$) was too weak to measure the lifetime. The lifetime in H_2O was determined to be 2.5 μs by extrapolating the curve. A linear relation between the reciprocal of the lifetime and the mole fraction of solvents was also observed in MeOH–D_2O mixed solvents. The lifetime increased by the deuterium effect, and it was determined to be about 20 μs in D_2O.

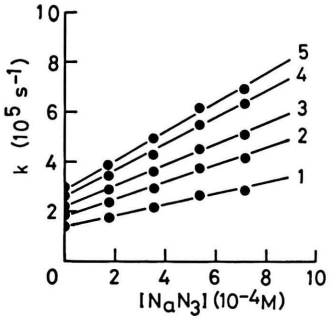

Fig. 3. Decay rate constant (k) of singlet oxygen as a function of NaN_3 concentration in MeOH–H_2O mixed solvents. Concentration of Ery, $3.6 \cdot 10^{-5}$ M; contents (v/v %) of MeOH for Curves 1, 2, 3, 4 and 5, 100, 90, 80, 70 and 60, respectively; temperature, 30 °C; excitation, 520 nm dye laser light.

Fig. 3 shows the decay rate constant (k; eq. (5)) of singlet oxygen as a function of NaN_3 concentration in MeOH–H_2O mixed solvents. All the curves were linear at any mixing fraction of solvents. The slope of the curve increased with the decrease of the MeOH content. The slope gives the quenching rate constant (k_q) for singlet oxygen by NaN_3. The plot of $\log k_q$ against the reciprocal of the solvent polarity (dielectric constant, ε) gave a linear curve (Curve 1) as shown in Fig. 4. The plot of $\log k_d$ gave

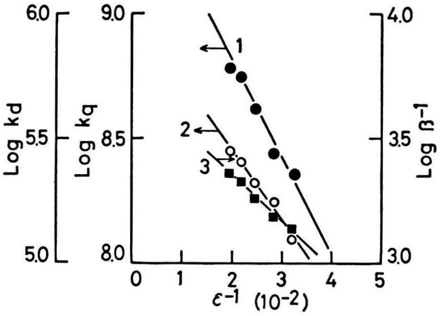

Fig. 4. Semi-log plots of k_q, k_d and β^{-1} against the reciprocal of polarity (ε) of MeOH–H_2O mixed solvents. k_q, obtained from the slope of curves in Fig. 3, k_d, obtained from Fig. 2; $\beta = k_q \cdot k_d$; ε, obtained from the data in ref. 9; Curves 1, 2 and 3, $\log k_q$, $\log k_d$ and $\log \beta^{-1}$, respectively.

also a straight line (Curve 2) in the polarity range investigated. The k_d value can not be determined with good precision by the kinetic analysis, but β defined by $\beta^{-1} = k_q/k_d$ is satisfactorily determined. For this reason, β was frequently used in photochemistry so far. The plot (Curve 3) of $\log \beta^{-1}$ *vs.* ε^{-1} exhibited a linear curve.

Young *et al.* [5] obtained a linear relation between $\log (1/\beta)$ and $1/\varepsilon$ for the photooxidation of 2,5-diphenylfuran in MeOH–H_2O mixed solvents ($1/\beta = k_q \cdot \tau^1O_2$). Gupta and Rohatgi-Mukherjee [12] also obtained the same relation for the photooxidation of I^- in MeOH–H_2O mixed solutions, and proposed a charge-transfer intermediate for the quenching for singlet oxygen by iodide ion. Cohen *et al.* [13] have obtained a linear relation between the log of the quenching rate constant (k_q) for triplet benzophenone or fluorenone by amines and $1/\varepsilon$. They proposed the following relation between log k_q and $1/\varepsilon$;

$$\log k_q = \Delta G_{ET} = IP(D_o) - E(Ac^-/Ac) - {}^3E(Ac) - e_o{}^2/\varepsilon a, \qquad (8)$$

where ΔG_{ET}, $IP(D_o)$, $E(Ac^-/Ac)$, ${}^3E(Ac)$, e_o, ε and a are free energy change, ionization potential of amines (donor, D_o), oxidation-reduction potential of electron acceptor (Ac), triplet energy of acceptor, electron charge, solvent dielectric constant (polarity) and encounter distance, respectively. We [14] have obtained a linear relation between $\log k_q$ and the ionization potential of various amines, and suggested that the quenching of singlet oxygen by amines might proceed through a partial charge-transfer intermediate between singlet oxygen and amines such as $[\text{Amine}^+ \cdots {}^1O_2^-]$. The linear relation (Curve 1) in Fig. 4 also suggests the involvement of the above intermediate in the quenching process. The slope of Curve 1 gives the value of $e_o{}^2/a$ in eq. (8).

Young *et al.* [5] and Gupta *et al.* [12] determined the slope of the curve of $\log \beta^{-1}$ *vs.* ε^{-1} in MeOH–H_2O mixed solvents. The values are given in Table I with ours. The quenching rate (β^{-1}) of I^- is the largest among three quenchers, and the quenching

Table I. Slope of the curve of $\log (1/\beta)$ *vs.* $1/\varepsilon$.

Quencher/Solvent	Slope	Ref.
2,5-diphenylfuran/MeOH–H_2O	42.6	[5]
I^-/MeOH–H_2O	77.9	[12]
NaN_3/MeOH–H_2O	19.2	

reaction for singlet oxygen by I^- is very sensitive to the solvent polarity.

Assuming that k_q is the rate constant for the reaction: $N_3^- + {}^1O_2 \rightarrow [N_3 \cdots {}^1O_2^-]$, the activation energy for the reaction was obtained from the temperature dependence of k_q (Fig. 5). The obtained activation energy was small, 1.72 (Curve 1, MeOH) and 4.92 kcal/mol (Curve 2, 60% MeOH–H_2O). The polarity (ε) is 30.7 in MeOH and 52.5 in 60% MeOH aqueous solution. The activation energy was larger in higher solvent polarity. Long and Kearns [4] obtained about 1 kcal/mol as the activation energy of quenching reaction for singlet oxygen (1,3-diphenylisobenzofuran in $CHCl_3$), and Koch [15] 3.5 kcal/mol (2,5-diphenylfuran in toluene).

The effect of viscosity on the lifetime ($\tau {}^1O_2$) of singlet oxygen and k_q was examined in MeOH–EG mixed solvents. The results obtained are shown in Table II; $\tau {}^1O_2$ increased with the increase of the solvent viscosity. This may be due to the inhibition for the collision deactivation of singlet oxygen in highly viscous solvents; k_q also increased with the increase of the solvent viscosity. Usually, the increase of the solvent viscosity results in a diminution of k_q. Some unknown factor such as interaction between quencher (or singlet oxygen) and EG might play an important role for the quenching mechanism. At present, the data is too short to explain the viscosity effect of k_q. The dielectric constant of MeOH–EG mixed solvents is much lower than that of water and does not undergo a large change by the mixing ratio of solvents ($\varepsilon_{MeOH} = 32.6$; $\varepsilon_{EG} = 37.7$). Young *et al.* [5] reported that the quenching rate (β^{-1}) for singlet oxygen by 2,5-diphenylfuran increased with increasing the viscosity of solvents (MeOH–EG).

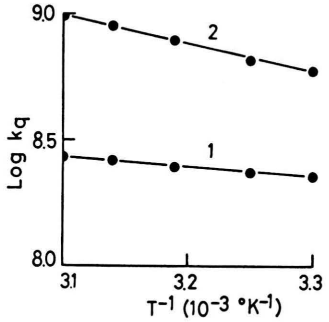

Fig. 5. Temperature dependence of the quenching rate constant (k_q) for singlet oxygen by NaN_3 in MeOH–H_2O solvents. Concentration of Ery, $3.6 \cdot 10^{-5}$ M; Curves 1 and 2, 100 and 60% (v/v) MeOH, respectively; temperature, 30 °C; excitation, 520 nm dye laser light.

Table II. Effects of solvent viscosity on lifetime ($\tau {}^1O_2$) of singlet oxygen and quenching rate constant (k_q) for singlet oxygen by NaN_3.

Solvent MeOH–EG (EG v/v %)	Viscosity (cp)	$\tau {}^1O_2$ (μs)	k_q (10^8/M · s)
0	0.54	8.00	2.32
10	0.73	8.30	2.50
20	1.05	8.63	2.97
30	1.45	9.13	3.83
40	1.90	9.70	4.92
50	2.42	10.42	6.87

Viscosity, calculated from the data of ref. 5.

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