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Thermal Lensing Study of Singlet Oxygen Reactions

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Abstract: A time-resolved thermal lensing technique has been used to determine the lifetimes of singlet oxygen ($^1\Delta_g$) in the various solvents produced by energy transfer from several sensitizers, and also to study a photosensitized oxygenation of several singlet oxygen acceptors. In order to determine rate constants from the observed signals, we carried out in detail an analysis of the thermal lensing signal. It was shown that this technique can directly follow the concentration of singlet oxygen in solution. The absolute rate constants for reaction of singlet oxygen with several acceptors were determined. The rate constant of $^1O_2$ with β-carotene in Freon 113 was found to be 9.5×10^9 M^{-1} s^{-1}. The technique was also shown useful for determination of reaction enthalpies of photooxygenation in the time-resolved manner. The enthalpy change of reaction of 1,3-diphenylisobenzofuran with $^1O_2$ was determined to be 35 kcal/mol in methanol.

I. Introduction

The thermal lensing technique is well known to be extremely sensitive and allows one to measure exceptionally weak absorption spectra.[2] The technique has been extensively used to study vibrational overtone spectroscopy[3] and two-photon spectroscopy.[4] It has also been used in the study of analytical chemistry.[5] The thermal lensing technique was also shown to applicable to measurement of the lifetime of a nonemitting metastable excited species.[6-9] An observation of the buildup time of the thermal lens gave us information for the rate of thermal energy deposition into the sample and thus for the excited-state lifetime. Furthermore, since the thermal lensing measurement is essentially a calorimetric determination of the very small temperature gradient induced by relaxation of excited species, this technique may provide us information on the enthalpy change for photochemical reactions. Although the technique has these advantages, an application to the photochemical reaction in solution is rare.[8,9]

Reactions of singlet oxygen, $^1O_2$ ($^1\Delta_2$), have been extensively studied because of its importance in photochemical and photobiological processes,[10-12] in most of which the presence and role of $^1O_2$ in the photochemical reaction are deduced from chemical products, scavenger trapping, and/or other secondary evidence.[12] Recently Krasnovsky[13] and Khan and Kasha[14] demonstrated the possibility of the direct observation of $^1O_2$ infrared emission at 1268 nm ($^1\Delta_g \rightarrow {}^3\Sigma_g^-$) by sensitizing dye in solution. Indeed, the observation of $^1O_2$ emission is the most direct method to indicate its involvement in various photooxidation reactions. However, since the quantum yield of $^1O_2$ emission is very small, and since a sensitive and fast-responding detector is not easily available at that wavelength range, their studies were almost limited to steady-state experiments.

An alternative way to detect $^1O_2$ may be the observation of its nonradiative transition to the ground state by using the thermal lensing technique. In the thermal lensing experiment, one observes only a nonspecific refractive index change in the sample, and, therefore, it is not so direct a method as the emission measurement. However, the following advantages are expected in the application of this technique to the dye-sensitized photooxidation reaction. First, $^1O_2$ can be directly detected by the thermal lensing technique with high sensitivity. Secondly, this technique may be applicable to the kinetic study of $^1O_2$ in solution in as short a time as a few hundred nanoseconds. Furthermore, the technique may provide us information on reaction enthalpy changes in the photooxygenation of $^1O_2$ acceptors.

In the present work, we demonstrated the observation of $^1O_2$ sensitized by dyes in solution by using the thermal lensing technique. To verify the general utility of the technique, we examined the quenching rate constants and reaction enthalpies for the photooxidation reactions of several $^1O_2$ acceptors. The results of these studies are reported in this paper.

II. Determination of Rate Parameters

Analysis of the thermal lensing signal produced by a pulsed laser excitation has been reported by several research groups. The lensing signal due to a short-lived excited species has been analyzed by Twarowski and Kliger,[4] while, Flynn and his co-workers[6] and Friedrich and Klem[7] have reported the analyses for the decay of metastable excited species. The analysis described by Flynn et al. is mainly concerned with the density change of the gas-phase sample created by relaxation of vibrationally excited species decaying with a rate comparable to an acoustic transient time ($\tau_a = w_p/v_s$; w_p is the beam radius of excitation laser and v_s is the velocity of sound). However, under fairly tight focusing conditions, the acoustic transit time in solution was found to be less than 100 ns in the present experimental setup. Thus, the acoustic effect discussed by them may reasonably be neglected for the analysis of the lensing signal created by a rather long-lived excited species such as $^1O_2$; the lifetime of $^1O_2$ is in the range of a few microseconds to a few milliseconds in various organic solvents. In this time domain, thermal conduction plays an important role as discussed by Friedrich and Klem.[7] Therefore, we extended the analysis predicted by the latter authors to the determination of the rate of the thermal transient observed in an irradiated dye solution. We shall follow closely the analyses and notations used by previous workers.[4,7]

To analyze a thermal lensing signal produced by irradiation of dye solution, it is necessary to consider the following set of reactions:

$$D_0 \xrightarrow{h\nu} {}^1D^* \quad (1)$$

$$^1D^* \rightarrow D_0 + h\nu_f \quad (2)$$

$$^1D^* \rightarrow D_0 \quad (3)$$

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[1] (a) Keio University, since April 1981. (b) Kanazawa University.

[2] (a) Whinnery, J. R. *Acc. Chem. Res.*, **1974**, *7*, 225. (b) Kliger, D. S. *Ibid.* **1980**, *13*, 129.

[3] (a) Swofford, R. L.; Long, M. E.; Albrecht, A. C. *Science* **1976**, 191. (b) Albrecht, A. C. In "Advances in Laser Chemistry"; Zewail, A. H., Ed.; Springer-Verlag: Berlin, 1978; p 235.

[4] (a) Twarowski, A. J.; Kliger, D. S. *Chem. Phys.*, **1977**, *20*, 253. (b) Twarowski, A. J.; Kliger, D. S. *Ibid.* **1977**, *20*, 259.

[5] Dovichi, N. D.; Harris, J. M. *Anal. Chem.* **1979**, *51*, 728.

[6] (a) Grabiner, F. R.; Siebert, D. S.; Flynn, G. W. *Chem. Phys. Lett.* **1972**, *17*, 189. (b) Siebert, D. R.; Grabiner, F. R.; Flynn, G. W. *J. Chem. Phys.* **1974**, *60*, 1564.

[7] Friedrich, D. M.; Klem, S. A. *Chem. Phys.* **1979**, *41*, 153.

[8] Daree, K. *Opt. Commun.* **1971**, *4*, 238.

[9] (a) Fuke, K.; Sakamoto, S.; Ueda, M.; Itoh, M. *Chem. Phys. Lett.* **1980**, *74*, 546. (b) Fuke, K.; Ueda, M.; Itoh, M. *Ibid.* **1980**, *76*, 372. (c) Fuke, K.; Hasegawa, A.; Ueda, M.; Itoh, M. *Ibid.* **1981**, *84*, 176.

[10] Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395, and references cited therein.

[11] Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104.

[12] Wasserman, H. H.; Murray, R. W. "Singlet Oxygen"; Academic Press: New York, 1979.

[13] (a) Krasnovsky, A. A., Jr. *Photochem. Photobiol.* **1979**, *29*, 29. (b) Krasnovsky, A. A., Jr. *Chem. Phys. Lett.* **1981**, *81*, 443.

[14] (a) Kahn, A. U. *Chem. Phys. Lett.* **1980**, *72*, 112. (b) Kahn, A. U.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6047.

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$$^1D^* \rightarrow {}^3D^*;\quad \phi_{st} \tag{4}$$

$$^3D^* + {}^3O_2 \rightarrow D_0 + {}^3O_2 \tag{5}$$

$$^3D^* \rightarrow D_0 \tag{6}$$

$$^3D^* + {}^3O_2 \rightarrow D_0 + {}^1O_2;\quad \phi_{et} \tag{7}$$

$$^1O_2 \xrightarrow{k_d} {}^3O_2;\quad \phi_d \tag{8}$$

$$^1O_2 + A \xrightarrow{k_A} AO_2;\quad \phi_A \tag{9}$$

$$^1O_2 + A \xrightarrow{k_{A'}} {}^3O_2 + A;\quad \phi_{A'} \tag{10}$$

The energy levels for these states are shown schematically in Figure 1. A fraction of the energy absorbed initially by a dye may be released through processes 2–7 within a few hundred nanoseconds in an aerated or oxygenated dye solution. In the absence of $^1O_2$ acceptor (A), the rest of absorbed energy, which is redistributed as the excitation energy of $^1O_2$, is degraded to heat through process 8 with a much slower rate (k_d). In the presence of an appropriate $^1O_2$ acceptor, the occurrence of an oxygenation reaction (eq 9) may introduce additional energy owing to the enthalpy change (ΔH_r) in the overall reaction:

$$A + {}^1O_2 \rightarrow AO_2 \tag{11}$$

The nonradiative processes 3–10 are all responsible for the heat generation observed in the thermal lensing experiment. Among these processes, reactions 2–7 are rapid and will be completed within nearly the same time as the acoustic transit time. Thus, it is reasonable to treat the heat generation through these processes as instantaneous in the following analysis. The produced $^1O_2$ may decay with the rate constant:

$$k = k_d + (k_A + k_{A'})[A] \tag{12}$$

The heat (cal cm^{-1} s^{-1}) generated through the above nonradiative processes between r and $r + dr$ in an optically thin sample within the time interval t and $t + dt$ is expressed as

$$Q(r,t)\,dr\,dt = 4J^{-1}Nw_p^{-2}H(t)\exp(-2r^2/w_p^2)r\,dr\,dt \tag{13}$$

where $J = 4.184$ J cal^{-1}, N is the initial excitation population of dye molecules, and w_p is the pulsed beam radius. Here, we assumed a gaussian TEM$_{00}$ excitation. From the above reaction scheme, a heating function, $H(t)$, is given as

$$H(t) = \Delta E_0\delta(t) + \phi_{st}\phi_{et}[(\phi_d + \phi_{A'})\Delta E_d + \phi_A(\Delta E_d + \Delta H_r)]k\exp(-kt) \tag{14}$$

where the thermal energy generated through processes 3–7 is simply expressed as ΔE_0 joule per excited state and $\delta(t)$ is a δ function for time. ΔE_d and ΔH_r are shown in Figure 1. Following Friedrich and Klem,[7] the temperature rise, ΔT, at radius r and time t in the sample is expressed as

$$\Delta T(r,t) = (2DN/\kappa J w_p^2)\int_0^t H(t-\tau) \times (1 + 2\tau/t_c)^{-1}\left[1 - (r/w_p)^2\frac{2}{1 + 2\tau/t_c}\right]d\tau \tag{15}$$

where κ is the thermal conductivity (cal cm^{-1} s^{-1} °C), and D is the thermal diffusivity (cm^2 s^{-1}). $t_c = w_p^2/4D$ is the thermal time constant. This temperature rise generates a local refractive index change in the medium, which is equivalent to a lens having a focal length of

$$1/F(t) = (8DlN/\kappa J w_p^2)\,(d\eta/dT)\int_0^t H(t-\tau)(1 + 2\tau/t_c)^{-2}\,d\tau \tag{16}$$

where l is the thickness of thermal lens and $d\eta/dT$ is the temperature coefficient of the refractive index. This refractive index change is monitored by a CW laser such as a He-Ne laser. The effect of the thermal lens on the monitoring beam is observed as a change in the intensity of the monitoring laser at the beam center, i.e., passing through the pinhole located in front of the detector as shown in Figure 2. The thermal lensing signal, $S(t)$, is defined as $S(t) = [I(t) - I(\infty)/I(t)]$, where $I(t)$ is the intensity at time t after the excitation. $I(\infty)$ is the intensity at a time sufficiently long that the lens has disappeared. According to the ray analysis predicted by Twarowski and Kliger,[4] the lensing signal, $S(t)$, is approximately related to the above focal length by

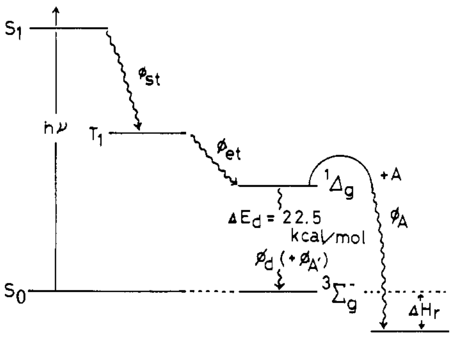

Figure 1. A schematic diagram showing the energy levels of sensitizer, molecular oxygen, and reaction product.

$$S(t) \approx 2z/F(t) \tag{17}$$

where z is the distance from the focal point of the converging lens to the sample. Thus the time development of the thermal lensing signal is given by

$$S(t) \simeq \alpha\int_0^t H(t-\tau)(1 + 2\tau/t_c)^{-2}\,d\tau \tag{18}$$

where

$$\alpha = 16DlN\,(d\eta/dT)z/\kappa J w_p^4$$

Substituting the expression for $F(t)$ from eq 14 into eq 18, we obtain

$$S(t) \simeq \alpha\int_0^t\{\Delta E_0\delta(t-\tau) + \phi_{st}\phi_{et}[(\phi_d + \phi_{A'})\Delta E_d + \phi_A(\Delta E_d + \Delta H_r)]k\exp[-k(t-\tau)](1 + 2\tau/t_c)^{-2}\}\,d\tau \tag{19}$$

Noting that several assumption were made in the derivation of eq 18, care should be taken to satisfy the experimental conditions pointed out in ref 4.

In particular, when the decay time ($1/k$) is much less than t_c (about 70 ms in the present experimental setup), we can reduce eq 19 to more practical form as follows. In this case, the denominator of the integrant in eq 19 is nearly constant in the time domain of interest, and integration gives

$$S(t) \simeq \alpha\{\Delta E_0 + \phi_{st}\phi_{et}[(\phi_d + \phi_{A'})\Delta E_d + \phi_A(\Delta E_d + \Delta H_r)] \times [1 - \exp(-kt)]\} \tag{20}$$

If we take the plateau value, S_m, which corresponds to the S value at the time when all the excited species decay, the thermal lensing signal is simply related to k as follow:

$$\ln[S_m - S(t)] = \ln\beta - kt \tag{21}$$

where

$$\beta = \alpha\phi_{st}\phi_{et}[(\phi_d + \phi_{A'})\Delta E_d + \phi_A(\Delta E_d + \Delta H_r)]$$

Using eq 21, k can be determined from the slope of a plot of ln $[S_m - S(t)]$ against time. From the preliminary results for the numerical calculations of eq 19 assuming $t_c = 70$ ms, the latter approximate method to determine the rate was found to be valid for a decay time less than a few hundred microseconds. Thus, all rates in the present work were evaluated by using eq 21.

If the decay time of interest is longer than the above-mentioned time, the simulation calculation using eq 19 is required to determine a rate from the thermal lensing signal. In this case, the thermal time constant, t_c, which depends on D and w_p, should be

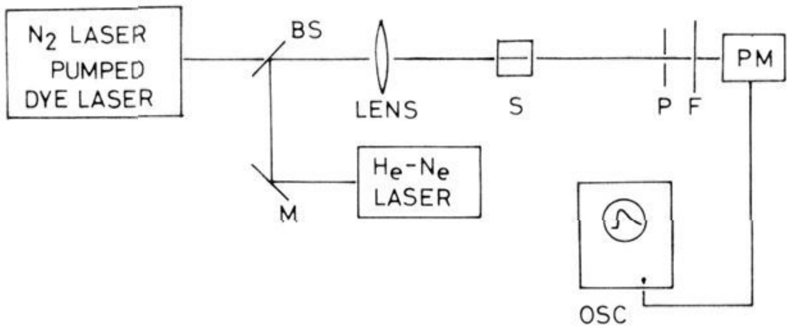

Figure 2. Apparatus used in the thermal lensing experiment: BS, beam splitter; S, sample; M, mirror; P, pinhole; F, filters; PM, photomultiplier; OSC, oscilloscope.

measured separately using an appropriate reference sample having a short enough decay time. The procedure for the determination of t_c is found in ref 4.

III. Experimental Section

The apparatus used in the thermal lensing experiment is shown in Figure 2. A nitrogen-pumped dye laser (Molectron UV-12, DL-14) was used as an excitation laser. The dye used in the laser was Coumarin 485 (520 nm) from Exciton Chemical. A small aperture was introduced between the oscillator and amplifier of the DL-14 to improve the beam quality of the dye laser. The mode structure was checked by a photodiode array (MEL 1024K) and was predominantly in the fundamental mode. The beam from a He–Ne laser (NEC 5330G) was made collinear with the dye laser beam, and the two beams were focused into the sample cell with a 15-cm focal length lens. The position of the sample cell (path length was 2 to 10 mm) was optimized by seeking the location which maximized the thermal lensing signal. An 0.8-mm diameter pinhole was placed 1 m from the sample so that only the center portion of the He–Ne laser beam was monitored. The He–Ne laser light passing through the pinhole was detected by an HTV R666 photomultiplier. Photomultiplier output was fed into 450-ohm load resister and recorded on a Tektronix 7904 oscilloscope. A differential comparator (Tektronix 7A13) was used to amplify small changes in the intensity of the monitoring laser. In many cases the output of the dye laser was appropriately attenuated by inserting a shutter between the nitrogen laser and dye laser in order to avoid a spherical aberration and to assure the linearity of thermal lensing signal.[15]

The following chemicals were used as received from the supplier: erythrosine, *meso*-tetraphenylporphine, 2,3-dimethyl-2-butene, β-carotene, *p*-(*tert*-butyl)catechol, 3-methylindole, Freon 113 (Nakarai Chemical), 1,3-diphenylisobenzofuran (Aldrich), and deuteriomethanol (Wako Chemicals). 2,5-Dimethylfuran (Nakarai Chemicals) was treated in a silica gel column before use. Dodecylammonium propionate (DAP) was obtained from Katayama Co. and was purified by recrystallization from cyclohexane.

Reversed micellar solutions were prepared by the method of Miyoshi and Tomita.[16] All measurements were made at room temperature.

IV. Results and Discussion

1. Evidence for Direct Detection of $^1O_2$. Since erythrosine (Ery) and *meso*-tetraphenylporphine (TPP) are known as good sensitizers for $^1O_2$ (quantum yields for $^1O_2$ formation are 0.68[17] for Ery and 0.88[18] for TPP), we used them to produce $^1O_2$. It was found that these sensitizers have a strong triplet–triplet absorption band at 632.8 nm which makes it difficult to observe the thermal transients, as discussed below. To circumvent this problem, the sample solutions were oxygenated by bubbling with oxygen so that the triplet lifetimes of these sensitizers were reduced. Figure 3 shows typical thermal lensing signals produced by irradiation of (a) Ery in ethanol and (b) TPP in cyclohexane. It is clearly seen that the lensing signals still build up slowly after the triplet dye molecules completely decay, and the magnitude of the signals reaches the plateau value within 30 μs in ethanol and 50 μs in cyclohexane.[19] Although the signal-to-noise ratio is not good, plots of ln $[S_m - S(t)]$ vs. time for these signals by means of eq 21 are reasonably linear as shown in Figure 4. From the slopes, the decay times were found to be 11 μs in ethanol and 20 μs in cyclohexane. These results are in good agreement with literature values for the lifetime of $^1O_2$ in each solvent. In order to confirm the assignment of these transient species to $^1O_2$, we measured the decay times of thermal transients in various organic solvents. We also carried out similar experiments for Ery in dodecylammonium propionate (DAP) reversed micellar solutions. The concentration of Ery was adjusted to 1×10^{-5} M and those of DAP and water were 0.04 and 0.1 M, respectively. The results are summarized

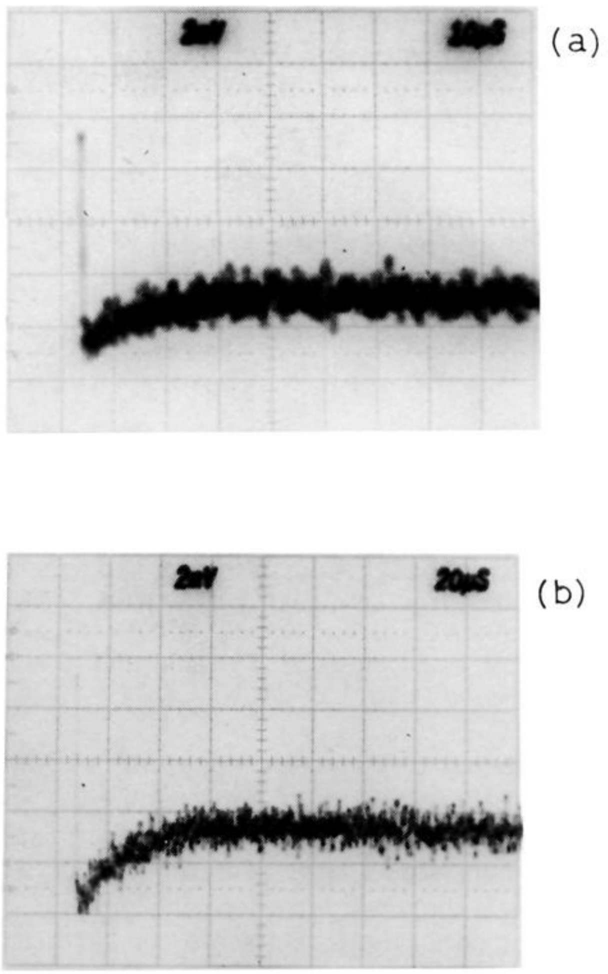

Figure 3. Typical oscilloscope traces of the thermal lensing signals produced by irradiation of (a) Ery in ethanol (time scale 10 μs/div) and (b) TPP in cyclohexane (time scale 20 μs/div).

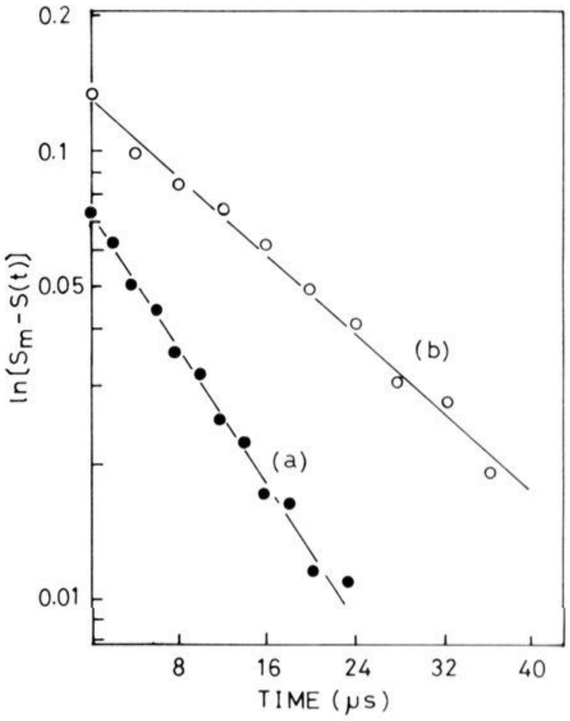

Figure 4. Plot of ln $[S_m - S(t)]$ vs. time for the signals shown in Figure 3.

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[15] In the case that the absorbed power is too large, the focal length of thermal lens may become short and eq 17 may no longer be valid. Preliminary experiments showed that, under these conditions, the linearity of the lensing signal was lost and a spurious rise of the lensing signal was observed as seen in Figure 2 of ref 4b. Thus, in the present experiment, special care was taken to avoid these situations.

[16] Miyoshi, N.; Tomita, G. *Z. Naturforsch., Teil B* **1980**, *35*, 731.

[17] Usui, Y. *Chem. Lett.* **1973**, 743.

[18] Olmsted, J., III *J. Am. Chem. Soc.*, **1980**, *102*, 66.

[19] The spikes observed in the oscilloscope traces in Figure 3 and the other figures shown later are due to the triplet–triplet absorption of dye molecules. The fast rise of signal due to the heat generation through processes 3–7 are superimposed on this absorption and these fast change are invisible in this time domain.

Table I. Lifetimes of Thermal Transient Produced by Irradiation of Dye Solutions Compared with the Lifetime of $^1O_2$ in Various Solvents

solvent	$1/k_d$ (μs) this work Ery	TPP	Ery/DAP	lifetime of $^1O_2$ (lit.)
methanol	9			7,[a] 11[b]
CH_3OD	40			
ethanol	11			12[a]
pyridine	17	14		17,[c] 33[b]
cyclohexane		20	17	17[a]
dioxane		21		32[b]
benzene		23	20	24[a]
acetone	25	30		26[a]
acetonitrile	36			30[a]
dichloromethane		54	52	
chloroform		62		60[a]

[a] Values are taken from ref 20. [b] R. H. Young, D. Brewer, and R. A. Keller, *J. Am. Chem. Soc.*, 95, 375 (1973). [c] S. R. Fahrenholtz, F. H. Doleiden, A. M. Trozzolo, and A. A. Lamola, *Photochem. Photobiol.*, 20, 505 (1974).

in Table I compared with reported values for the lifetime of $^1O_2$. The present results agree with the reported lifetimes of $^1O_2$ in all solvents within experimental errors. Moreover, the lifetime in deuteriomethanol shows a large deuterium effect, which is frequently used as a diagnostic test for $^1O_2$.[20]

On the other hand, the triplet sensitizer has been known to interact directly with ground-state sensitizers, usually with hydrogen atom to form an ion radical.[21] This reaction intermediate might also be a possible candidate for the observed thermal transient. However, experiments in DAP reverse micellar solutions may rule out this possibility. According to a study by Correll and his co-workers,[22] all the cosolubilized water molecules in nonpolar solvent may be tied up in the core of the DAP reverse micelle when the concentration of the water is less than 0.19 M vs. concentration of 0.04 M DAP. Ery may be bound to water inside the reverse micelles. The ion radicals mentioned above are expected to be trapped in the micelle, while $^1O_2$ may escape freely from the micellar phase to the bulk solution phase.[23] On the other hand, the lifetimes of $^1O_2$ in solutions (pyridine, ethanol, and acetone) were independent of the sensitizers (Ery and TPP), as shown in Table I. Further, the $^1O_2$ lifetimes in the DAP reverse micelle were consistent with those in the nonpolar solvents within experimental error. The facts suggest that the $^1O_2$ lifetimes in the reverse micelle are those in the nonpolar solvent phase out of the reverse micelle. Therefore, the thermal transient observed here is not due to the reaction intermediate such as an ion-radical formation of sensitizer mentioned above, but due to the formation and decay of $^1O_2$.

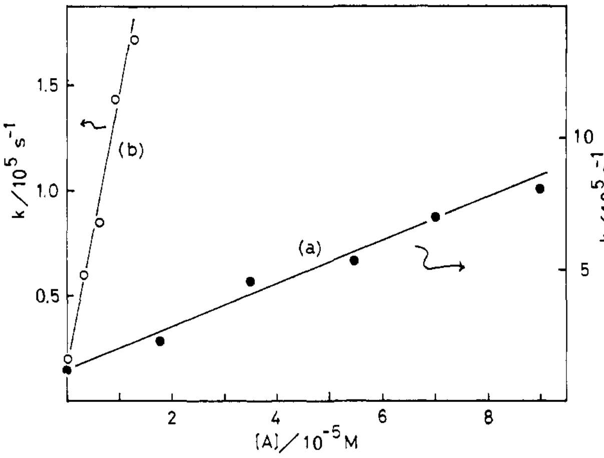

Figure 5. Plots of the experimental first-order rate constant vs. the concentration of (a) DPBF in methanol and (b) β-carotene in dichloromethane.

Table II. Rate Constants for Quenching/Reaction of $^1O_2$ with Acceptors

	$(k_A + k_A')/M^{-1}\,s^{-1} \times 10^{-8}$			
	this work			
acceptor	Ery[a]	TPP[b]	Ery/DAP[c]	lit.[e]
TME	0.3	0.4	0.1	0.47 (0.4)
DMF	3.8			4.0
DPBF	8.3		5.3	8.0
β-carotene		130 95[d]		130 30[d]
p-tert-butylcatechol		0.04		
3-methylindole		0.06		

[a] In methanol. [b] In dichloromethane. [c] In cyclohexane. [d] In Freon 113. [e] Reference 23.

The total thermal lensing signal consists of a fast nonradiative transition including the sensitization of $^1O_2$ (processes 3–7 in the reaction scheme) and a slow nonradiative transition from $^1O_2$ to $^3O_2$ (process 8). The ratio of the magnitude of the lensing signal due to the latter and former was found to be small (less than 0.2) as shown in Figure 3. This is partly due to the fact that only a fraction of the excitation energy absorbed by the sensitizer ($h\nu$ = 55 kcal mol^{-1}) is degraded to the thermal energy through process 8 (ΔE_d = 22.7 kcal mol^{-1}) with an efficiency of $\phi_{st}\phi_{et}$. Further, if there is an excited singlet absorption band ($S_n \leftarrow S_1$) of the sensitizer at the excitation wavelength, this absorption may increase the fast signal because of the short lifetime of the S_1 state, and may also suppress the above ratio. In this process, the additional photon energy absorbed in the $S_n \leftarrow S_1$ transition may increase the total amplitude of the lensing signal, but not increase the population of $^1O_2$. These facts prevent an accurate measurement of the lifetime of $^1O_2$. However, this situation may be greatly improved by introducing a signal-averaging technique.

2. Quenching Rate Constants for $^1O_2$ Acceptors. In the preceding section, we demonstrated that the present technique can directly follow the time-dependent concentration of $^1O_2$ produced by dye sensitization. Accordingly, the quenching rate constant for a $^1O_2$ acceptor may be directly obtained from the slope of a plot of the decay rate constant (k) vs. the concentration of an acceptor by means of eq 12 and 21. In order to demonstrate the general utility of the method to determine a quenching rate constant, we examined the quenching rate constants for several $^1O_2$ acceptors. In Figure 5 are shown plots of k for 1,3-diphenylisobenzofuran (DPBF) in methanol and for β-carotene in dichloromethane. From the slopes, the quenching rate constants obtained were 8.3×10^8 and 1.3×10^{10} M^{-1} s^{-1} for DPBF and β-carotene, respectively. The results for k determined in the present work are summarized in Table II and compared with literature values. The present results in free solution for 2,3-dimethyl-2-butene (TME), 2,3-dimethylfuran (DMF), DPBF, and β-carotene agree fairly well with those reported previously. The results in DAP/cyclohexane reversed micellar solution show somewhat lower rates compared with those in free solution.

As for β-carotene, the quenching rate constant has been extensively studied by using various techniques,[24] because it is frequently used as a diagnostic tool for involvement or noninvolvement of $^1O_2$ in organic or biological oxygenation reactions. The most reliable rate constant for β-carotene is belived to be $1.5 \pm 0.5 \times 10^{10}$ M^{-1} s^{-1}.[25] The present result for β-carotene in dichloromethane is in excellent agreement with this value. Macheson and his co-workers reported the rate constant (3×10^9 M^{-1} s^{-1}) for β-carotene in Freon 113,[26] which was substantially

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(20) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.*, **1972**, *94*, 7244.

(21) Koizumi, M.; Kato, S.; Mataga, N.; Matuura, T.; Usui, Y. "Photosensitized Reactions"; Kagakudojin: Kyoto, 1978; Chapter 6.

(22) Correll, G.; Chesser, R. N. III; Nome, F.; Fendler, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 1254.

(23) Usui, Y. In "Singlet Oxygen – Reaction with Organic Compounds and Polymers"; Ranby, B., Rabek, J. F., Eds.; Wiley: New York, 1978; p 203.

(24) Bellus, D. In ref 23, p 61.

(25) Foote, C. S. In ref 12, Chapter 5.

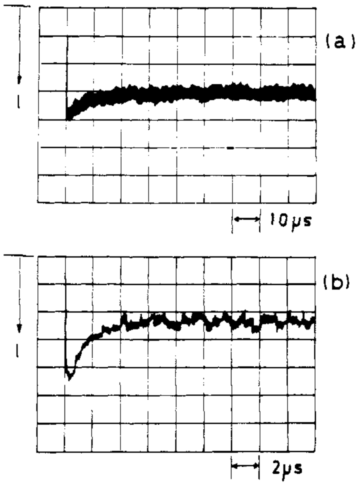

Figure 6. Typical oscilloscope traces of the thermal lensing signals produced by irradiation of Ery in methanol (a) in the absence (time scale 10 μs/div) and (b) presence of 6×10^{-4} M DPBF (time scale 2 μs/div).

lower than the above standard value. Several authors have criticized their result.[27] However, it is not clear whether the difference is caused by systematic errors from the different equipment used by Macheson et al., or caused by a solvent effect. To clarify this problem, we examined the rate constant for β-carotene in Freon 113 using TPP as the sensitizer. To solublize TPP, 4% dichloromethane was added to Freon 113. The rate constant obtained was 9.5×10^9 M^{-1} s^{-1}, which is nearly the same as that in dichloromethane. The error in Macheson's result probably arose from underestimation of the quenching rate constant of $^1O_2$ by ground-state oxygen, which was required to evaluate the rate for the $^1O_2$ acceptor in their high-pressure experiment.[28]

3. Reaction Enthalpies of Photooxygenation for $^1O_2$ Acceptor. Although the dye-sensitized photooxygenation reactions involving $^1O_2$ have been extensively studied, the enthalpy changes accompanying photooxygenation have not been studied to date except for the work of Olmsted.[18] As mentioned in section 1, the thermal lensing experiment may provides us information of an enthalpy change in the photooxygenation reaction of $^1O_2$ acceptor in the time-resolved manner. In order to obtain an experimental certification for this, we made an attempt to determine the reaction enthalpies (ΔH_r) for DPBF, TME, and β-carotene. When $\phi_A \Delta H_r$ in eq 20 is not negligibly small compared with $\phi_d \Delta E_d$, the addition of suitable acceptor may result in the enhancement of the thermal lensing signal. Figure 6 shows the typical thermal lensing signals produced by irradiation of Ery in methanol (a) in the absence and (b) presence of DPBF (6×10^{-4} M). These signals clearly show that the addition of DPBF causes a decrease in the decay time of $^1O_2$ and the enhancement of the signal at the same time. A similar enhancement was observed for TME, but not for β-carotene.

To evaluate ΔH_r from the observed changes in the magnitude of signals, we consider the following analysis. In principle, the enthalpy change can directly be determined by using eq 20 with a knowledge of α and ϕ_A. However, practically, it is very difficult to determine the value of α accurately because it requires the estimation of the initial population of $^1O_2$ and the beam radius of the excitation laser in the sample cell. Further, it is experimentally difficult to match the many assumptions involved in deriving eq 18. Consequently, we developed the following comparison method to determine ΔH_r.

Table III. Enthalpy Changes for Reaction of $^1O_2$ with Acceptors

acceptor	ΔH_r, kcal/mol, in solvent: dichloromethane[a]	methanol[b]
β-carotene	0	0
TME	25	4
DPBF		35

[a] TPP was used as the sensitizer. [b] Ery is used as the sensitizer.

In addition to measuring the thermal lensing signal for the sample containing a $^1O_2$ acceptor (S value designated here by a superscript s), we measured the signal for only dye solution (denoted by superscript r) under the same experimental conditions. In the absence of an acceptor, all of the photon energy of the formation and decay of $^1O_2$ may degrade to heat through energy transfer to solvent molecules. The plateau value of the thermal lensing signal, defined in eq 21, is given by:

$$S^r_m = (S^r_m)_0 + (S^r_m)_1 \simeq \alpha(\Delta E_0 + \phi_{st}\phi_{et}\Delta E_d) \qquad (22)$$

where $(S^r_m)_0$ and $(S^r_m)_1$ are the magnitudes of signals corresponding to the thermal energy generated through the formation and decay processes of $^1O_2$, respectively. The values $(S^r_m)_0$ and $(S^r_m)_1$ are readily obtained from the observed S^r_m value and the intercept of the similar plot as shown in Figure 4. Therefore, we have the following ratio (R^r) as reference:

$$R^r = (S^r_m)_1/(S^r_m)_0 \simeq \phi_{st}\phi_{et}(\Delta E_d/\Delta E_0) \qquad (23)$$

In the presence of the $^1O_2$ acceptor, excess energy, ΔH_r, may be liberated in the sample, and the plateau value in this case is given as

$$S^s_m = (S^s_m)_0 + (S^s_m)_1 \simeq \alpha[\Delta E + \phi_{st}\phi_{et}(\Delta E_d + \phi_A \Delta H_r)] \qquad (24)$$

where $(S^s_m)_0$ and $(S^s_m)_1$ are the thermal lensing signals of $^1O_2$ formation and decay in the presence of quencher; and the relation, $\phi_d + \phi_A + \phi_{A'} = 1$ in eq 21 for decay processes of $^1O_2$, is used. Then, the ratio (R^s) is

$$R^s = (S^s_m)_1/(S^s_m)_0 \simeq \phi_{st}\phi_{et}(\Delta E_d + \phi_A \Delta H_r)/\Delta E_0 \qquad (25)$$

Therefore, the ratio of eq 25 to eq 23 gives

$$R^s/R^r = 1 + \phi_A(\Delta H_r/\Delta E_d) \qquad (26)$$

Consequently, ΔH_r can be determined from the observed ratio, R^s/R^r, and the quenching quantum yield (process 9), ϕ_A $(=k_A[A]/\{k_d + (k_{A'} + k_A)[A]\})$. Since it has been well accepted that DPBF and TME quench chemically $^1O_2$,[18,29] we can reasonably assume that $\phi_A \simeq k[A]/(k_d + k_A[A])$. We also adjust the concentration of the acceptor to reduce the decay time of $^1O_2$ to one-tenth of the intrinsic lifetime in each solvent so as to be able to separate the value of $(S^s_m)_0$ from the value, S^s_m, in eq 24. Thus, ϕ_A should be about 0.9 in the present analysis. This method may suppress an error which arises from scatter of the output of the excitation laser and give ΔH_r without knowledge of α.

The results of ΔH_r for β-carotene, TME, and DPBF are shown in Table III. Although the present results include a fairly large experimental error (ca. ±6 kcal mol^{-1}), the enthalpy change obtained for β-carotene is consistent with the results by the energy transfer quenching.[27] Results for TME were 25 and 4 kcal mol^{-1} in dichloromethane and in methanol, respectively, while ΔH_r for DPBF in methanol was 35 kcal mol^{-1}. Olmsted has also determined the enthalpy changes of reaction of $^1O_2$ with TME and DPBE in several nonpolar solvents by using steady-state photochemical calorimetry.[18] The enthalpy changes reported by him are about a factor of 1.4 larger than those obtained here. Since the solvents used and the experimental time domains (between a few hundred ns and 10 μs in the present work and between 1 and 15 min in the Olmsted's work) are different from each other, the direct comparison of two data seems to be difficult.

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(26) Macheson, I. B. C.; Lee, J. E.; Yamanishi, B. S.; Wolbarsht, M. L. *J. Am. Chem. Soc.* **1974**, *96*, 3343.

(27) (a) Foote, C. S.; Ching, T. Y. *J. Am. Chem. Soc.* **1975**, *97*, 6209. (b) Herkstroeter, W. G. *Ibid.* **1975**, *97*, 4161.

(28) The preliminary result for a high-pressure thermal lensing experiment using TPP as the sensitizer shows that the decay time of $^1O_2$ in Freon 113 (containing 4% dichloromethane) is considerably reduced even at an oxygen pressure of 13 atm.

(29) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 462.

As for DPBF, the mechanism of photooxygenation is still a subject of controversy.[30] The reaction of DPBF with ${}^1O_2$ to form *o*-dibenzoylbenzene involves the apparent loss or transfer of an atom of oxygen, and thus the overall photochemical yield is expected to be two times the quantum yield of singlet oxygen. The work of Usui[23] on methylene blue sensitized photooxygenation of DPBF in methanol and tetrachloroethane supports the above prediction. However, Olmsted[18] reported that the photochemical quantum yield was almost unity, even though he carried out the experiment in a time domain similar to that of Usui. In order to interpret the present result of ΔH_r for DPBF, we must consider these mechanistic ambiguities. However, Rio and Scholl[31] suggested that the initial product is an endoperoxide which is relatively stable, while the overall reaction in methanol to form *o*-benzoylbenzene intercepted by methoxy hydroperoxide is complex. Therefore, considering the present experimental time domain, the value of ΔH_r may be ascribed to the enthalpy change to form endoperoxide.

The enthalpy change obtained here for TME in two solvents shows a considerable discrepancy (Table II). A possible interpretation for this is the solvent effect on the photooxygenation reaction of TME to form butene hydroperoxide. The reaction product hydroperoxide seems to be more stabilized in methanol than in dichloromethane owing to the formation of hydrogen bonding with methanol. However, this speculation is in conflict with the present results of ΔH_r. A satisfactory explanation for this discrepancy of ΔH_r in two solvents is not readily apparent at the present stage.

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(30) Wasserman, H. H.; Lipshutz, B. H. In ref 12, p 434.

(31) Rio, G.; Scholl, M. J. *J. Chem. Soc., Chem. Commun.* **1975**, 474.

New Model for the Interior of Polyelectrolyte Coatings on Electrode Surfaces. Mechanisms of Charge Transport through Protonated Poly(L-lysine) Films Containing $Fe^{III}(edta)^-$ and $Fe^{II}(edta)^{2-}$ as Counterions

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Abstract: A model is proposed for the interior of a swollen, polycationic coating equilibrated with a supporting electrolyte solution containing both electroactive and electroinactive counteranions. The coating is divided (conceptually) into two regions. The first, termed the "Donnan domains", represents the region where the counterions are confined by electrostatic forces; the second comprises the remaining volume of the coating that is assumed to be occupied by the supporting electrolyte solution. Some expected effects of this two-part structure on the electrochemical responses obtained in both steady-state and transient experiments with coated electrodes are discussed and compared with experimental results obtained with the $Fe^{III}(edta)^-/Fe^{II}(edta)^{2-}$ redox couple. The polycationic coatings employed were prepared from protonated poly(L-lysine) deposited on graphite electrodes. This particular combination of polyelectrolyte and incorporated redox couple yields rates of propagation of charge through the coating that are remarkably high in both of the regions, indicating that the open, swollen structure of the coating is particularly favorable for rapid motion of counterions. The coupling between the two propagation pathways by means of electron exchange is also quite rapid. The experimental data adhere well to the predictions of the equations derived on the basis of the two-phase model which may prove generally applicable to electrodes bearing polyelectrolyte coatings.

In the first experimental account of the exploitation of polyelectrolyte-coated electrodes to examine the kinetics of redox self-exchange reactions,[1] a simplified model, adapted from earlier work by Levich,[2] was employed to analyze steady-state data obtained with rotating disk electrodes. Subsequent theoretical analyses of the mechanisms and kinetics of charge propagation within polymer and polyelectrolyte coatings[3-6] have indicated that more intricate models may be required to account for the wide range of electrochemical responses that are obtained from electrodes coated with polymers or polyelectrolytes.[7] The kinetics of redox self-exchange processes occurring within coatings on electrodes is perhaps the simplest general case of interest, and a theoretical treatment of the kinetic behavior to be expected for the case of simple self-exchange on the basis of a more detailed model of the interior structure of polyelectrolyte coatings has been presented.[3] It proved possible to arrive at an analytical expression for the steady-state current at a coated, rotating disk electrode under all experimental conditions. In this report we present an experimental test of this new model by comparing the predictions it leads to with the observed electrochemical responses.

The essential feature of the new model employed for polyelectrolyte coatings is the existence of two phases within the coating.

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(1) Shigehara, K.; Oyama, N.; Anson, F. C. *Inorg. Chem.* **1981**, *20*, 518-522.

(2) Levich, V. G. "Physicochemical Hydrodynamics"; Prentice-Hall: Englewood Cliffs, N.J., 1962.

(3) Anson, F. C.; Saveant, J. M.; Shigehara, K. *J. Phys. Chem.* **1983**, *87*, 214.

(4) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Saveant, J. M. *J. Electroanal. Chem.* **1982**, *1*, 131.

(5) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1982**, *134*, 163.

(6) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* **1982**, *142*, 1.

(7) Recent relevant references were cited in ref 3.