

INVESTIGATION OF TRIPLET STATE AND SINGLET OXYGEN DYNAMICS OF BENZOPHENONE IN POLAR AND NONPOLAR SOLUTIONS WITH TIME-RESOLVED TWO-COLOR THERMAL LENSING METHOD

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Abstract - The heat generated by nonradiative decay dynamics induces thermal lens effect. From such an effect, photodynamic properties of solutions can be investigated with two-color pulsed thermal lens experiments which have the time resolution of down to nanoseconds. In this study, using nanosecond two-color thermal lens method, we investigated the triplet state of benzophenone and the singlet oxygen state dynamics in various oxygen concentration solvents. The measured triplet state lifetimes, singlet oxygen relaxation times and singlet oxygen formation quantum yields are in good agreement with the reference values. From these parameters the existence of the triplet exciplex formation between benzophenone and benzene is proved, and it is also suggested that the relaxations of triplet states of benzophenone undergo coupled dynamics with some of singlet oxygens in oxygen-rich conditions.

INTRODUCTION

Thermal lens is one of powerful tools in obtaining parameters about many photophysical reactions which undergo through nonradiative processes.^{1,2} Observation of the building-up times of the thermal lens signals gives us information on the rate of thermal energy deposition into the system and thus for the excited-state dynamics.³ So, this method has recently begun to be utilized as tool which is complementary to other well-established spectroscopic methods, providing energetic and kinetic information about transient species (excited singlets, triplets, isomers, radicals, *etc.*) formed by light absorption.⁴ Particularly, for dark molecular systems, this technique is very powerful in investigating the properties of the excited states.

In photophysical dynamics, photophysical properties of the triplet state are difficult to be directly obtained because of very weak radiative transition due to spin-forbidden transition characteristics.⁵ However, by using thermal-lensing technique, triplet state lifetimes and quantum yields of molecular systems can be measured simultaneously. So this technique may be applicable to the kinetic study of $^1\text{O}_2$ in solution with the time resolution of nanoseconds. These singlet oxygens are formed through energy transfer processes from triplet states of photosensitizers to the dissolved oxygen molecules. Reactions of singlet oxygen are important in many photochemical and photobiological processes.³

Among them, the dynamics of $^1\text{O}_2$ are particularly important in the photodynamic therapy. The mechanism of photodamages of the biological cells in photodynamic therapy involves the intermediacy of singlet molecular oxygen.⁶ Whereas the previous determinations of the dynamics have involved the use of indirect chemical techniques, the time-resolved thermal lensing method directly measures the absolute values with no requirement for the use of a reference sample.^{7,8}

The triplet state and singlet oxygen state dynamics have been studied under different experimental conditions such as temperature, solvent, sensitizer concentration and the power of excitation light.^{9,10} In this study, we investigated the dynamics of triplet state and singlet oxygen with benzophenone in various solvents under different oxygen concentration solvents. Benzophenone is an efficient compound for the thermal lens experiment since it has fluorescence quantum yield of nearly zero and triplet quantum yield of unit in degassed solution.^{11,12} We also indirectly proved the existence of the triplet exciplex formation of benzophenone with benzene, and it was expected that some of singlet oxygens and triplet state of benzophenone relaxed coupled with together in oxygen-rich solvents.¹³

MATERIALS AND METHODS

Chemicals. Benzophenone was purchased from Eastman organic chemical co. and recrystallized in ethanol. Ethanol (Merck, special grade), benzene (Yakuri, special grade), hexane (Cica-Merck, HPLC grade) were used without further purification. N_2 gas (99.999%) and O_2 gas (99.999%) were

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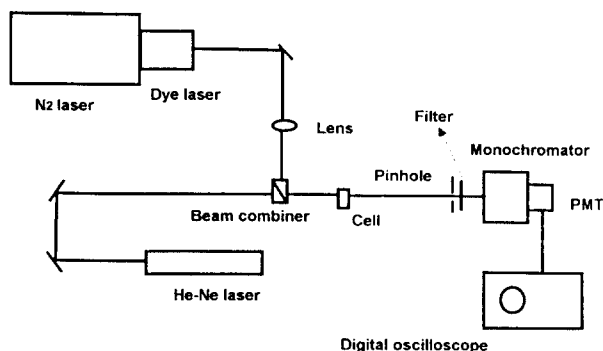


Figure 1. Time-resolved two-color thermal lens experimental setup.

used for bubbling processes. The flow rates of N_2 gas and O_2 gas are 2.1 NL/min and 2.5 NL/min, respectively. The samples were bubbled for 25 minutes. The absorbance were adjusted in the range of 0.4 ~ 0.9 O.D. after bubbling procedures.

Apparatus. The UV-VIS spectra of the sample and the steady-state fluorescence spectra were obtained by the spectrophotometer (Shimadzu UV-160A) and the spectrofluorimeter (Hitachi F-2000). The two-color thermal lens experimental setup is illustrated in Figure 1. Picosecond N_2 laser-pumped dye laser (Laser Photonics LN1000) was used as an excitation light source. The ethanol solution was excited at 383 nm and the benzene and the hexane solutions were excited at 380 nm. He-Ne laser(Uniphase 1130P) beam of 632.8 nm was used as a probe beam. The two beams were combined and collimated by using the Glan-Thomson polarizer. The excitation beam was focussed into the cuvette by a 150 mm focal length lens. The probing He-Ne laser beam was passed, after the sample cuvette, through a pinhole (300 μ m) and a monochromator (Acton Research Co. Spectro-275), and detected by a photomultiplier (Hamamatsu R928). The signal was amplified by preamplifier (Stanford Research Systems, model SR445) which was terminated with 50 Ω , and averaged over 2,048 times by 500 MHz digital oscilloscope (HP, 54520A) and then processed by a computer.

RESULTS AND DISCUSSION

Most excitation energies in the first excited singlet state of benzophenone solutions are flowed into the triplet state in fast time (\sim ps). Some of this triplet energies are nonradiatively decayed into the S_0 state in a time scale of microseconds* and the other energies are flowed into the singlet oxygen state. This transferred energy is also nonradiatively decayed into the ground state of oxygen molecule in a time scale of microseconds.' These energy dynamics were measured by pulsed two-color thermal lens method in this study. The approximated diagram of these dynamics is illustrated in Figure 2.

We obtained the triplet state lifetimes (τ_1) and the singlet oxygen relaxation times (τ_2), as presented in Figure 2, by nonlinear regression fitting with the two-color thermal lens signal. The fitting equation is written as,

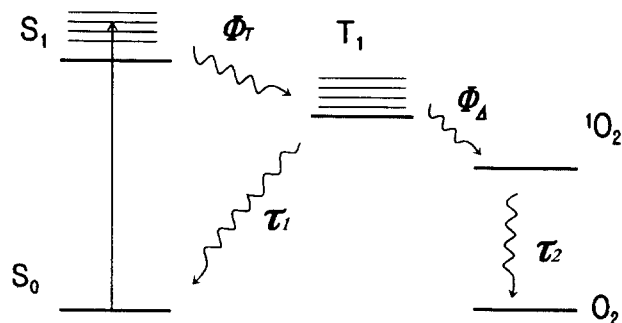


Figure 2. Brief diagram of the photodynamics of the triplet state and the singlet oxygen.

$$I(t) = a_1 \cdot \exp(-t/\tau_1) + a_2 \cdot \exp(-t/\tau_2) \quad (1)$$

where a_1 and a_2 are the amplitudes of the triplet state relaxation component and the singlet oxygen relaxation component, respectively. τ_1 is the triplet state lifetime and τ_2 is the singlet oxygen relaxation time. The typical time evolution of thermal lens signal, fitted line, and its fitting residuals are shown in Figure 3. The corresponding values of a_1 , τ_1 , a_2 and τ_2 for the sample solutions at three different conditions(atmosphere, O_2 bubbling, N_2 bubbling) are shown in Table 1. The fitted τ_1 , τ_2 values are in good agreement with the reference values of the corresponding sample solutions.^{14,15,16} It is found that, in ethanol sample, the triplet state lifetimes τ_1 and the singlet oxygen relaxation time, τ_2 are changed, depending

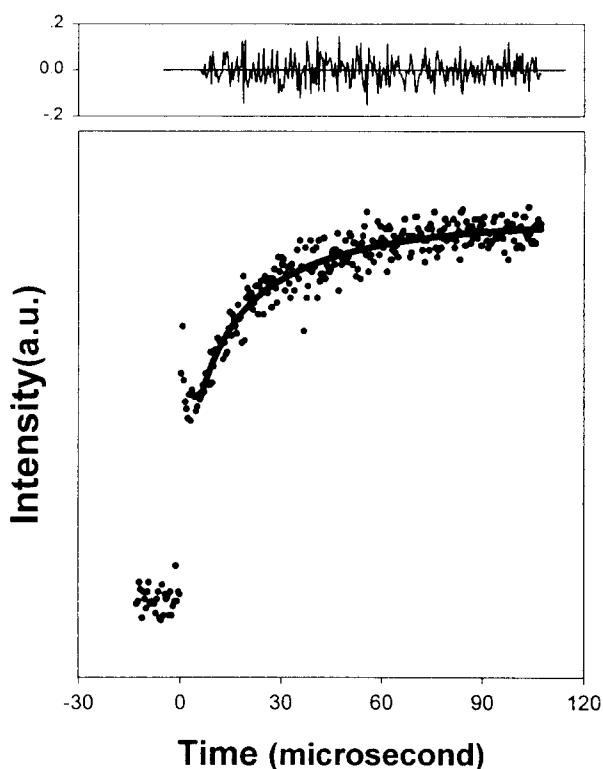


Figure 3. Typical time evolution of the thermal lens signal (dotted), the fitted line, and its fitting residuals.

Table 1. Fitted parameters at different solvents and corresponding reference values.

		Atmosphere	O ₂ bubbling	N ₂ bubbling	Ref. values
Benzene	A ^{a)}	50	46	50	
	B ^{b)}	50	54	50	
	$\tau_1(\mu\text{s})$	9	9	9	5 ^{c)}
	$\tau_2(\mu\text{s})$	32	33	37	31.2 ^{c)} , 24 ^{d)}
Hexane	A ^{a)}	50	50	46	
	B ^{b)}	50	50	54	
	$\tau_1(\mu\text{s})$	8	9	10	
	$\tau_2(\mu\text{s})$	33	31	35	31.4 ^{c)}
Ethanol	A ^{a)}	40	11	50	
	B ^{b)}	60	89	50	
	$\tau_1(\mu\text{s})$	50	44	53	
	$\tau_2(\mu\text{s})$	15	17	14	15.3 ^{c)} , 12 ^{d)}

$$^a) A = \frac{a_1}{a_1 + a_2} \times 100(\%)$$

$$^b) B = \frac{a_1}{a_1 + a_2} \times 100(\%)$$

a_1 and a_2 are the amplitudes of the triplet state relaxation component and the singlet oxygen relaxation component, respectively.

^{c)}Ref. [16]. ^{d)}Ref. [14]. ^{e)}Ref. [15].

upon the dissolved O₂ concentrations. However, in benzene and hexane solutions, the lifetime shifts were not observed as the dissolved O₂ concentration changed.

The singlet oxygen quantum yields were calculated from the singlet oxygen component of the thermal lens signal amplitude with the following equation (2).⁴ But the triplet state quantum yields could not be obtained since the oxygen was not fully degassed from the solution by nitrogen bubbling process.^{5,17} The calculated singlet oxygen quantum yields in various conditions are presented in Table 2.

$$\Phi_{\Delta} = \frac{U_{slow} h\nu_{ex} - \Phi_f E_f}{U_{tot} E_{\Delta}} \quad (2)$$

where U_{slow} and U_{tot} are the slow rising amplitude of singlet oxygen state component and the total amplitude of the thermal lens signal, respectively. $h\nu_{ex}$ is the photon energy of the excitation laser, Φ_f is the fluorescence quantum yield of the sensitizer solution, E_f is the average photon energy of the fluorescence, and E_{Δ} is the energy of the singlet oxygen state. The singlet oxygen quantum yields of the benzene and the hexane solutions and that of the oxygen-bubbled ethanol solution are almost unity.

Table 2. Measured singlet oxygen quantum yields(Φ_{Δ}) at different solvents.

	Benzene	Hexane	Ethanol
Atmosphere	0.99	0.99	0.83
O ₂ bubbling	0.97	0.99	0.99
N ₂ bubbling	0.99	0.99	0.81

However, in the degassed and atmospheric ethanol sample solutions, the quantum yields are significantly smaller than that in the oxygen bubbling condition.

The singlet oxygen formation is considered to be dependent on the oxygen solubility of solvent and the diffusion of oxygen molecule in solvent, *i.e.* the viscosity of the solvent. The solubility of oxygen in pentane is 0.576¹⁸ at 20°C, so the solubility of hexane is expected to be around this value at this temperature. But, the solubility of oxygen in benzene and ethanol solvents are 0.174¹⁸ and 0.154,¹⁸ respectively. On the other hand, at 20°C, the viscosity of hexane is 0.31 cP¹⁹ and the viscosity of benzene and ethanol are 0.65 cP¹⁹ and 1.21 cP¹⁹, respectively. Therefore, oxygen molecules are dissolved more in hexane and diffuse faster. So the triplet state quenching process of oxygen molecule in hexane solvent is expected to be the most efficient. The experimental results that triplet state lifetimes are smaller than those in ethanol sample and quantum yields are higher support this expectation.

However, the benzene and ethanol solutions have similar solubility for oxygens and the viscosity of benzene is not much less than that of ethanol, compared with the viscosity difference between hexane and ethanol. In contrast to these facts, the singlet oxygen quantum yields are higher in benzene solutions and the triplet states relax much faster in benzene than in ethanol. That is, the oxygen quenching process is more efficient in ethanol solvent than in ethanol solvent. In order to consider the diffusion effect of oxygen molecules in these solvents, we calculated the average travelling distance of diffusing oxygen molecule in each solvent with the Einstein-Sutherland hydrodynamic equations,²⁰ assuming the stick boundary condition. In this calculation of the averaged travelling distance of diffusing oxygen molecules, the diffusion equation is

$$D = kT/f \quad (3)$$

where k, T are Boltzmann's constant and temperature, respectively, and f is the frictional coefficient:

$$f = 6 \pi \eta \gamma_h F \quad (4)$$

Here η represents viscosity and the shape factor F is

$$F = (1 - P^2)^{1/2} / P^{2/3} \ln \{ [1 + (1 - P^2)^{1/2}] / P \} \quad (5)$$

where the shape of oxygen molecule is modeled as a prolate ellipsoid and it is defined that $P = b/a$, $a > b$. In these calculations, the stick boundary condition is assumed because, in the translational diffusion process, the oxygen molecule breaks the intermolecular couplings between the solvent molecules. The hydrodynamic radius, r_h is,

$$r_h = [(3/4 \pi)(M/N_0)(V_2)]^{1/3} \quad (6)$$

in which M is the molecular weight and N_{θ} is the Avogadro number and V_2 is the partial specific volume. In this equation, the additional solvent volume effect is ignored because, in contrast to the macromolecule case such as protein, molecular oxygen does not have the hydrogen bonding effect and the extensive van der Waals effect with the solvent which results the complex structural effect. With the known bond lengths and van der Waals radii, the molecular axial lengths a and b are obtained to be 446 pm and 150 pm, respectively. From $P = b/a = 0.34$, the shape factor F is evaluated to be 1.11. From the partial specific volume of $1.41 \times 10^{-7} \text{ m}^3 \text{ g}^{-1}$, the hydrodynamic radius r_h is calculated to be $1.22 \times 10^{-10} \text{ m}$ by equation (6). Then, the frictional coefficients in benzene and ethanol solvents become $1.65 \times 10^{-12} \text{ kg s}^{-1}$ and $3.08 \times 10^{-12} \text{ kg s}^{-1}$, respectively. From above frictional coefficients and equation (3), the diffusion constant in benzene and ethanol solvents are $2.45 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $1.31 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, respectively. From these calculated values, the average distance travelled by diffusing particles in a time, $\langle x^2 \rangle^{1/2} = 2Dt$, could be obtained. The average travelling distances of oxygen molecule during 50 μs which is the longest triplet lifetime in ethanol are 0.495 μm in benzene solvent and 0.362 μm in ethanol solvent, respectively. Since the focussed beam spot size is about 20 μm in its diameter, the above distance values are very short distances. That is, the diffusion effect, in other words, the viscosity effect is not important and only the oxygen molecules in vicinity of benzophenone molecules can mostly contribute to the quenching process of the triplet state of benzophenone, consequently, converted into the singlet oxygen molecules. The amount of oxygen molecule is almost same near the benzophenone molecule due to the similar oxygen solubilities of both solvents. From these results, we can conclude that the cross-section of oxygen quenching reaction in the benzene solvent is greater than that in ethanol solvent. That is, benzophenone in benzene solvent has the greater contacting area for the quenching molecular oxygens. It indicates that benzophenone forms the triplet exciplex with benzene solvent as reported by Wolf *et al.*²¹

Considering the fitting parameters, in the benzene and hexane sample solutions, the differences of the A , B amplitudes between each conditions are negligibly small and the quantum yields in all oxygen quenching conditions are almostly same. Therefore, all solution conditions are considered to be same in each solvent. That is, their differences in the lifetimes are assumed to be in the error range. But, the A , B amplitudes differences between one another conditions in ethanol sample are considerable, namely, the respective quenching states are considered to be quite different, which implies that the differences in the lifetimes could be out of the error range. Therefore, it is thought that the lifetimes are shifted under various oxygen rich conditions in ethanol solution. In oxygen bubbled ethanol sample, the lifetime of triplet state of benzophenone is smaller than those of

the other bubbling conditions. There are two possibilities for the reason of these phenomena. In oxygen rich condition, the sensitizer can be quenched more rigorously and then the sensitizer relaxes more rapidly. Another possibility is that the triplet state of benzophenone is relaxing coupled with the generated singlet oxygen molecule to the singlet ground state of benzophenone molecules. The slower singlet oxygen state lifetime supports the latter mechanism, because if only the oxygen quenching process exists, the singlet oxygen must relax faster in oxygen bubbling condition. But, in contrast, the singlet oxygen relaxes more slowly in oxygen rich condition than the other conditions. The above facts indicate that the singlet oxygen state have more probability to be coupled to the benzophenone triplet state during their relaxation processes as the dissolved O_2 concentration increases.

CONCLUSION

We could obtain the lifetimes in some accuracy and investigate the dynamics of oxygen quenching mechanism. In benzene solvent, the existence of triplet exciplex is indirectly proved by the hydrodynamic diffusion rate calculation and the experimental results of the benzophenone triplet state and singlet oxygen dynamics, such as lifetimes and quantum yields data. And, also, the coupling mechanism of benzophenone triplet state with the singlet oxygen is suggested as the peculiar energy dynamic behaviour. The better the degassing process is, the more benzophenone triplet state dynamics can be understood in detail due to the absence of gas quenching process. That is, the variation of the energy coupling of benzophenone with the solvent by changing the solvent properties and the extent of photoreactions with the solvent in triplet excited state of benzophenone could be more investigated under such degassing condition. The more detailed studies are on progress with improved degassing condition.

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