Effects of Nonradiative Energy Transfer on Photodimerization of a Stilbazolium Cation on Ag and GaAs Substrates: Infrared Reflection Absorption and Emission Spectroscopic Studies

Masato Yamamoto and Koichi Itoh*

Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169, Japan

Atsuko Nishigaki and Shigeru Ohshima

Department of Biomolecular Science, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan Received: September 20, 1994; In Final Form: December 22, 1994[®]

Infrared reflection absorption (IRA) and fluorescence spectroscopies were applied to elucidate photodimerization processes induced by irradiation at 340 nm of stilbazolium cations (C18S) incorporated in Langmuir-Blodgett (LB) films of fully deuterated arachidic acid (DA) on the silver and GaAs substrates. A spacer layer consisting of monomolecular LB films of DA was inserted between the substrates and the mixed LB monolayers ($C_{18}S$: DA = 1:4). Both the rate and the extent of photodimerization increased with the thickness of the spacer layer (d). The quantum yield of excimer fluorescence also increased with d. Analyses of these results confirmed that photodimerization proceeded through an excimer of C18S and that the reduction in the dimerization rate observed for the samples with smaller numbers of spacer layers was mainly due to an increase in the rate of nonradiative energy transfer to the substrates. The energy transfer on the GaAs substrate depended on d^{-3} , which conformed to a well-known classical theory based on the standard Förster-type energy transfer. On the other hand, the energy transfer rate on the silver substrate was proportional to d^{-1} , which did not agree with the classical theory. Change in the intensity of an excimer fluorescence band near 490 nm was observed from 15 monolayers of a mixed LB film ($C_{18}S:DA = 1:4$) on a silver substrate as a function of t in the temperature range 77-320 K. Above 300 K, the intensity decreased precipitously with t, indicating the advance of photodimerization; the activation energy of the process was determined to be 28.4 kJ/mol. On the contrary, the intensity showed appreciable increase below 200 K and dimerization hardly proceeded. This phenomenon was interpreted as due to a photoinduced orientation change of $C_{18}S$, resulting in a state which was more favorable for the excimer formation and hence stronger fluorescence. However, only very few excimers had thermal energy larger than the activation energy so that dimers were scarcely produced below 200 K. In the temperature range 200-300 K, the intensity at first increased and then decreased gradually; the result could be reproduced by assuming that both the orientation change and the photodimerization occurred at the same time.

Introduction

Experimental as well as theoretical studies have been performed on lifetimes and quantum yields of fluorescence from excited molecules on metal and semiconductor surfaces.¹⁻⁹ In these studies the Langmuir-Blodgett monolayer assembly technique or an evaporation method was used to create a spacer layer of variable thickness between the substrates and the luminescent molecules. In this manner, the lifetime and the quantum yield were measured as a function of distance (d) of the molecule from the surfaces. At distances much less than the emission wavelength the lifetime decreased monotonically toward zero. This was attributed to nonradiative transfer of energy from the excited molecule to the surface. A classical model for the energy transfer has been developed in great detail, in which the excited molecule was treated as a point dipole and the substrate was described as a continuous medium of permittivity, $\epsilon(\nu)$.¹⁻⁴ The theory predicted the dependence of the nonradiative energy transfer rate on d^{-3} . The classical theory, however, could not explain experimental results at small d^{4-9} Some of the shortcomings of the classical theory have been overcome by introducing the wave vector dependence of

0022-3654/95/2099-3655\$09.00/0 © 1995 American Chemical Society

the permittivity, in which the effects of surface-plasmon polariton (SPP) excitation⁷ and/or electron-hole pair excitation process⁸ were considered as important factors in the nonradiative energy transfer process.

Nonradiative and radiative energy transfer processes from excited states of molecules have serious effects on photochemical reactions of molecules adsorbed on solid surfaces. Hence, if the extent and quantum efficiency of the reaction are measured as a function of the distance of the reacting molecules from the surface, the results would give ample information on the mechanism of the energy transfer processes. In previous papers^{10,11} we applied Fourier-transform infrared reflection absorption (IRA) spectroscopy to investigate the photodimerization process of N-(1-octadecyl)-4-stilbazolium cation (abbreviated as C₁₈S), shown in Figure 1, embedded in Langmuir-Blodgett (LB) films of perdeuterated arachidic acid (abbreviated as DA). According to Quina and Whitten,¹² the photodimerization of C₁₈S proceeded through the formation of an excimer which showed a fluorescence peak near 490 nm. In the present paper, the LB assembly technique was used to fabricate spacer layers of DA of different thickness (d), on silver and GaAs substrates, and to place mixed LB monolayers of C18S and DA $(C_{18}S:DA = 1:4)$ on top of the spacer. The extent of the

^{*} Abstract published in Advance ACS Abstracts, February 15, 1995.



Figure 1. Structure of C₁₈S and its photodimerization scheme.

photodimerization of $C_{18}S$ as a function of *d* was determined by the IRA spectroscopy; at the same time, the intensity and quantum efficiency of the fluorescence at 490 nm were measured to obtain information on the radiative and nonradiative energy transfer processes paralleling the photodimerization reaction. The results reveal new aspects of the reactions, as will be discussed in detail in the following sections.

Experimental Section

Materials. $C_{18}S$ was synthesized as a *p*-chlorobenzenesulfonate salt by the literature method¹² and purified by recrystallization from 2-propanol. The purity of the sample was checked by measuring a ¹H-NMR spectrum by the use of a 400-MHz JEOL GSX-400 NMR spectrometer. The spectrum confirmed that $C_{18}S$ assumed a trans conformation with respect to the central C=C bond.

Substrates. A silver film of 100 nm was prepared on a glass slide by a thermal evaporation method. A GaAs wafer (Sumitomo Electronics Co. Ltd.) was washed successively with trichloroethylene, acetone, Semikoclean (Furuuti Chemicals Co. Ltd.) and finally purified water for 10 min in an ultrasonic bath.

Fabrication of LB Film Samples. A Kyowa Kaimen Kagaku, HBM-AP2, Langmuir trough with a Whilhelmy balance was used for LB film fabrication. Trough water was purified with a Millipore water purification system (Milli-Q, 4-bowl), and the pH value was adjusted to 6.8 in order to make DA taking an acidic form in the LB film. A monolayer was spread on the trough water at 20 °C by dropwise addition of a sample solution in chloroform (C₁₈S:DA = 1:4, 5×10^{-3} mol/L). Monolayers were transferred to the substrate by a vertical dipping method, at a surface pressure of 30 mN/m and a dipping speed of 10 mm/min. The transfer ratio of the spacer layer on the silver substrate was 0.95 ± 0.05 , while the ratios of odd and even numbers of the mixed LB monolayers were 0.97 and 0.92, respectively. The transfer ratio of the spacer layers on a GaAs substrate was 1.00 ± 0.05 , and those of even and odd numbers of the mixed LB monolayers were 1.0 and 0.95, respectively. The LB films on silver and GaAs substrates are denoted as (Ag m + n) and (GaAs m + n), respectively; m and n indicate the number of the spacer monolayers of DA and that of the mixed monolayers ($C_{18}S:DA = 1:4$), respectively. *m* was changed in the range 0-11, but n was fixed at 3 for the IRA measurements and for the emission measurements at 77 K. As for the measurement of the fluorescence lifetime at room temperature, n was fixed at 7.

IRA Measurement. Photodimerization of the LB film samples was induced by irradiation at 340 nm; excitation light was obtained from a 150-W xenon lamp through a Hoya U340 filter. IRA spectra were measured by using a JEOL JIR-5500 Fourier-transform infrared spectrophotometer equipped with a liquid nitrogen cooled MCT detector with a resolution of 4 cm⁻¹. IRA spectral changes due to the photoirradiation of the mixed LB monolayers on a silver substrate (Ag 0 + 21) were measured at 100 K by using a homemade cryostat¹³ under a base pressure

of 10^{-9} Torr. The incidence angle was fixed at 80 and 70° for the silver and GaAs substrates, respectively. *p*-Polarization light was used in both cases.

Measurement of Emission Spectra. Fluorescence spectra were measured by using a Hitachi 850 emission spectrophotometer. An Oxford cryostat (DN1754) was used to regulate the sample temperature in the 77–320 K range. Excitation light at 340 nm of the spectrometer induced the photodimerization of $C_{18}S$ in the LB film samples. In contrast to the IRA spectra, the fluorescence spectral changes associated with the photodimerization were measured without irradiation by the 150-W xenon lamp.

Measurement of Relative Quantum Efficiency of Fluorescence. Fluorescence lifetimes were measured by using timecorrelated single photon counting.¹⁴ A low-pressure hydrogen discharge lamp was used as an excitation source; the lamp was operated at a repetition of 30 kHz and with a pulse width of about 2 ns. Samples were irradiated through an interference band-path filter (Toshiba KL-33), and emission was detected through a cut-off filter (Toshiba Y-43) to eliminate scattered light. Data were analyzed with the exponential series method, and the simplex method¹⁵ was applied to optimize the fitting. The decay curves were fitted by a sum of two exponentials

$$G(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$
(1)

where τ_i and A_i (i = 1, 2) represent the lifetime and its statistical weight, respectively. The integrated fluorescence intensity, I, was obtained by the following equation⁹

$$I = \tau_1 A_1 + \tau_2 A_2 \tag{2}$$

and the relative quantum efficiency is defined as $\Phi = I/I_0$, where I_0 is the fluorescence intensity for the sample in the absence of energy transfer.

Results and Discussion

Relation between the Extent of Photodimerization and the Thickness of LB Monolayers. The rate of photodimerization was measured by monitoring the change in the $\nu(C=C)$ band intensity at 1626 cm⁻¹ of C₁₈S induced by 340-nm irradiation of the mixed LB monolayers ($C_{18}S:DA = 1:4$). Figure 2 represents the variations of the band intensities with irradiation time (t) observed for the LB films on silver (part A) and GaAs substrates (part B); the intensity is normalized to the corresponding intensity observed prior to the irradiation. The extent of photodimerization, Θ , is defined as the ratio of the number of photodimerized $C_{18}S$ molecules to the initial number of $C_{18}S$ and can be expressed as $\Theta = 1.0 - R$, where R is the relative intensity of the ν (C=C) band. The LB technique may yield complicated assemblies of $C_{18}S$ in the mixed monolayers. The steady decrease in the relative intensity observed in Figure 2, however, indicates that, as discussed in a previous paper,¹⁰ the C₁₈S molecules in each monolayer exist in a more or less phaseseparated state favorable for photodimerization. From Figure 2 it is clear that the rate and the extent of photodimerization increase with the thickness of the LB monolayers on both the silver and GaAs substrates. The intensities of the ν (C=C) bands of the samples on both substrates measured before irradiation increase linearly with the number of monolayers, at least in the region of n = 1-9; the result indicates that the olefinic double bond of C₁₈S on each substrate keeps a constant orientation in the region. Thus, the reduction in the rate and the extent of photodimerization observed for the LB films with smaller n cannot be explained in terms of an unfavorable stacking state



Figure 2. Relative intensity change of the ν (C=C) band of C₁₈S in the mixed LB films as a function of irradiation time: (A) (Ag 0 + 1 ~ 15), (B) (GaAs 0 + 1 ~ 15) (see text).

of the $C_{18}S$ molecules in these LB films. Presumably, for samples with smaller n, the excitation energy of $C_{18}S$ is nonradiatively transferred to the substrate, which reduces the rate and the extent of photodimerization. If this is the case, the rate and the extent of photodimerization should be significantly affected by the distance between the $C_{18}S$ molecule and the substrates. In order to get more quantitative information, the following experiments were performed using the samples with spacer layers.

Effect of the Spacer Thickness (d) on Photodimerization. Figure 3A,B shows the IRA spectra of (Ag 3 + 3) and (GaAs3 + 3), respectively. It is clear that, after 3 min of irradiation, there occurs an appreciable decrease in the relative intensity of the ν (C=C) band near 1625 cm⁻¹ to the 1644-cm⁻¹ band due to a ring stretching vibration of the pyridiniumyl group; the decrease is ascribed to the photodimerization of $C_{18}S^{10}$ Although the signal/noise ratio of the ν (C=C) band for (GaAs 3 + 3 (Figure 3(B)) is rather poor compared to that for (Ag 3 + 3) (Figure 3A), accurate estimation of the rate and the extent of photodimerization still can be made. Figure 4A,B represents the relative intensity of the ν (C=C) band against irradiation time for (Ag $0 \sim 7 + 3$) and (GaAs $1 \sim 9 + 3$), respectively. The results establish that both the rate and the extent of the photodimerization reaction increase with d. However, the band intensities prior to the irradiation for each series of the LB films are almost constant, irrespective of d. This means that the orientation of $C_{18}S$ relative to the surfaces is almost the same for each series and that the reduction in the rate and the extent observed for the samples with smaller m, i.e., smaller d, cannot be ascribed to an unfavorable stacking state. Thus, the results confirm that the reduction arises from an increased nonradiative energy transfer from the excited state of C₁₈S to the substrate.

Effect of the Spacer Thickness (d) on Excimer Fluorescence. Figure 5 shows the emission spectra for (Ag $0 \sim 13 + 3$) and (GaAs $0 \sim 15 + 3$); they give rise to a broad band around

490 nm without vibrational structure even at 77 K, indicating that the emission is due to the fluorescence of excimers.¹² Up to T = 200 K, photodimerization does not take place under irradiation of excitation light at 340 nm (vide infra). When d is reduced, the fluorescence intensity (I) decreases appreciably. This is clarified by plotting I against d, as shown in Figure 6, where I is normalized to the intensity (I_0) observed for a sample in which the nonradiative energy transfer is absent; I_0 was measured by inserting a glass plate with a thickness of 1 mm between the mixed LB monolayers and the substrates. (Each value of I was obtained immediately after the beginning of the measurement because, as shown in Figure 10, I increases with time at 77 K.) The relative quantum efficiency (I/I_0) , obtained by the steady-state fluorescence measurement, may be affected noticeably by the interference effects at surfaces.^{4,9} In order to exclude such effects and to obtain a more reliable relative quantum yield (Φ), the fluorescence lifetime measurement was performed at room temperature. The result for (Ag $0 \sim 27 +$ 7) is summarized in Figure 7. Since excitation light used for the lifetime measurement was very weak, photodimerization can be ignored. In the case of (GaAs $0 \sim 15 + 7$), a precise measurement of Φ could not be performed because the fluorescence intensities at room temperature were very weak, especially for samples with smaller m. The feature of the plot in Figure 7 is similar to that observed for (Ag $0 \sim 9 + 3$) in Figure 6. From Figures 6 and 7, we can recognize that the fluorescence intensity for the LB films on silver shows a rapid increase in the region of m = 0-9 and attains a constant value for $m \ge 12$. On the other hand, the fluorescence intensity of the LB films on GaAs shows only a slight increase with m below 9, and an abrupt increase for $m \ge 9$. Thus, there is an appreciable difference in the dependence of the fluorescence intensity on the spacer thickness between the LB films on silver and those on GaAs.



Figure 3. IRA spectral changes in the 1580-1680-cm⁻¹ region induced by irradiation at 340 nm for 3 min: (A) (Ag 3 + 3), (B) (GaAs 3 + 3).

The rate constant, k, of the deactivation process of an excimer state on a solid substrate can be expressed by

$$k = k_{\rm nr} + k_{\rm i} + k_{\rm r} + k_{\rm d},\tag{3}$$

where k_{nr} , k_i , k_r , and k_d are the rate constants for nonradiative deactivation, nonradiative energy transfer from the excimer to the substrate, radiation, and photodimerization reaction, respectively. The quantum efficiency of excimer fluorescence, η , is defined by

$$\eta = \frac{k_{\rm r}}{k_{\rm nr} + k_{\rm i} + k_{\rm r}} \tag{4}$$

for the case where the photodimerization does not take place (i.e., $k_d = 0$). When nonradiative energy transfer due to the interaction with the surfaces can also be ignored (i.e., $k_i = 0$), the corresponding quantum efficiency, q, is expressed as follows:

$$q = \frac{k_{\rm r}}{k_{\rm nr} + k_{\rm r}} \tag{5}$$

It can be assumed that the ratio, η/q , is equal to the relative

intensity of excimer fluorescence, I/I_0 , obtained from the lifetime measurements, i.e.

$$\frac{I}{I_0} = \frac{\eta}{q} \tag{6}$$

From eqs 4, 5, and 6, we obtain

$$\frac{I_0}{I} - 1 = \frac{k_i}{k_r} q \tag{7}$$

Under the assumption that the ratio of the decay rates, k_i/k_r , depends on

$$\frac{k_{\rm i}}{k_{\rm r}} = \beta d^{-\gamma} \tag{8}$$

where β is a constant and *d* is the distance between an excited molecule (i.e., an excimer state of C₁₈S) and the substrate surface, and from eqs 7 and 8, the following equation is obtained:

$$\log\left(\frac{I_0}{I} - 1\right) = -\gamma \log d + \log(\beta q) \tag{9}$$



Figure 4. Relative intensity change of the ν (C=C) band of C₁₈S in the mixed LB films as a function of irradiation time: (A) (Ag 0 ~ 7 + 3), (B) (GaAs 1 ~ 9 + 3).



Figure 5. Fluorescence spectra of $C_{18}S$ at 77 K for the mixed LB films with various numbers of spacer layers: (A) (Ag $0 \sim 13 + 3$), (B) (GaAs $0 \sim 15 + 3$).

Values of $\log(I_0/I - 1)$ derived from Figure 6 are plotted against log d in Figure 8; d is expressed by the number (m) of the spacer monolayers. The solid line drawn along the data for the GaAs substrate and the dashed line along the data for the silver substrate correspond to $\gamma = 3$ and 1, respectively. The lines reproduce the experimental results except for smaller d. (As it



Figure 6. Relative intensity change of the excimer fluorescence of $C_{18}S$ at 77 K in the mixed LB films as a function of the number (m) of spacer layers: (D) data for (Ag $0 \sim 11 + 3$), (**D**) data for (GaAs $0 \sim 15 + 3$).

can be recognized from Figure 5, the fluorescence intensity is very weak for the LB films with smaller m. Hence, the plot for m = 1 on the silver substrate and those for $m \le 5$ on the GaAs substrate in Figure 8 may be subject to large error.) If the reduction in the fluorescence efficiency is caused by the nonradiative energy transfer due to the Förster-type dipoledipole interaction mechanism, the rate, k_i , should depend on d^{-3} (i.e., $\gamma = 3$).³ The rate for the LB films on the GaAs substrate in the region of $m \ge 7$ agrees with the prediction. On the other hand, the energy transfer rate for the LB films on the



Figure 7. Relative quantum yield change of the excimer emission of $C_{18}S$ at room temperature in the mixed LB films on the silver substrate as a function of the number (m) of spacer layers (see text).



Figure 8. Plots of $\log (I_0/I - 1)$ vs $\log (m)$ derived from the data in Figure 5: (\Box) Data for the silver substrate, (\blacksquare) data for the GaAs substrate. A solid line drawn along the data for the GaAs substrate and a dashed line along the data for the silver substrate correspond to eq 9 with $\gamma = 3$ and 1, respectively.

silver substrate shows a d^{-1} dependence, which is a large deviation from the classical theory.⁴⁻⁹ Presumably, other factors which contribute at smaller *d*, such as electron—hole and/or surface—plasmon excitations, may explain the deviation. More experimental as well as theoretical studies are needed to obtain better understanding about the d^{-1} dependence of k_i .

Relation between the Extent of Photodimerization and the Fluorescence Intensity. The extents of photodimerization, Θ_d , obtained from the *R* values at t = 30 s in Figure 4A,B, are plotted against m in Figure 9. The reaction extents for the LB films on the silver substrate increase precipitously in the region of m = 0-3 and level off in the region above 7. On the other hand, the extents for the GaAs substrate are much reduced in the region of m = 0-3 and show a steady increase in the region above 3.



Figure 9. Plots of the reaction extent (Θ_d) versus the number of the spacer layers (m) (see text): (\Box) data for the silver substrate, (\blacksquare) data for the GaAs substrate. A solid line drawn along the data for the GaAs substrate and a dashed line along the data for the silver substrate indicate the values calculated by using the eq 12 with $\gamma = 3$ and 1, respectively.

 Θ_d is proportional to the quantum efficiency, Φ_d , of the photodimerization reaction. If Φ_d is represented in a manner similar to that in eq 4, the following equation is obtained:

$$\Phi_{\rm d} = c\Theta_{\rm d} = \frac{ck_{\rm d}}{k_{\rm nr} + k_{\rm i} + k_{\rm r} + k_{\rm d}} \tag{10}$$

where c is a constant. By defining the extent and quantum efficiency of the reaction in the absence of energy transfer as Θ_{d0} and Φ_{d0} , respectively, we obtain the following equation:

$$\frac{\Phi_{\rm d}}{\Phi_{\rm d0}} = \frac{\Theta_{\rm d}}{\Theta_{\rm d0}} = \frac{1}{1 + \frac{k_{\rm i}}{k_{\rm nr} + k_{\rm r} + k_{\rm d}}} \tag{11}$$

The value of $k_{nr} + k_r + k_d$ can be considered as a constant because it is independent of the spacer thickness. Then, eq 11 leads to the following equation by using eq 8

$$\Theta_{d} = \frac{\Theta_{d0}}{1 + \left(\frac{\alpha}{d}\right)^{\gamma}}$$
(12)

where α denotes $\{\beta k_r/(k_{nr} + k_r + k_d)\}^{1/\gamma}$ and has a physical meaning of the spacer thickness corresponding to $\Theta_d = \Theta_{d0}/2$. The solid line along the data for the GaAs substrate in Figure 9 indicates the values calculated by using eq 12 with $\gamma = 3$ ($\alpha = 6.7$), and the dashed line along the data for the silver substrate, the calculated values with $\gamma = 1$ ($\alpha = 1.3$). The calculated values fit well with the experimental points, indicating that the method of the analysis of the fluorescence intensities in the preceding section can also be applied to the analysis of the extent of photodimerization. The result confirms that photodimerization on the silver and GaAs substrates proceeds through the formation of excimers. The fit between the calculated and the experimental values in Figure 9 proves that the reduction in the rate of photodimerization for the LB films on both the silver



Figure 10. Relative intensity change of the excimer fluorescence of $C_{18}S$ in the mixed LB film (Ag 0 + 15) as a function of irradiation time at various temperature.

and GaAs substrates with smaller m is mainly due to the enhanced nonradiative energy transfer from the excimers to the substrate.

Temperature Dependence of the Emission Spectra on the Silver Substrate. In order to gain insight into the temperature dependence of the photodimerization of $C_{18}S$ in the mixed LB films, the fluorescence intensity at 490 nm was recorded for (Ag 0 + 15) with irradiation time (t) at various temperatures; the results are illustrated in Figure 10, in which the intensity is normalized to the value at t = 0. In the temperature range above 300 K, the intensity decreases with t, which is explained by the occurrence of photodimerization induced by the excitation light (340 nm) for the fluorescence measurement. In the temperature range 77–200 K, the intensity does not show any decrease, but instead increases with t. These intensity changes as a function of t can be approximated by the following exponential functions:

$$I_{\rm L} = 1.6 - 0.6 \exp(-k_{\rm L}t) \quad (77 \le T \le 200 \text{ K}) \quad (13)$$

$$I_{\rm H} = 1.0 \exp(-k_{\rm H}t) \quad (296 < T < 320 \text{ K})$$
 (14)

The rate constants, k_L and k_H , which determine the features of the intensity changes in the lower and higher temperature ranges, respectively, are plotted against 1/T in Figure 11. From the slopes of the Arrhenius plots, the activation energy was calculated to be 0.84 kJ/mol for the lower temperature process and 28.35 kJ/mol for the higher temperature one (i.e., the photodimerization). As can be seen from Figure 10, the fluorescence intensity at first increases and then gradually decreases at 280 K; such a behavior is observed for the intensity



Figure 11. Arrhenius plots of $\ln(k_L)$ vs 1/T (A) and $\ln(k_H)$ vs 1/T (B) (see text)

change in the temperature range 200-290 K. This feature can be explained as a composite of the two processes mentioned above and approximated by the following equation:

$$I_{\rm M} = \{1.6 - 0.6 \exp(-k_{\rm L}t)\} \exp(-k_{\rm H}t)$$
(15)

The change at 280 K can be well reproduced with the following values: $k_{\rm L} = 0.068 \text{ s}^{-1}$ and $k_{\rm H} = 0.027 \text{ s}^{-1}$. The values of $k_{\rm L}$ and $k_{\rm H}$ calculated by using the activation energies are 0.114 and 0.022 s^{-1} , respectively. While the calculated and experimental values of $k_{\rm H}$ are in good agreement, the calculated $k_{\rm L}$ value is almost two times larger than the experimental one. The disagreement in $k_{\rm L}$ is explained as that the fitting in terms of eq 13 is rather phenomenological and the equation does not have a physical meaning; a qualitative interpretation of the photophysical process with a rate constant $k_{\rm L}$ is discussed below. Contrarily, $k_{\rm H}$ has a mechanistic significance. It represents the rate constant of the dissociation of excimers, which leads to dimerization. The activation energy for this process, 28.4 kJ/ mol, is considered as the energy necessary for an excimer to undergo a stereospecific change in forming a dimer. Presumably, only very few molecules can acquire enough thermal energy to surmount this energy barrier below 200 K, resulting in an apparent absence of the dimerization process at that temperature range.

In order to account for the origin of the fluorescence intensity increase observed below 200 K, the IRA spectral changes due to irradiation at 340 nm were measured at 100 K for a mixed LB film consisting of 21 monolayers on a silver substrate, (Ag 0 + 21). The 1628- and 1645-cm⁻¹ bands, which are assigned to ν (C=C) and a stretching vibration of the pyridiniumyl moiety of C₁₈S, respectively, show appreciable intensity changes. Figure 12 summarizes these intensity changes together with that of the 879-cm⁻¹ band; the 879-cm⁻¹ band has been assigned to a CH out-of-plane vibration of the olefinic moiety and disappears upon dimerization of C₁₈S.¹⁰ On irradiation at 100 K, however, the 879-cm⁻¹ band shows appreciable intensity increase, indicating that the photodimerization does not take place. The irradiation at 100 K did not cause the appearance of the 891and 781-cm⁻¹ bands, which are due to a cis form of C₁₈S.¹⁰ On the basis of these results, it is concluded that the intensity changes are due to an orientation change of $C_{18}S$ in the LB films. The appreciable intensity decrease in the ν (C=C) band indicates that the change proceeds from a less tilted orientation



Figure 12. Relative intensity changes of the IRA bands at 1645 (\Box), 1628 (\odot), and 879 cm⁻¹ (\blacktriangle) for a mixed LB film (Ag 0 + 21) at 100 K as a function of irradiation time. (see text).

of the C=C bond to a more tilted one with respect to the surface normal of the silver substrate. Presumably, the orientations of $C_{18}S$ in the original LB films are thermodynamically in a metastable state (or a trapped state). During the repetition of formation and dissociation of excimers, there proceeds a conversion of the orientation to a more stable state, which favors the formation of an excimer and gives stronger excimer fluorescence. In addition to the intensity increase in the temperature range 77–200 K, we also observed a slight blue shift of the fluorescence (not shown in this paper), which suggests that a change in the molecular orientation has occurred.

Conclusions

IRA and fluorescence spectroscopies were applied to study the effect of nonradiative energy transfer from an excimer of $C_{18}S$ to substrate surfaces (silver and GaAs) on its photodimerization reaction. The reaction extent and the relative quantum efficiency of excimer fluorescence were measured as a function of the distance (d) from C₁₈S to the substrate. The results show that the nonradiative energy transfer appreciably reduces the photodimerization reaction and the reaction proceeds through the formation of an excimer. The *d* dependence of the reaction rate and the fluorescence efficiency for the samples on the GaAs substrate is explained by the classical Förster-type dipole—dipole interaction between the excited state and the substrate. However, those for the samples on the silver substrate cannot be explained in terms of the classical theory. More experimental as well as theoretical studies are needed to elucidate these points.

The temperature dependence of the photodimerization process of $C_{18}S$ embedded in the LB films of DA on silver was also studied. The results show that photodimerization of $C_{18}S$ with an activation energy of 28.4 kJ/mol proceeds mainly upon irradiation at 340 nm in the temperature range above 300 K. On the other hand, in the temperature range below 200 K, the dimerization does not take place and there is an appreciable increase in excimer fluorescence with an activation energy of 0.84 kJ/mol. This is interpreted as due to a change in the molecular orientation on the substrate, caused by photophysical processes in the LB films.

References and Notes

(1) Drexhage, K. H. In Progress in Optics; Wolf, E., Ed.; North Holland: Amsterdam, 1974; Vol. VII.

(2) Kuhn, H. J. Chem. Phys. 1970, 53, 101.

(3) Chance, R. R.; Prock, A.; Silbey, R. In Advances in Chemical Physics; Prigogine, I., Rice, S. A., Eds.; Wiley: New York, 1978; Vol. 37, p 1.

(4) Waldeck, D. H.; Alivisatos, A. P.; Harris, C. B. Surf. Sci. 1985, 158, 103.

(5) Goncher, G. M.; Parsons, C. A.; Harris, C. B. J. Phys. Chem. 1984, 88, 4200.

- (6) Hayashi, T.; Caster, T. G.; Boyd, R. W. Chem. Phys. Lett. 1983, 94, 461.
 - (7) Weber, W. H.; Eagen, C. F. Opt. Lett. 1979, 4, 236.
 - (8) Avouris, P.; Persson, B. N. J. J. Phys. Chem. 1984, 88, 837.
- (9) Ohshima, S.; Kajiwara, T.; Hiramoto, M.; Hashimoto, K.; Sakata, T. J. Phys. Chem. 1986, 90, 4474.

(10) Yamamoto, M.; Wajima, T.; Kameyama, A.; Itoh, K. J. Phys. Chem. 1992, 96, 10365.

(11) Itoh, K.; Yamamoto, M.; Wajima, T. J. Mol. Struct. 1993, 293, 311.

- (12) Quina, F. H.; Whitten, D. G. J. Am. Chem. Soc. 1977, 99, 877.
- (13) Fujii, S.; Osaka, N.; Itoh, K. Surf. Sci. 1994, 306, 381.
- (14) O'Connor, D. V.; Phillips, D. Time-Correlated Single Photon Counting; Academic Press, Inc.: Orlando, FL, 1984.

(15) Deming, W. D. Statistical Adjustment of Data; John Wiley: New York, 1943.

JP942523X