BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(2), 437—441 (1976)

Triplet Excimer of Phenanthrene in Fluid Solution. Dynamic Analysis of Time-Resolved Phosphorescence

Masayuki Aikawa, Takeshi Takemura, and Hiroaki Baba

Division of Chemistry, Research Institute of Applied Electricity, Hokkaido University, Sapporo 060

(Received October 27, 1975)

The excimer phosphorescence of phenanthrene in isooctane at temperatures over a range of 300—77 K has been studied by means of a photon-counting technique. At temperatures above the melting point of isooctane a broad emission spectrum with its intensity maximum at 525 nm was obtained, which is essentially different from the structured phosphorescence spectrum obtained in rigid media at 77 K. The time dependence of the spectral shape and intensity of the phosphorescence emission affords strong evidence that the broad emission spectrum originates from the triplet excimer. A scheme of the triplet excimer formation involving a self-quenching pathway of the triplet monomer is proposed to interpret the time and concentration dependence of the monomer and excimer phosphorescence.

Although there have been many studies on the triplet excimer of aromatic hydrocarbons, the occurrence of excimer phosphorescence in solution has not yet been established.[1–4] In previous papers we have confirmed the existence of the triplet excimer for naphthalene and 1-chloronaphthalene in 2,2,4-trimethylpentane (isooctane) at 293 K through the photostationary and transient phosphorescence measurements.[5,6]

Langelaar *et al.* first reported the excimer phosphorescence of phenanthrene in viscous solution, but they have subsequently shown that the emission was due to an impurity.[7,8] They have also shown, however, kinetic evidence in favor of triplet excimer formation in some aromatic hydrocarbons including phenanthrene in fluid solutions.[9,10] On the other hand, in a study on the photo-dissociation of the *cis* dimer of 9-(hydroxymethyl)phenanthrene and other phenanthrene derivatives in a rigid matrix at 77 K, Chandross and Thomas have concluded that phenanthrene does not form a triplet excimer as well as a singlet excimer even under favorable conditions.[11] Thus, it is necessary to further study the phenanthrene triplet in fluid solution in order to settle the question whether the triplet excimer does exist.

In the present work, we have observed a broad phosphorescence spectrum with a maximum near 525 nm for phenanthrene in isooctane solution at 187 or 293 K. This spectrum is essentially different from the structured phosphorescence spectrum of phenanthrene obtained in EPA at 77 K. The broad spectrum may be attributed to emission either from an impurity triplet produced by T–T energy transfer or from the triplet excimer of phenanthrene. In order to elucidate this problem we measured time-resolved spectra of phenanthrene phosphorescence in fluid solution. An analysis of the time-dependent behavior of the phosphorescence after flash excitation leads to strong evidence that the phenanthrene triplet excimer exists even in fluid solution.

Experimental

A sample of commercial phenanthrene was purified carefully by the following successive processes. To remove a small quantity of anthracene from phenanthrene, the sample was refluxed with maleic anhydride in spectro-grade benzene for 20 hours. The mixture was filtered, the filtrate was shaken with a sodium hydroxide solution, and phenanthrene contained in the organic layer was freed from the solvent by distilling the latter under reduced pressure.[12,13] The sample was then recrystallized several times from spectroquality ethanol, passed through a silica-gel column with petroleum benzine as the solvent, and finally sublimed *in vacuo*. Spectro-grade isooctane was also treated with a silica-gel column. The solution of phenanthrene in 1 cm square quartz cell was fully degassed by repeated freeze-thaw cycles (7 or 8 times).

Emission and excitation spectra were measured with a high-resolution, high-sensitivity photon-counting emission spectrophotometer constructed in our laboratory. The time-resolved phosphorescence spectra, as well as the intensity of phosphorescence or delayed fluorescence emission as a function of time, were measured with the aid of a spectrophosphorimeter which was designed, on the basis of the photon-counting method, for obtaining emission decay curves in a time range of 10^2 to 10^{-5} s. In this phosphorimeter, either a continuous Xe arc lamp combined with a light-chopping system or a Xe flash lamp was used as a pulsed light source. The design and performance of these two apparatuses have been described in a previous paper.[6]

The phosphorescence spectra were corrected for the spectral sensitivity of the monochromator-photomultiplier system after the method reported in a previous paper[14] using a standard tungsten filament lamp. The phosphorescence quantum yields were determined by comparing the corrected phosphorescence spectra with a corrected fluorescence spectrum of quinine sulfate in 0.5 M sulfuric acid, which has a fluorescence quantum yield of 0.51.

Results

Figure 1 shows the phosphorescence spectra of phenanthrene in isooctane at 77 K and 187 K. In the spectrum at 187 K a broad emission band is seen near 525 nm which is absent at 77 K. A phosphorescence spectrum similar to that at 187 K was also obtained at 293 K. The structured phosphorescence band at 187 K or at 293 K in a region near 470 nm, which is practically identical with the spectrum at 77 K in location and band shape, can be attributed to the monomer phosphorescence emission of phenanthrene. The excitation spectrum in fluid solution monitored at the 520 nm emission peak (Fig. 1), as well as that monitored at 465 nm, is in good agreement with the absorption spectrum. This suggests that the broad emission band originates from phenanthrene itself.

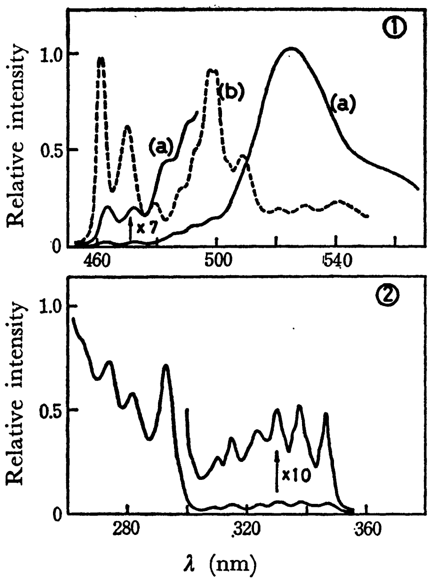


Fig. 1. Corrected phosphorescence and excitation spectra of phenanthrene in isooctane $(2.5 \times 10^{-5}\ \mathrm{M})$. (1) Phosphorescence spectrum: **a**, at 187 K; **b**, at 77 K. (2) Excitation spectrum at 187 K, monitored with respect to the 520 nm phosphorescence peak.

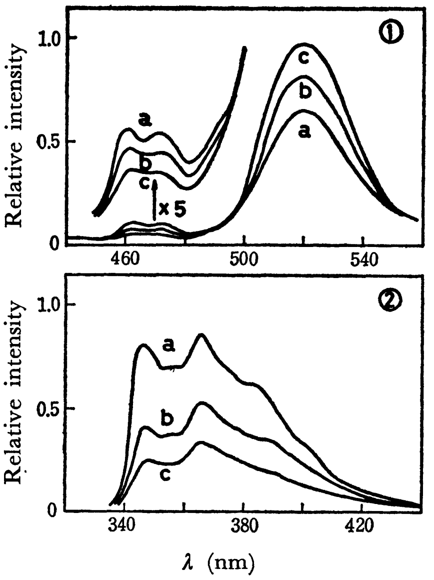


Fig. 2. Time-resolved phosphorescence (1) and delayed fluorescence (2) spectra in isooctane $(1 \times 10^{-4}\ \mathrm{M})$ at 293 K (uncorrected for instrumental response). The spectra denoted by **a**, **b**, and **c** were observed at 140, 305, and 635 μs, respectively, after flash excitation.

The time-resolved phosphorescence and delayed fluorescence spectra in isooctane at 293 K are shown in Fig. 2. The intensities of both the phosphorescence at about 465 nm and the delayed fluorescence decrease monotonously with time after flash excitation, whereas the broad structureless band with its maximum at about 525 nm grows with time.

The emission intensity as a function of time after flash excitation, monitored at a given wavelength, will be denoted by $I(t)$. Figure 3 illustrates the $I(t)$ curves for phosphorescence in isooctane at 293 and 187 K. The $I(t)$ curve observed at 465 nm and at 187 K is composed of two exponential decays but that at 293 K represents a first order decay within our experimental errors. On the other hand, the $I(t)$ curve detected at 520 nm shows a rise for small values of t and decay for large t. It is also seen that the value of t at which $I(t)$ reaches a maximum becomes much smaller on increasing the phenanthrene concentration. We can thus assign the broad emission band with the intensity maximum at about 525 nm to the triplet excimer of phenanthrene on the basis of the following considerations.

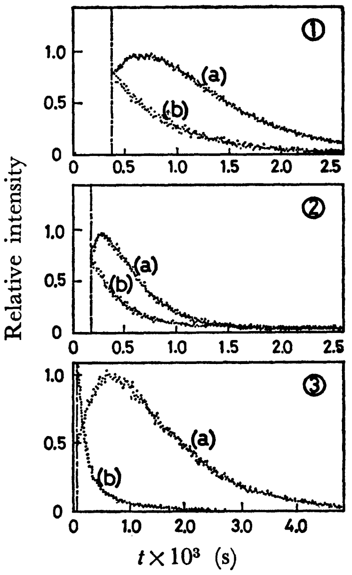


Fig. 3. Some representative $I(t)$ curves for phenanthrene in isooctane. Temperatures and solute concentrations: (1) 293 K, 1.8×10^{-4} M; (2) 293 K, 1.24×10^{-3} M; (3) 187 K, 2.1×10^{-3} M. Monitoring wavelengths: **a**, 465; **b**, 520 nm. Dashed lines show the time width of pulsed light source.

Under our experimental conditions where the excitation intensity is low and the solution is of very low viscosity, the kinetic scheme for the deactivation of the triplet states involving the triplet excimer formation may be expressed in general as follows:[9,15]

$$\begin{tikzcd}[column sep=small] {}^3\mathrm{M}^* \arrow[d, shift right] \arrow[d, squiggly, shift left] & + & {}^1\mathrm{M} \arrow[r, shift left, "\vec{k}"] & {}^3\mathrm{D}^* \arrow[l, shift left, "\overleftarrow{k}"] \arrow[d, shift right] \arrow[d, squiggly, shift left] \\ k_{1\mathrm{r}}\ \ k_{1\mathrm{q}} & & & k_{2\mathrm{r}}\ \ k_{2\mathrm{q}} \end{tikzcd} \tag{1}$$

Here, ^{1}M, ^{3}M*, and ^{3}D* stand for the ground singlet monomer, excited triplet monomer, and excited triplet dimer (triplet excimer), respectively; k_{1r}, k_{1q}, k_{2r}, and k_{2q} are the radiative (r) and non-radiative (q) decay constants for the triplet monomer and excimer; and $\vec{k}$ and $\overleftarrow{k}$ denote the rate constants for the formation and dissociation of the triplet excimer, respectively.

Delayed fluorescence could be observed because of its high intensity. The triplet–triplet annihilation, however, need not be considered in the scheme, since the triplet concentration in our experiments was so low that the annihilation should not contribute appreciably to the triplet decay. The decay rate constant for the delayed fluorescence observed is twice the rate constant obtained from the tail portion of the phosphorescence $\boldsymbol{I}(t)$ curve at 465 nm (see Fig. 2).

Solution of the rate equations for the kinetic scheme (1), under the appropriate initial conditions, yields the following expressions for the quantum intensity of the monomer and excimer phosphorescence at time t.

$$\boldsymbol{I}_{\mathrm{m}}(t) = \frac{k_{1\mathrm{r}}(\theta_2 - X)}{(\theta_2 - \theta_1)}\{\mathrm{e}^{-\theta_1 t} + A\mathrm{e}^{-\theta_2 t}\} \tag{2}$$

$$\boldsymbol{I}_{\mathrm{d}}(t) = \frac{k_{2\mathrm{r}}\overrightarrow{k}[{}^1\mathrm{M}]}{(\theta_2 - \theta_1)}\{\mathrm{e}^{-\theta_1 t} - \mathrm{e}^{-\theta_2 t}\} \tag{3}$$

where

$$\theta_{1,2} = \frac{1}{2}[X + Y \mp \{(Y - X)^2 + 4\overrightarrow{k}\overleftarrow{k}[{}^1\mathrm{M}]\}^{1/2}] \tag{4}$$

and

$$\begin{aligned} A &= (X - \theta_1)/(\theta_2 - X) \\ X &\equiv k_1 + \overrightarrow{k}[{}^1\mathrm{M}] \qquad k_1 = k_{1\mathrm{r}} + k_{1\mathrm{q}} \\ Y &\equiv k_2 + \overleftarrow{k} \qquad\qquad\quad k_2 = k_{2\mathrm{r}} + k_{2\mathrm{q}} \end{aligned} \tag{5}$$

Equations (2) and (3) predict that the monomer should display a curve consisting of two exponential decays and that the excimer phosphorescence should yield a rise-and-decay curve. The $\boldsymbol{I}(t)$ curves monitored at 465 and 520 nm correspond well to $\boldsymbol{I}_{\mathrm{m}}(t)$ given by Eq. (2) and $\boldsymbol{I}_{\mathrm{d}}(t)$ given by Eq. (3), respectively. This provides the conclusive evidence that the emission at 520 nm is due to the triplet excimer of phenanthrene.

For both $\boldsymbol{I}(t)$ curves monitored at 465 and 520 nm, the plot of log $\boldsymbol{I}(t)$ *vs.* t at long times after flash excitation gives the first-order decay constant, θ_1. The value of θ_2 can be obtained from the difference between the $\boldsymbol{I}(t)$ curve observed for the excimer emission and the first order decay curve extrapolated towards shorter times by the use of θ_1. The θ_2 value can also be obtained by using the initial part of the $\boldsymbol{I}(t)$ curve for the monomer.

The initial decay related to θ_2 was observed in the monomer $\boldsymbol{I}(t)$ curve at 187 K, but not at 293 K. This is because the excitation pulse used was not sufficiently short to monitor the fast decay at 293 K.

There may be a possibility that the broad phosphorescence is ascribed to an impurity emission. Energetically, however, reversible energy transfer is not likely to occur[16,17] owing to a large energy difference between the phosphorescence 0–0 band at 463 nm and the phosphorescence maximum at 520 nm. Therefore, if the emission assigned to the excimer phosphorescence were to be due to an impurity triplet, $^3\mathrm{Q}^*$, the broad phosphorescence should arise from irreversible triplet–triplet energy transfer from phenanthrene to the impurity. In this case, the kinetic scheme (1) is modified by substituting $^1\mathrm{Q}$ for $^1\mathrm{M}$ and $^3\mathrm{Q}^*$ for $^3\mathrm{D}^*$, and the following expression is obtained for the time dependence of the intensity of monomer emission:

$$\boldsymbol{I}_{\mathrm{m}}(t) = C\exp\{-(k_1 + \overrightarrow{k}[{}^1\mathrm{Q}])t\} \tag{6}$$

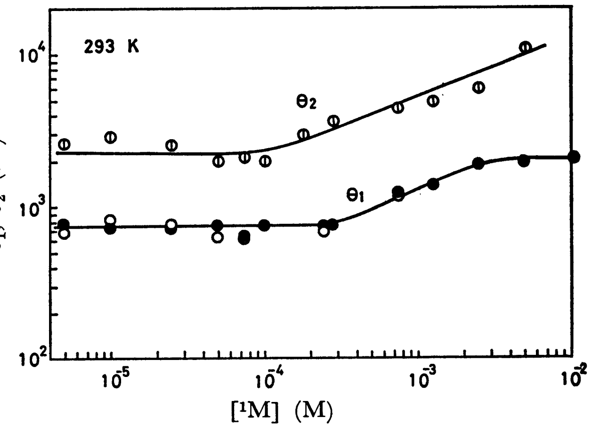


Fig. 4. Plots of θ_1 and θ_2 against the concentration of phenanthrene in isooctane at 293 K. The values of θ_1 are obtained from the $\boldsymbol{I}(t)$ curves monitored at 465 (○) and 520 nm (●), and the values of θ_2 are obtained at 520 nm (⦶).

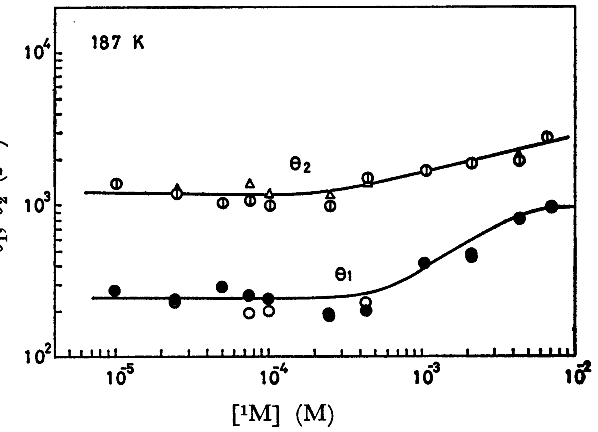


Fig. 5. Plots of θ_1 and θ_2 against the concentration of phenanthrene in isooctane at 187 K. The symbol (△) refers to the values of θ_2 which are obtained from the $\boldsymbol{I}(t)$ curves monitored at 465 nm, and the other symbols are the same as in Fig. 4.

The $\boldsymbol{I}(t)$ curve for the monomer phosphorescence observed at 465 nm is then expected to show a single exponential decay with a rate constant $k_1 + \overrightarrow{k}[{}^1\mathrm{Q}]$. This expectation contradicts the experimental fact that the initial fast decay was observed in the monomer $\boldsymbol{I}(t)$ curve at 187 K, and therefore the possibility of impurity emission is ruled out. Thus additional evidence is obtained that the emission at 525 nm is due to the triplet excimer of phenanthrene.

The plots of θ_1 and θ_2 obtained at 293 K and 187 K against [^{1}M] are shown in Figs. 4 and 5, respectively. As [^{1}M] increases, θ_1 first increases and then reaches a constant value at relatively high values of [^{1}M], while θ_2 increases monotonously. It is also seen from Fig. 5 that the monomer and the excimer $\boldsymbol{I}(t)$ curves at 187 K lead to consistent values both for θ_1 and for θ_2.

The rate constants $\overrightarrow{k}$, $\overleftarrow{k}$, k_1, and k_2 at a given temperature can be evaluated from the data on θ_1 and θ_2 as a function of [^{1}M] by using the following limiting properties.[15] (i) As [^{1}M] becomes small, θ_1 and θ_2

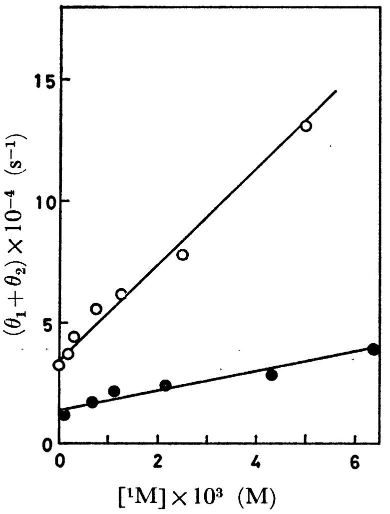


Fig. 6. Plots of $\theta_1+\theta_2$ against the concentration of phenanthrene at 293 (○) and 187 K (●).

Table 1. Rate constants for phenanthrene in isooctane solution

Temperature K	$k_1\times 10^{-2}$ s^{-1}	$k_2\times 10^{-3}$ s^{-1}	$\vec{k}\times 10^{-6}$ $M^{-1} s^{-1}$	$\overleftarrow{k}\times 10^{-3}$ s^{-1}
187	2.5	1.0	0.4	0.2
293	7.5	1.9	2.0	0.6

approach constant values which represent k_1 and $k_2+\overleftarrow{k}$. As shown in Figs. 4 and 5, θ_1 and θ_2 become constant in the concentration range of 10^{-6}—10^{-4} M. (ii) At higher concentrations ($>10^{-2}$ M in the case of phenanthrene), θ_1 becomes k_2. (iii) At any value of $[^1M]$, Eq. (4) yields the following relation:

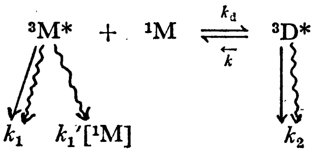
$$\theta_1 + \theta_2 = k_1 + k_2 + \overleftarrow{k} + \vec{k}[^1M] \tag{7}$$

As expected from Eq. (7), the plots of $\theta_1+\theta_2$ against $[^1M]$ (Fig. 6) give good straight lines with slopes, $\vec{k}$ equal to 2.0×10^6 and 0.4×10^6 $M^{-1} s^{-1}$, respectively, at 293 and 187 K. The behavior of θ_1 and θ_2 as predicted from the limiting conditions (i) through (iii) is consistent with our experimental results. The rate constants, $\vec{k}$, $\overleftarrow{k}$, k_1, and k_2 at 293 and 187 K thus determined are summarized in Table 1.

Discussion

The equilibrium constant of the excimer formation reaction (1) in the triplet state is defined as $\boldsymbol{K}_e=\vec{k}/\overleftarrow{k}$, which is calculated to be 3.3×10^3 M^{-1} at 293 K and 2.0×10^3 M^{-1} at 187 K. The energy difference ($\Delta \boldsymbol{E}$) between the 0–0 phosphorescence band of the monomer at 463 nm and the phosphorescence maximum of the triplet excimer at 525 nm is about 2600 cm^{-1} (7.3 kcal). The value of $\boldsymbol{K}_e$ is much the same as those observed in singlet excimers, but the $\Delta \boldsymbol{E}$ value is very small compared with the corresponding values for singlet excimers of aromatic hydrocarbons, in which $\Delta \boldsymbol{E}$ is nearly constant and equal to ~6000 cm^{-1}.[16] The entropy change, $\Delta \boldsymbol{S}$, accompanying the triplet excimer formation is obtained from $\boldsymbol{K}_e$ and $\Delta \boldsymbol{E}$ after the manner in which $\Delta \boldsymbol{S}$ was estimated for the singlet excimer.[15] The absolute value of $\Delta \boldsymbol{S}$ thus determined seems to be too small (less than 1 cal mol^{-1} deg^{-1} at 293 K).

In view of those circumstances, we introduce a self-quenching pathway of $^3M^*$ into the scheme (1):



$$\begin{tikzcd} {}^3M^* + {}^1M \arrow[r, shift left, "k_d"] \arrow[d, squiggly, "k_1"'] \arrow[d, squiggly, shift left=4, "k_1'[^1M]"] & {}^3D^* \arrow[l, shift left, "\overleftarrow{k}"] \arrow[d, squiggly, "k_2"] \\ {} & {} \end{tikzcd} \tag{9}$$

Evidently the rate constants k_1 and $\vec{k}$ defined in the scheme (1) correspond, respectively, to $k_1+k_1'[^1M]$ and k_d in the scheme (9). The values of $\vec{k}$ as determined from the dependence of $\theta_1+\theta_2$ on $[^1M]$ (Eq. (7) and Fig. 6) must then be identified as the values for $k_1'+k_d$. It is conceivable that most of the encounters of the triplet-state monomer with the ground-state lead to the quenching of the former, and thus it is possible that k_1' may be ten times as large as k_d. The rate constant k_d will then be smaller than $\vec{k}$ by a factor of 10; in other words, the photoassociation equilibrium constant, $\boldsymbol{K}_a=k_d/\overleftarrow{k}$ in the scheme (9) may become far smaller than $\boldsymbol{K}_e$. Thus, if we tentatively assume that $\boldsymbol{K}_a=10^2$ M^{-1} at 300 K, we can obtain reasonable values for $\Delta \boldsymbol{S}$, the enthalpy of the triplet excimer formation $\Delta \boldsymbol{H}$, and the repulsion energy between two unexcited monomer molecules $\boldsymbol{I}_G$, using $\Delta \boldsymbol{E}=7.3$ kcal mol^{-1}. The results are: $\Delta \boldsymbol{S}=-10$ cal mol^{-1} deg^{-1}, $\Delta \boldsymbol{H}=-5.5$ kcal mol^{-1}, and $\boldsymbol{I}_G=2$ kcal mol^{-1}.

We believe that the triplet excimer formation of aromatic hydrocarbons is a general phenomenon as in the case of the singlet excimer formation. It is probable that the stabilization responsible for the triplet excimer is due to the charge resonance interaction,[4,17,18] which depends critically on the distance, R, and the orbital overlap between the triplet and ground state molecules contrary to the dipole-dipole interaction.[19] Thus, the triplet excimer formation requires a specific arrangement between the two molecules within the solvent cage. This seems to correspond to the fact that the formation rate constant is much smaller than the diffusion-controlled rate constant, as is shown by our experimental results (Table 1). It may be concluded that the difference between those two rate constants results from the frequency factor.

It is well known that the T–T energy transfer rate in fluid solution is very nearly the diffusion-controlled rate when the triplet level of donor lies higher than that of the acceptor by 3—4 kcal/mol or more.[20–22] T–T energy transfer distance, 6—10 Å between donor and acceptor in fluid solution[23] is much larger than the interaction distance of triplet excimer which may be 3—3.5 Å on the analogy of singlet excimer. The difference between the T–T energy transfer and triplet excimer formation, though both processes require overlaps of the orbitals of the two molecules, is that the former can occur even within one or two encounter with very weak interaction, in comparison with the latter which depends on the suitable overlap. There have been many negative results about the problem whether or not the orientation is detectable for the T–T energy transfer in solution.[24,25] Our result suggests, however, that the triplet excimer formation needs specific and critical requirement for the orientation between two molecules.

In the concentration range used in our experiments, the precursor of the triplet excimer is very likely the triplet monomer rather than the singlet excimer. In higher concentration region, the possibility of the latter cannot be ruled out.

References

1) G. Castro and R. M. Hochstrasser, *J. Chem. Phys.*, **45**, 4352 (1966).

2) E. C. Lim and S. K. Chakrabarti, *Mol. Phys.*, **13**, 293 (1967).

3) C. T. Lin and M. A. El-Sayed, *Chem. Phys.*, **5**, 315 (1974).

4) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **41**, 3131 (1964).

5) T. Takemura, H. Baba, and Y. Shindo, *Chem. Lett.*, 1091 (1974).

6) T. Takemura, M. Aikawa, and H. Baba, *J. Amer. Chem. Soc.*, in press.

7) J. Langelaar, R. P. H. Rettschnick, A. M. F. Lambooy, and G. J. Hoytink, *Chem. Phys. Lett.*, **1**, 609 (1968).

8) J. Langelaar, Thesis, University of Amsterdam (1969).

9) J. Langelaar, R. P. H. Rettschnick, and G. J. Hoytink, *J. Chem. Phys.*, **54**, 1 (1971).

10) J. Langelaar, G. Jansen, R. P. H. Rettschnick, and G. J. Hoytink, *Chem. Phys. Lett.*, **12**, 86 (1971).

11) E. A. Chandross and H. T. Thomas, *J. Amer. Chem. Soc.*, **94**, 2421 (1972).

12) D. D. Phillips, "Organic Syntheses," Vol. 34, p. 31 (1954).

13) L. Feldman, P. Pantages, and M. Orchin, *J. Amer. Chem. Soc.*, **73**, 4341 (1951).

14) H. Baba and S. Suzuki, This Bulletin, **35**, 683 (1962).

15) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London (1970), p. 301.

16) J. B. Birks, M. D. Lumb, and I. H. Munro, *Proc. Roy. Soc.*, **A280**, 289 (1964).

17) J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1964).

18) S. I. Choi, J. Jortner, S. A. Rice, and R. Silbey, *J. Chem. Phys.*, **41**, 3294 (1964).

19) M. Inokuti and F. Hirayama, *ibid.*, **43**, 1978 (1965).

20) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960); K. Sandros, *ibid.*, **18**, 2355 (1964).

21) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

22) P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968).

23) T. Takemura, M. Aikawa, and H. Baba, This Bulletin, **47**, 2476 (1974).

24) K. B. Eisenthal, *J. Chem. Phys.*, **50**, 3120 (1969).

25) A. Adamczyk and D. Phillips, *J. Chem. Soc., Faraday II*, **70**, 537 (1974).