THE HYDROGEN BONDING EFFECT OF PYRIDINE ON THE DEACTIVATION OF THE EXCITED STATES OF ACRIDONE

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(Received January 15, 1976)

Summary

The interaction between the ground and excited acridone and pyridine has been investigated by an emission–absorption flash and a laser technique. The hydrogen bonding equilibrium was observed in the ground state (K = 4.5 M^{-1} at 22 °C). The triplet acridone interacts with pyridine (rate constant, $8 \times 10^8 \ M^{-1} \ s^{-1}$) to produce the hydrogen-bonded triplet which decays with the rate constant of $3.3 \times 10^6 \ s^{-1}$ in benzene, yielding the radical which is stable even in the presence of oxygen. The fluorescence yield and the lifetime increase considerably by the hydrogen bond formation with pyridine. In pyridine where all of acridone seems to be hydrogen-bonded, the radical formation from the singlet excited state was not observed. Since $\Phi_{ST} + \Phi_f \simeq$ 1 in benzene and 0.37 in pyridine, it was concluded that the deactivation other than fluorescence and intersystem crossing is enhanced by the hydrogen bond formation.

Introduction

It is well-known that fluorescence is quenched thoroughly by the formation of hydrogen bond between two π-electronic systems [1]. This phenomenon was conceptionally explained by Mataga *et al.* to be the delocalization of π-electrons through hydrogen bond.

Recently, Rehm and Weller [2] studied theoretically the quenching mechanism and proposed that the spontaneous H atom transfer reaction is probable. Shortly after, we investigated the interactions of excited 2-naphthol and 1-anthrol with pyridine and quinoline [3, 4], and confirmed the fluorescence quenching due to H atom transfer in the non-relaxed encounter

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complex. Therefore, the H atom transfer reaction as an important process of the deactivation is expected to occur in other hydrogen bonding systems.

We have studied the hydrogen bonding interaction between excited acridone and pyridine in benzene by using an emission–absorption flash [5] and a laser technique. This system seems to be very interesting, because fluorescence of acridone is not quenched by the hydrogen bond formation with pyridine [6] but the fluorescence yield and lifetime are greatly increased.

Experimental

Materials

Acridone (G. R. grade, Tokyo Kasei) was treated with activated charcoal in hot acetic acid, and then recystallized from ethanol. N-Methylacridone was prepared from N-methylacridinium iodide [7], and recrystallized from ethanol. All other reagents were purified by standard methods.

Apparatus and Procedure

Absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer. Fluorescence spectra were measured with a modified Hitachi EPU spectrophotometer. The flash energy was usually about 130 J. FWHM is about 10 μs. A Hoya-U2 filter was usually used for excitation. A passive Q-switched ruby laser provides a 15 ns pulse of about 0.15 J, and its second harmonics was used for excitation. Lifetime measurements were made with a phasefluorometer modulated at 10.7 MHz. An NEC He–Cd laser (325 nm) was used for the modulated light source. Measurements were made at room temperature. The solutions were degassed by freeze–pump–thaw cycles. The methods of measuring transient absorption spectra and time-integrated fluorescence intensities during flashing were essentially the same as reported [5].

Results and Discussion

Hydrogen bonding equilibrium in the ground state

The absorption spectra of acridone in benzene at various concentrations of pyridine are shown in Fig. 1. Isosbestic points were observed at 372, 382, and 391 nm up to pyridine concentrations of about 1 M. Further increase in pyridine concentration causes a progressive red shift of the spectrum*. In the case of N-methylacridone, the spectrum exhibits a little red shift by the addition of pyridine, but no isosbestic point was observed. From these results, it is clear that there is an equilibrium of hydrogen bond formation between acridone and pyridine in the ground state, although in a previous study this

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*The absorption maximum of the longest wavelength band lies at 25,840 cm^{-1} in benzene and at 25,130 cm^{-1} in pyridine.
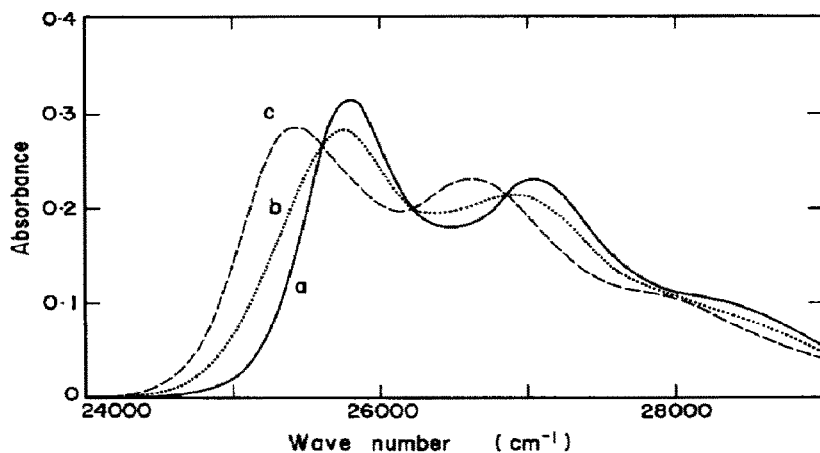
Fig. 1. The absorption spectra of acridone. [Pyridine] : (a) 0 M, (b) 0.1 M, (c) 0.75 M.
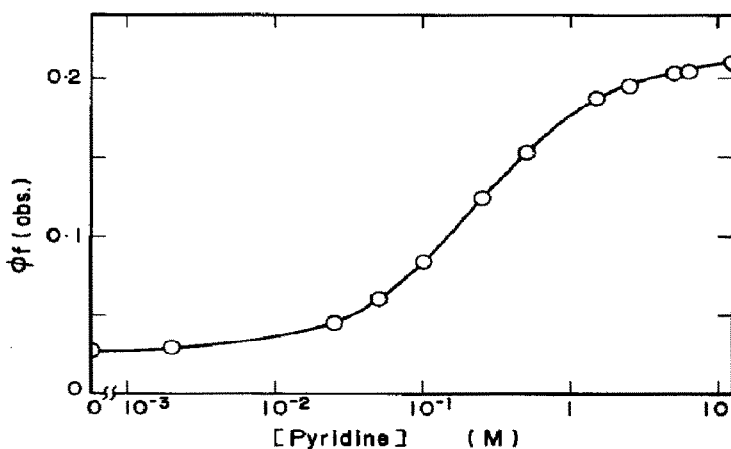

Fig. 2. The dependence of apparent fluorescence yield of acridone on pyridine concentration.

fact was unnoticed [5]. The equilibrium constant K = 4.5 M^{-1} (at 22 °C) was evaluated by analyzing Fig. 1.

Fluorescence spectrum, yield, and lifetime

The fluorescence spectrum of acridone changes slightly in the shape by the addition of pyridine and exhibits a little red shift [5]*. The apparent fluorescence yield increases considerably with increasing pyridine concentration as shown in Fig. 2. The fluorescence lifetime (τ_0) is 0.78 ns in benzene and 2.5 ns in pyridine. Owing to too short lifetime in benzene, the interaction

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*The fluorescence maximum lies at 25,330 cm^{-1} in benzene and at 24,480 cm^{-1} in pyridine.
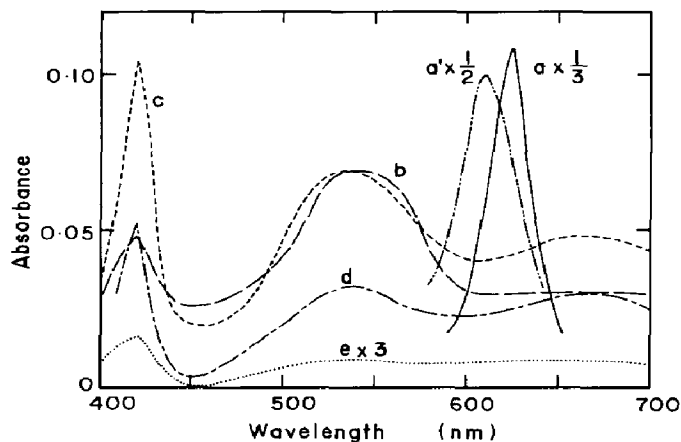
Fig. 3. The transient spectra of acridone.

between the singlet excited state of free species and pyridine could not be investigated.

Triplet state of acridone

Figure 3(a) is the transient absorption spectrum observed in the benzene solution which decays as a first-order process. Its decay rate increases by the addition of anthracene, ferrocene, pyridine, and oxygen. When anthracene was added, triplet energy transfer from acridone to anthracene was observed. Hence, the spectrum (Fig. 3(a)) is attributed to the T–T absorption spectrum of acridone.

The decay rate of triplet acridone increases with increasing acridone concentration. As shown in Fig. 4, the observed rate constant of triplet decay, k_{obs}, is satisfactorily linear with respect to the initial concentration of acridone, $[A]_0$:

$$k_{obs} = k_1 + k_2 [A]_0$$

From the intercept and slope of the plot, we obtain:

$$k_1 = 5 \times 10^4 \text{ s}^{-1} \quad \text{and} \quad k_2 = 7 \times 10^9 \ M^{-1} \text{ s}^{-1}.$$

The quenching rate constant of the triplet by ferrocene which is an excellent triplet quencher [8, 9], k_F, has been obtained from the similar experiment:

$$k_F = 8 \times 10^9 \ M^{-1} \text{ s}^{-1}$$

The decay rate of triplet acridone increases with increasing pyridine concentration up to about 0.1 M and remains a constant in the range of 0.1 M to 1 M (Fig. 5). Therefore, it is safely concluded that all of the triplet molecules is hydrogen-bonded with pyridine above 0.1 M. The decay constant of the hydrogen-bonded triplet in benzene was obtained as 3.3×10^6 s^{-1}. The T–T absorption spectrum in pyridine is shown in Fig. 3(a'), and its decay constant was found to be 2.5×10^6 s^{-1}. The decrease in the decay rate at
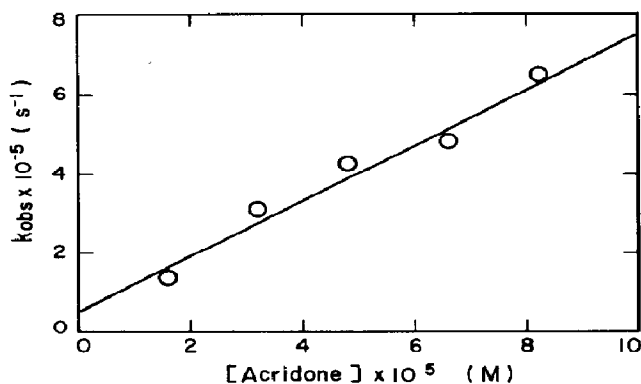
Fig. 4. The relation between the observed first order decay constant of acridone triplet and the initial concentration of acridone.
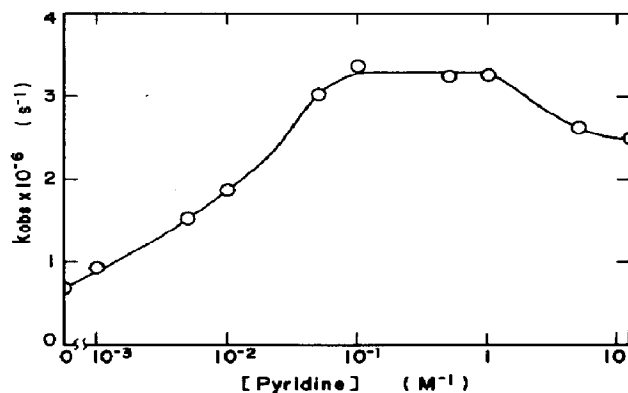

Fig. 5. The relation between the observed first order decay constant of acridone triplet and pyridine concentration.

the pyridine concentration higher than 1 M seems to be due to the solvent effect.

Reaction intermediates

After the T–T absorption spectrum disappeared, quite a different spectrum (Fig. 3(b)) was observed in the benzene solution. This transient spectrum decays as a second order process with the rate constant k/ϵ (540 nm) = 6.2×10^5 cm/s. The yield of the transient decreases by the addition of anthracene, ferrocene, and oxygen. When pyridine concentration is high enough to interact with the triplet effectively, the other spectrum (Fig. 3(c)) was observed. This spectrum decays as a second-order process with the rate constant k/ϵ (540 nm) = 1.4×10^5 cm/s.
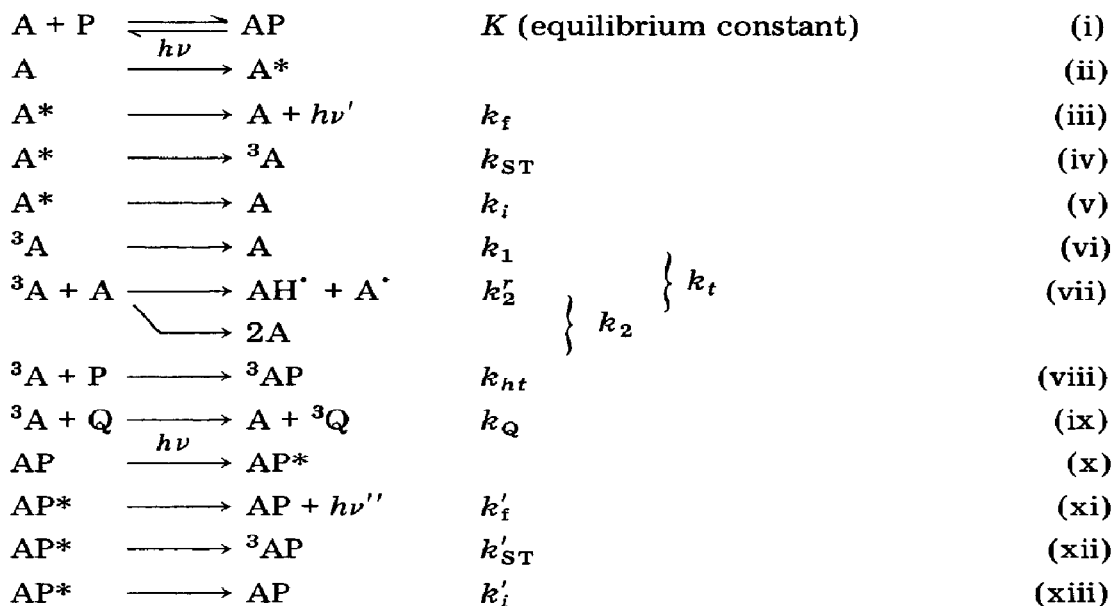
In the aerated solutions, the similar spectra (d) and (e) in Fig. 3 were observed both in the presence and the absence of pyridine respectively. The spectrum (Fig. 3(d)) decays as a second order process with the rate constant k/ϵ (540 nm) = 1.3×10^5 cm/s, and the yield increases with increasing pyridine concentration up to about 0.01 M. In this concentration range of
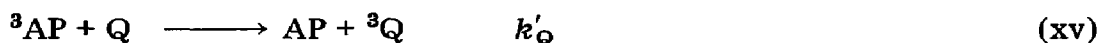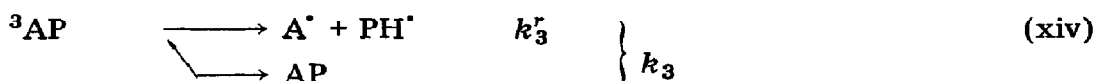
pyridine, both the formation of hydrogen bond in the ground state and the collisional quenching of the singlet excited state are negligible. Therefore, the reactive state should be the triplet alone.

The spectra (c) and (d) are quite similar, but the spectrum (b) is different from others. Furthermore the decay constants of the spectra (c) and (d) are nearly equal. Thus it may be clear that the spectra (c) and (d) are attributed to the same intermediate (A$\cdot$) which is stable even in the presence of oxygen, and that the spectrum (b) is superimposed by another intermediate (AH$\cdot$) which may be reactive with oxygen. The triplet decay rate increases with increasing acridone concentration as described above, and the yield of these intermediates also increases. The following reactions are plausible for intermediate formations.

(triplet)   (A)   (AH$\cdot$)   (A$\cdot$)

(triplet)   (P)   (H-bonded triplet)   (PH$\cdot$)
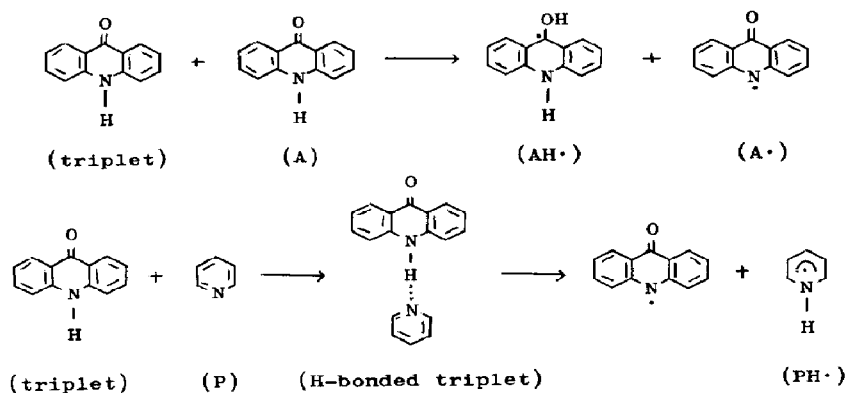
On the basis of the above results, we can summarize the reaction scheme as:

$$A + P \rightleftharpoons AP \qquad K \text{ (equilibrium constant)} \qquad \text{(i)}$$

$$A \xrightarrow{h\nu} A^* \qquad\qquad\qquad\qquad\qquad \text{(ii)}$$

$$A^* \longrightarrow A + h\nu' \qquad k_f \qquad\qquad\qquad \text{(iii)}$$

$$A^* \longrightarrow {}^3A \qquad k_{ST} \qquad\qquad\qquad \text{(iv)}$$

$$A^* \longrightarrow A \qquad k_i \qquad\qquad\qquad\qquad \text{(v)}$$

$${}^3A \longrightarrow A \qquad k_1 \qquad\qquad\qquad\qquad \text{(vi)}$$

$${}^3A + A \longrightarrow AH^{\cdot} + A^{\cdot} \qquad k_2^r \qquad\qquad \text{(vii)}$$
$$\qquad\qquad \searrow 2A$$

$${}^3A + P \longrightarrow {}^3AP \qquad k_{ht} \qquad\qquad\qquad \text{(viii)}$$

$${}^3A + Q \xrightarrow{h\nu} A + {}^3Q \qquad k_Q \qquad\qquad \text{(ix)}$$

$$AP \xrightarrow{h\nu} AP^* \qquad\qquad\qquad\qquad\qquad \text{(x)}$$

$$AP^* \longrightarrow AP + h\nu'' \qquad k_f' \qquad\qquad \text{(xi)}$$

$$AP^* \longrightarrow {}^3AP \qquad k_{ST}' \qquad\qquad\qquad \text{(xii)}$$

$$AP^* \longrightarrow AP \qquad k_i' \qquad\qquad\qquad\qquad \text{(xiii)}$$

$$^3AP \quad \longrightarrow A^\cdot + PH^\cdot \quad k_3^r \quad \Bigg\} \, k_3 \qquad (xiv)$$
$$\qquad\quad \searrow \longrightarrow AP$$

$$^3AP + Q \quad \longrightarrow AP + {}^3Q \quad k_Q' \qquad (xv)$$

According to the above scheme, various concentration effects on the yield of radicals ($AH^\cdot$ and $A^\cdot$) were analyzed.

First the process (vii) was examined. The yield of the radicals is related to acridone concentration as*:

$$[AH^\cdot]_0 = [A^\cdot]_0 = \Phi_{ST} \, I_{ab}^0 \cdot \frac{k_2^r[A]}{k_1 + k_2[A]} \qquad (1)$$

where subscript 0 denotes the concentration immediately after flashing, and $I_{ab}^0 = \int I_{ab} \, dt$ is the total quantity of light absorbed during one flash. $\int I_{ab} \, dt$ is given as a function of the fluorescence intensity during flash excitation by:

$$\int I_f(\lambda') dt = \alpha(\lambda')\Phi_f \int I_{ab} \, dt \qquad (2)$$

where $\alpha(\lambda')$ is a constant depending upon the experimental conditions. From eqns. (1) and (2), we can obtain the absorbance due to the transients immediately after flashing, $D(\lambda)_0$, as:

$$\frac{\int I_f(\lambda') dt}{D(\lambda)_0} = \frac{\alpha \, \Phi_f}{\Phi_{ST}} \cdot \frac{1}{[\epsilon_{A^\cdot}(\lambda) + \epsilon_{AH^\cdot}(\lambda)] d} \cdot \frac{k_2}{k_2^r} \cdot (1 + \frac{k_1}{k_2} \frac{1}{[A]}) \qquad (3)$$

where $\epsilon_{A^\cdot}(\lambda)$ and $\epsilon_{AH^\cdot}(\lambda)$ are the molar extinction coefficients of $A^\cdot$ and $AH^\cdot$ at wavelength λ, and $d = 10$ cm. Figure 6 shows the $\int I_f dt/D_0$ vs. $1/[A]$ plot from which we obtain $k_1/k_2 = 1 \times 10^{-5}$ M. From the value of $k_1 = 5 \times 10^4$ s^{-1}, we get $k_2 = 5 \times 10^9$ M^{-1} s^{-1} which is consistent with the value (7×10^9 M^{-1} s^{-1}) obtained from the acridone concentration effect on the triplet decay.

In a similar way, we studied the effect of ferrocene concentration on the yield of the transients, and obtained $k_F = 7 \times 10^9$ M^{-1} s^{-1} which agrees well with the value obtained above (8×10^9 M^{-1} s^{-1}).

Since the rate constant of process (viii) cannot be estimated directly from the apparent decay rate of the T–T absorption shown in Fig. 5, it was determined by the following way. When pyridine was added to the aerated solution, the following relation is derived from the above scheme, because $AH^\cdot$ is reactive with oxygen:

$$\frac{1}{D(\lambda)_0 - D(\lambda)_0^0} = \frac{1}{\Phi_{ST} I_{ab}^0} \cdot \frac{1}{\epsilon_{A^\cdot}(\lambda) d} \times$$

$$\frac{1}{k_3^r/(k_3 + k_{O_2}'[O_2]) - k_2^r[A]/(k_t + k_{O_2}[O_2])} \times$$

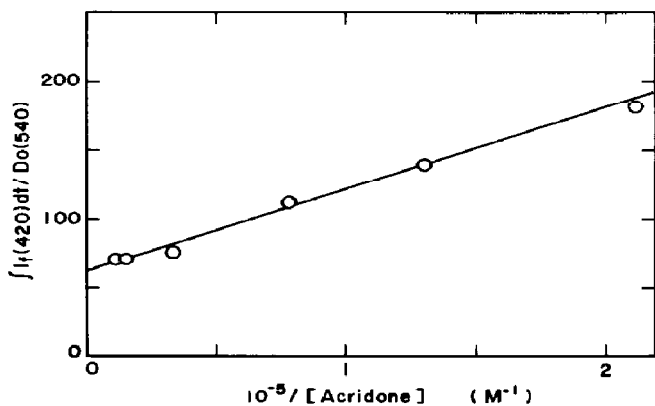*In the case of the deaerated benzene solution, $AH^\cdot$ and $A^\cdot$ would be produced in the same quantity.
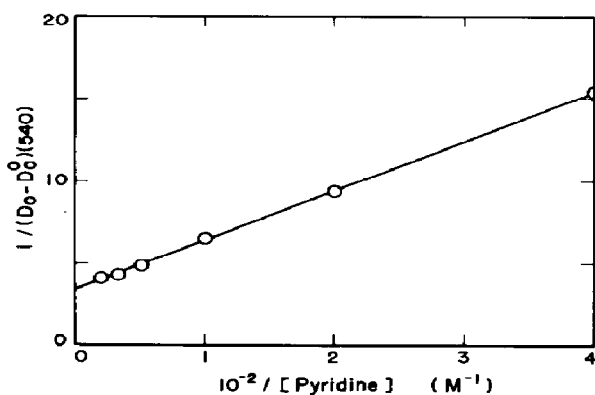
Fig. 6. Plot of $\int I_f dt/D_0$ vs. $1/[A]$.

Fig. 7. Plot of $1/(D_0 - D_0^0)$ vs. $1/[P]$.

$$(1 + \frac{k_t + k_{O_2}[O_2]}{k_{ht}[P]}) \tag{4}$$

where $D(\lambda)_0^0$ is the absorbance in the absence of pyridine. Figure 7 shows the $1/(D_0 - D_0^0)$ vs. $1/[P]$ plot, from which we get:

$$(k_t + k_{O_2}[O_2])/k_{ht} = 8.8 \times 10^{-3} \ M^{-1}$$

The triplet decay in the aerated benzene was measured by using the Q-switched ruby laser as $7 \times 10^6 \ s^{-1}$ ($[A] = 4.7 \times 10^{-5} \ M$). Thus we obtain $k_{ht} = 8 \times 10^8 \ M^{-1} \ s^{-1}$.

When pyrene was added to the pyridine solution (Q = pyrene in process (xv)), the absorbance ascribed to the radical A$^{\cdot}$ is given as:

$$\frac{1}{D(\lambda)_0} = \frac{1}{\Phi'_{ST} I^0_{ab} \epsilon_{A^{\cdot}}(\lambda)d} \cdot \frac{k_3}{k_3^r} \cdot (1 + \frac{k'_P}{k_3} [pyrene]) \tag{5}$$

Figure 8 shows the $1/D_0$ vs. [pyrene] plot, from which we obtain:
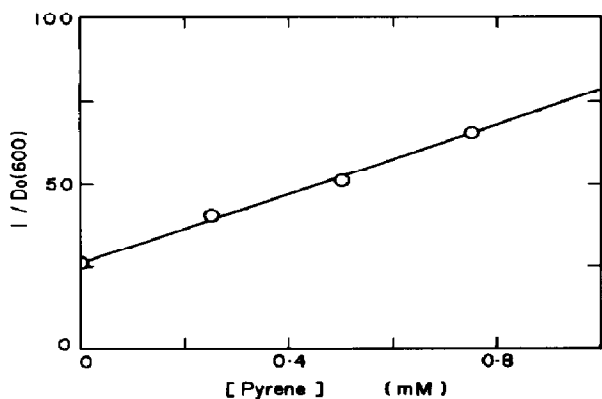
$$k'_P/k_3 = 2 \times 10^3 \ M^{-1}$$

Fig. 8. Plot of $1/D_0$ vs. [pyrene].

From the value of $k_3 = 2.5 \times 10^6$ s^{-1}, we have:

$$k'_{\rm P} = 5 \times 10^9 \ M^{-1} \ {\rm s}^{-1}$$

The linearity of the plot and the value of $k'_{\rm P}$ imply that the radical is not produced from the singlet excited state, but the triplet state alone.

Intersystem crossing probability

Intersystem crossing probability of acridone in benzene ($\Phi_{\rm ST}$) was determined by using an emission–absorption flash technique. Details of the method have been reported in a previous paper (relative method) [10]. In the case of acridone, however, the method had to be slightly modified, since the lifetime of triplet acridone is so short that the triplet yield cannot be obtained from the absorbance immediately after a flash.

Time dependence of the triplet concentration is expressed by:

$$\frac{{\rm d}[^3{\rm A}]}{{\rm d}t} = \Phi_{\rm ST} \, I_{\rm ab} - k_t \, [^3{\rm A}] \tag{6}$$

Integration of this equation gives the triplet yield as:

$$\Phi_{\rm ST} \int_0^\infty I_{\rm ab} \, {\rm d}t = k_t \int_0^\infty [^3{\rm A}] \, {\rm d}t \tag{7}$$

Thus the following modified equation was used:

$$\frac{\Phi_{\rm ST}^{\rm A}}{\Phi_{\rm ST}^{\rm R}} \cdot \frac{\epsilon_{\rm T}^{\rm A}(\lambda'')}{\epsilon_{\rm T}^{\rm R}(\lambda')} = k_t \cdot \frac{(\alpha\Phi_f)^{\rm A}}{(\alpha\Phi_f)^{\rm R}} \cdot \frac{\int D_{\rm T}^{\rm A}(\lambda''){\rm d}t / \int I_f^{\rm A}(\lambda){\rm d}t}{D_{\rm T}^{\rm R}(\lambda')_0 / \int I_f^{\rm R}(\lambda){\rm d}t} \tag{8}$$

where superscripts R and A denote anthracene (for reference) and acridone, respectively. The ratio of the molar extinction coefficients was determined by triplet energy transfer from acridone to anthracene. Time integrated absorbance was obtained easily from the oscillogram. Other ratios were determined in a similar manner as a previous paper [10]. The results were listed in Table 1. As $\Phi_f^{\rm R} = 0.27$ in benzene [11], $\Phi_{\rm ST}^{\rm R}$ is estimated to be 0.73 by assuming the relation, $\Phi_{\rm ST}^{\rm R} = 1 - \Phi_f^{\rm R}$. Thus we obtain $\Phi_{\rm ST} = 0.99 \pm 0.12$.

TABLE 1

Numerical values for determining the Φ_{ST} value in benzene

$\dfrac{\epsilon_T^A(620)}{\epsilon_T^R(430)}$	$\dfrac{(\alpha\Phi_f)^A}{(\alpha\Phi_f)^R}$	$\dfrac{\int D_T^A(620)\mathrm{d}t}{\int I_f^A(416.5)\mathrm{d}t}$	$\dfrac{D_T^R(430)_0}{\int I_f^R(416.5)\mathrm{d}t}$	k_t (s^{-1})	$\Phi_{ST}^R = 1 - \Phi_f^R$	Φ_{ST}^A
0.83	0.23	6.6×10^{-7}	4.8×10^{-2}	3.5×10^5	0.73	0.99

In pyridine the lifetime of acridone triplet is so short to observe by a conventional flash apparatus that the other modified method is necessary to be devised. When acridone alone is irradiated in the mixed solution of anthracene as an energy acceptor and acridone, we can easily obtain the following equation under the assumption that the triplet energy transfer occurs effectively:

$$\frac{\Phi_{ST}^A}{\Phi_{ST}^R} = \frac{(\alpha\Phi_f)^A}{(\alpha\Phi_f)^R} \cdot \frac{(D_T^R(\lambda')_0 / \int I_f^A(\lambda)\mathrm{d}t)}{(D_T^R(\lambda')_0 / \int I_f^R(\lambda)\mathrm{d}t)} \cdot (1 + \frac{k_3}{k_A[\text{anthracene}]}) \qquad (9)$$

By the use of various concentrations of anthracene and from the relation $\Phi_{ST}^R = 1 - \Phi_f^R = 0.80$ in pyridine, we have $\Phi_{ST}^A = 0.16$.

The above results imply that the deactivation other than fluorescence and intersystem crossing contributes appreciably in pyridine, because Φ_f value is 0.21 in pyridine.

The rate constants of various elementary reactions pertaining to the singlet and triplet excited states of acridone are listed in Table 2.

The present results concerning the singlet excited state seem to support the previous suggestion [5] that the levels of the singlet excited states, $^1(\pi\pi^*)$ and $^1(n\pi^*)$, change with the solvent dielectric constant. The intersystem crossing rate constant in pyridine is considerably smaller than that in benzene. This is a support for a suggestion that the emitting $^1(\pi-\pi^*)$ state is lowered by the effects of hydrogen bonding and higher dielectric constant in pyridine, while $^1(n-\pi^*)$ state lying presumably slightly higher than $^1(\pi-\pi^*)$ state is raised. The radiative rate constant in pyridine agrees with the value calculated by Strickler—Berg equation [12] and is larger than that in benzene. This might be explained by very small separation between $^1(\pi-\pi^*)$ and $^1(n-\pi^*)$ states, since the small separation might enhance the admixing of both states yielding the decrease in allowed charactor of the electronic transition. The rate constant of the deactivation other than fluorescence and intersystem crossing, k_i, was estimated from eqn. (10) and listed in Table 2:

$$k_i = 1/\tau_0 - (k_f + k_{ST}) \qquad (10)$$

Although the magnitude of k_i increases significantly by the hydrogen bond formation, it is exceptionally small compared with other hydrogen-bonded systems. In previous papers [3, 4] it has been suggested that in the singlet excited hydrogen-bonded species a transient H atom transfer is occurring.

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TABLE 2

Rate constants of elementary reactions pertaining to the excited acridone molecule in benzene and pyridine

Singlet excited state		Triplet state	
Free species	H-bonded species*	Free species	H-bonded species*
$k_f \simeq 3.5 \times 10^7 \ s^{-1}$	$k'_f \simeq 8.4 \times 10^7 \ s^{-1}$	$k_1 = 5 \times 10^4 \ s^{-1}$	$k_3 = 3.3 \times 10^6 \ s^{-1}$
$k_{ST} \simeq 1.2 \times 10^9 \ s^{-1}$	$k'_{ST} \simeq 6.4 \times 10^7 \ s^{-1}$	$k_2 = 5 \sim 7 \times 10^9 \ M^{-1} \ s^{-1}$	$k'_3 = 2.3 \times 10^6 \ s^{-1}$
$k_i < 1 \times 10^8 \ s^{-1}$	$k'_i \simeq 2.6 \times 10^8 \ s^{-1}$	$k_{ht} = 8 \times 10^8 \ M^{-1} \ s^{-1}$	
		$k_F = 7 \sim 8 \times 10^9 \ M^{-1} \ s^{-1}$	$k'_P \simeq 4.6 \times 10^9 \ M^{-1} \ s^{-1}$
			$k'_A \simeq 4.6 \times 10^9 \ M^{-1} \ s^{-1}$

*The prime means the rate constant in pyridine.

This may be also the case for the acridone–pyridine pair, since k_i increases by the hydrogen bond formation and the hydrogen-bonded acridone in the singlet excited state does not react. The unusual smallness of k_i may be explained by the very weak hydrogen bonding interaction between the singlet excited acridone and pyridine owing to the weak acid strength of acridone [13]

On the other hand, we could not conclude whether the bimolecular interaction between the singlet excited state of free species and pyridine is the radical formation reaction or the hydrogen bond formation, since the interaction cannot be examined owing to the short fluorescence lifetime. In previous papers [3, 4] it has been found that the eventual H atom transfer occurs through the non-relaxed encounter complex in the 2-naphthol–pyridine pair. According to Rehm and Weller's theory [2], H atom transfer reaction depends on the energy of the excited state, the oxidation–reduction potentials of fluorescer and quencher, and pK values of radicals produced. Therefore, the reaction should occur in the singlet excited state when it occurs in the triplet state. However, in both cases of 1-anthrol and 2-naphthol, it occurs more effectively in the triplet state than in the singlet excited state. This result suggests the imperfection of the theory and the existence of other factors overlooked. A possible factor is the relative strength of acid–base interaction. If this is large, the hydrogen bond formation followed by the proton transfer process might be important in the relaxation of the encounter complex. The singlet excited molecule is stronger acid than the triplet molecule in general, so that the H atom transfer is hard to occur in the singlet excited state*. Since in the case of acridone the acid strength is extremely weak compared with aromatic phenols, H atom transfer is presumably occurring in the encounter complex.

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*The H atom transfer in the singlet excited state was observed only for the 2-naphthol–pyridine system so far [4, 14].