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DEACTIVATION OF THE EXCITED STATES OF 1-ANTHROL BY AROMATIC *N*-HETEROCYCLES

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Summary

The interactions of the excited 1-anthrol with pyridine, quinoline, and acridine have been investigated in cyclohexane. Fluorescence of 1-anthrol is quenched dynamically by pyridine and quinoline at about a diffusion controlled rate. 1-Anthrol hydrogen bonded with pyridine or quinoline in the ground state does not produce any transient species detectable by a conventional flash apparatus and is non-fluorescent. The bimolecular interaction between the excited singlet 1-anthrol and pyridine leads to neither the enhancement of intersystem crossing nor reaction. The triplet 1-anthrol is not deactivated by pyridine, but by quinoline and acridine with the rate constants of $1.1 - 1.4 \times 10^9$ and 1.1×10^9 M^{-1} s^{-1}, respectively, yielding 1-anthroxyl radical. By means of the triplet energy transfer to the hydrogen bonded species, it was found that the radical is formed from the triplet state of the hydrogen bonded 1-anthrol. Acid dissociation constants of 1-anthrol were determined as pK = 10.0, ~10, and —0.07 for the ground, the triplet, and the singlet excited states, respectively. It was suggested that the acidities of both the hydrogen bonding donor and acceptor are closely correlated with the facility of the hydrogen atom transfer reaction in the excited states.

Introduction

When a fluorescent hydrogen bonding donor or acceptor forms the hydrogen bonded complex with an acceptor or a donor, the fluorescent ability of the complex is lost completely if the hydrogen bonding functions are involved in the π-electronic systems such as naphthol–pyridine [1, 5], carbazole–pyridine [2], and acridine dye–naphthol [3]. This phenomenon is interpreted in terms of the delocalization of π-electrons through the hydrogen bond [1 - 4]. Recently, Rehm and Weller [6] showed that the fluorescence quenching due to such a hydrogen bonding interaction cannot be explained by an electron transfer reaction but by a hydrogen atom transfer reaction.

In a previous paper [7] the 2-naphthol–pyridine pair in cyclohexane was studied by an emission–absorption flash technique. Both the excited singlet and the triplet states of 2-naphthol are quenched by pyridine yielding

2-naphthoxyl radical. However, hydrogen bonded 2-naphthol with pyridine in the ground state gives neither fluorescence nor transient absorption detectable by a conventional flash technique. In order to clarify the difference between the dynamic and the static quenching of fluorescence, the interactions between 1-anthrol (1-A) in the excited states and the hydrogen bonding acceptors such as pyridine, quinoline, and acridine have been investigated by the use of a fluorescence spectrophotometer and an emission–absorption flash apparatus. Further, the acid dissociation constants in the first singlet excited state and the lowest triplet state have been determined to obtain the information concerning the quenching phenomena.

Experimental

1-A was synthesized according to the method of Ferrero and Conzetti, and Schmidt [8], recrystallized from aqueous acetic acid several times, treated by thin-layer chromatography on silicagel G, and sublimed *in vacuo*. Quinoline was distilled under reduced pressure and stored *in vacuo*. Pyridine and cyclohexane were purified by the standard method.

Absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer. Fluorescence spectra and fluorescence yield were measured with a fluorimeter which consists of a Hitachi G-3 grating monochromator with 150 W Xe lamp for excitation and a Hitachi EPU prism monochromator with an EMI 9558 QB photomultiplier as an analyzing device. The spectral calibration factors were obtained by using standard fluorescence solutions described by Lippert *et al.* [9]. The fluorescence yield of 1-A in cyclohexane was determined by comparing with the known value of 0.30 for anthracene in cyclohexane [10]. Fluorescence lifetime was measured with a phase fluorimeter similar to that described elsewhere [11]. The input energy of flash lamps was 65 - 130 J and its FWHM was about 10 μs. Combination of a Hoya-U2 filter and a photographic plate glass was used for excitation.

The method for the analysis of transient absorption spectra and time integrated fluorescence intensities during a flash is essentially the same as a previous paper [12]. Cyclohexane solutions were degassed by freeze–pump–thaw method.

Results and Discussion

1-A forms a hydrogen bonded complex with pyridine and quinoline. Absorption and fluorescence spectra of 1-A in cyclohexane containing various amounts of pyridine are shown in Fig. 1. Isosbestic points appear at 355, 363, 373, 385, and 392 nm. Similar absorption spectral changes have been observed by the addition of quinoline (in cyclohexane), triethylamine (in liquid paraffin) [13] and dioxane (in iso-octane) [14]. The hydrogen bond equilibrium constants in the ground state, K at 25 °C, were determined to be 142 M^{-1} for

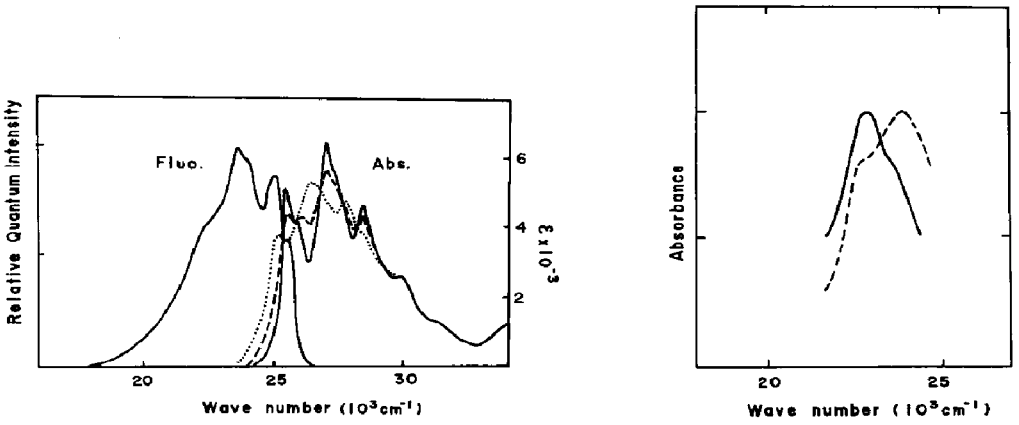


Fig. 1. Absorption and fluorescence spectra of 1-A in cyclohexane. [1-A] = 1×10^{-4} *M*. ———, [Pyridine] = 0 *M*; - - -, [pyridine] = 5×10^{-3} *M*; · · · · ·, [pyridine] = 1×10^{-1} *M*.

Fig. 2. Effect of pH on T–T absorption spectrum of 1-A in the mixed solvent of water and ethanol (9.5:0.5). ———, pH ≤ 9; - - - - -, pH ≥ 10.

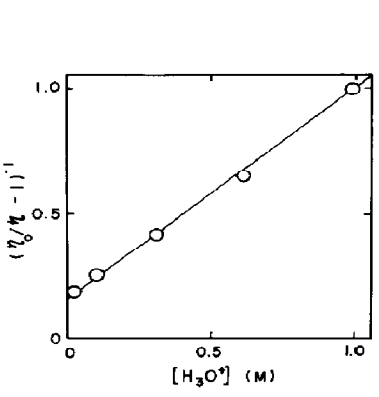
1-A–pyridine and 200 M^{-1} for 1-A–quinoline. These values are significantly larger than that for dioxane [14].

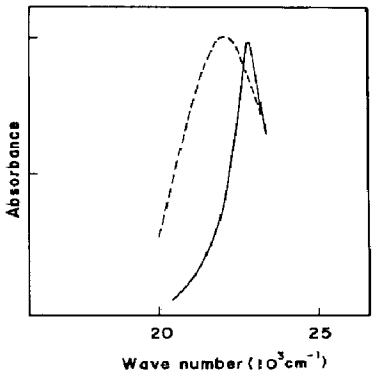
With the addition of pyridine or quinoline, the fluorescence of 1-A is quenched without any change in the fluorescence spectrum. Since in neat pyridine or quinoline no fluorescence was detected, it is clear that the observed fluorescence comes from free 1-A and the hydrogen bonded 1-A is not fluorescent. The fluorescence quenching rate constants were evaluated, as k_q = 1.2×10^{10} $M^{-1}s^{-1}$ for pyridine and 1.3×10^{10} $M^{-1}s^{-1}$ for quinoline by the use of the measured fluorescence lifetime τ_0 of 5.9 ns. The collisional quenching occurs at a diffusion controlled rate.

The difference in acid dissociation constants between an acid and a base is a measure of hydrogen bond energy when the acid–base pair is incorporated in an inert solvent. The p*K* value of 1-A in the ground state was determined spectrophotometrically as 10.0. At pH = 9 the T–T absorption spectrum of 1-A has a maximum at 440 nm, but at pH ≥ 10 the maximum lies at 420 nm as shown in Fig. 2. Therefore, the p*K* value in the triplet state is approximately 10 or a little smaller. The protolytic reactions of 1-A in the singlet excited state were examined by measuring relative fluorescence yields as a function of hydrogen ion concentration. The result was analyzed by [15]:

$$\frac{1}{\eta_0/\eta - 1} = \frac{1}{\vec{k}_T} + \frac{\overleftarrow{k}_T'}{\vec{k}_T}\,[H_3O^+] \qquad (1)$$

where η_0 is the fluorescence yield of undissociated 1-A, and η the yield at a given proton concentration, $[H_3O^+]$. From the plot shown in Fig. 3, $1/\vec{k}_T$ = 0.16 and $\overleftarrow{k}_T'/\vec{k}_T = 0.84$ M^{-1} were found. Using the measured fluorescence lifetimes of 1-A (τ = 3.2 ns) and of 1-anthrolate anion (τ' = 3.1 ns), we obtain $\vec{k} = 1.9 \times 10^9 s^{-1}$ and $\overleftarrow{k} = 2.2 \times 10^9$ $M^{-1}s^{-1}$ for the dissociation and association rate constants, respectively. Finally, $K^* = \vec{k}/\overleftarrow{k}$ was obtained as 0.86 *M* and $pK^* = -0.07$. These results are summarized in Table 1 together with the p*K* values for other related compounds.





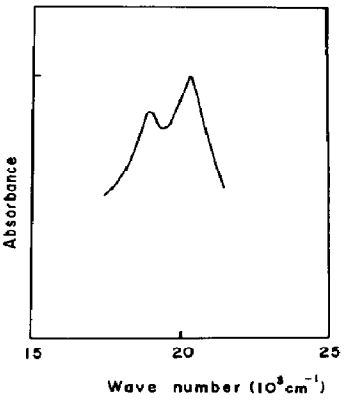


Fig. 3. Plot of $(\eta_0/\eta - 1)^{-1}$ *vs.* $[H_3O^+]$.

Fig. 4. T–T absorption spectra of 1-A. ———, Free 1-A in cyclohexane; ·····, hydrogen bonded 1-A in pyridine (this spectrum was measured by the use of 2-acetonaphthone as a triplet sensitizer).

Fig. 5. Absorption spectrum of 1-anthroxyl radical.

TABLE 1

pK values in the ground, first excited singlet and lowest triplet states.

	pK^G	pK^T	pK^S
1-Anthrol	10.0	$\leqslant 10$	−0.07
2-Naphthol	9.5	8.1 ~ 8.3[a]	2.81[b]
Acridine	5.5[c]	5.6[a]	10.65[b]
Quinoline	4.94[c]	6.0[a]	
Pyridine	5.23[c]		

[a] G. Jackson and G. Porter, Proc. R. Soc. (A), 260 (1961) 13.
[b] A. Weller, Z. Elektrochem., 61 (1957) 956; ibid., 64 (1960) 55; Z. Phys. Chem. (N.F.), 17 (1958) 224.
[c] A. Albert, R. Goldacre and J. Phillips, J. Chem. Soc., (1948) 2240.

The T–T absorption spectra of 1-A are shown in Fig. 4 [16]. In pyridine where all of the triplet 1-A is considered to be hydrogen bonded, the absorption maximum shifts to lower wavenumber by about 1000 cm^{-1} compared with that of free 1-A. The first order decay constants in cyclohexane and pyridine are $3.4 \times 10^3 s^{-1}$ and $5.8 \times 10^3 s^{-1}$, respectively.

The interactions between the triplet 1-A and the hydrogen bonding acceptors were investigated in cyclohexane at low acceptor concentration where practically no fluorescence quenching occurs. The decay rate of the triplet 1-A is not affected by the addition of pyridine, but increases with increasing quinoline concentration [Qu]. The observed first order rate constant k_{obs} is linear with respect to [Qu] less than 10^{-4} M:

$$k_{obs} = k_{dt} + k_{qt}\,[Qu]$$

The quenching rate constant was determined as $k_{qt} = 1.4 \times 10^9\ M^{-1}s^{-1}$. Above $10^{-4}\ M$ quinoline, the transient spectrum completely different from that of the T–T absorption was observed (Fig. 5). This spectrum decays as a second order process with the rate constant $k = 9 \times 10^5\ \epsilon$ cm s^{-1} (at 490 nm) and is observable even in the aerated solution.

The decay rate of the triplet 1-A also increases with the addition of acridine and the transient absorption spectrum after the triplet decay is the superposition of the spectrum of acridine C-radical [7] and the spectrum shown in Fig. 5. The observed decay rate is linear with respect to acridine concentration [acridine]:

$$k_{obs} = k_{dt} + k_{qt}\,[\text{acridine}]$$

and the quenching rate constant k_{qt} was found to be $1.1 \times 10^9\ M^{-1}s^{-1}$. This reaction is analogous to the 2-naphthol–acridine system [7] in which 2-naphthoxyl radical and acridine C-radical are produced. Hence the spectrum shown in Fig. 5 is attributed to that of 1-anthroxyl radical formed by the H atom release from the hydroxy group of 1-A.

The yield of 1-anthroxyl radical (R) measured at the end of a flash increases with increasing quinoline concentration up to $10^{-4}\ M$. Above 1 M quinoline, the hydrogen bond formation in the ground state is complete and no transient absorption is observed. However, the same spectrum as in Fig. 5 was obtained for the solution containing 1 M quinoline when anthracene was used as a triplet sensitizer. Therefore, the triplet hydrogen bonded with quinoline is the precursor of R. The following scheme concerning the fate of the triplet 1-A is established:

$$\begin{aligned}
&D \xrightarrow{h\nu} D^* && I_{ab}\\
&D^* \longrightarrow D^T && \Phi_{ST}\\
&D^T \xrightarrow{k_{dt}} D\\
&D^T + A \xrightarrow{k_{qt}} DA^T \begin{cases} \xrightarrow{k_r^t} R \\ \xrightarrow{k_d^t} D + A \end{cases}
\end{aligned} \qquad \text{(I)}$$

where D and A mean the hydrogen bonding donor (1-A) and acceptor, respectively. The absorbance of R at the end of a flash, $D_R^O(\lambda)$, is given as:

$$\frac{1}{D_R^O(\lambda)} = \frac{1}{\epsilon_R(\lambda) d \Phi_{ST} I_{ab}^0 \Phi_R}\left(1 + \frac{k_{dt}}{k_{qt}\,[Qu]}\right) \qquad (2)$$

where $\Phi_R = k_r^t/(k_r^t + k_d^t)$. The plot of $1/D_R^O(\lambda)$ *vs.* $1/[Qu]$ is given in Fig. 6, from which the ratio k_{dt}/k_{qt} was found to be $3.0 \times 10^{-6}\ M$. Since $k_{dt} = 3.4 \times 10^3 s^{-1}$ in cyclohexane, k_{qt} was determined as $1.1 \times 10^9\ M^{-1}s^{-1}$. This value agrees with $k_{qt} = 1.4 \times 10^9\ M^{-1}s^{-1}$ obtained from the effect of quinoline concentration on the triplet decay.

In order to investigate the processes occurring in the singlet excited state, the emission–absorption flash technique was used for higher pyridine concentrations. The time integrated fluorescence intensity measured at 444 nm during a flash, $\int I_f(444)dt$, and the absorbance of the T–T absorption at

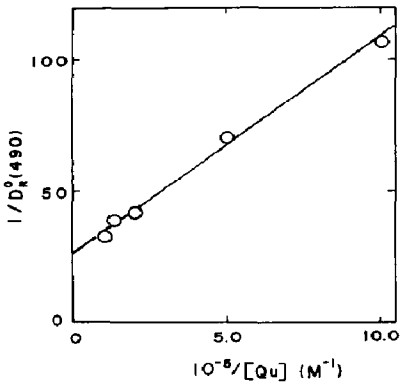


Fig. 6. Plot of $1/D_R^0$ *vs.* $1/[Qu]$.

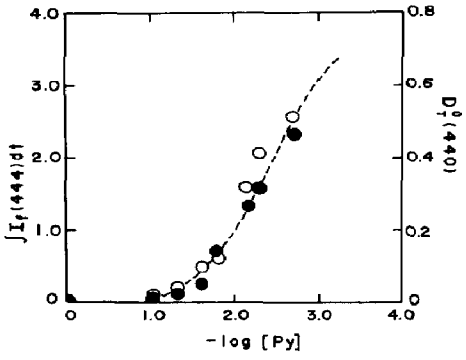


Fig. 7. Plot of $\int I_f(444)dt$, $D_T^0(440)$ *vs.* log [Py]. ○, $\int I_f(444)dt$; ●, $D_T^0(440)$.

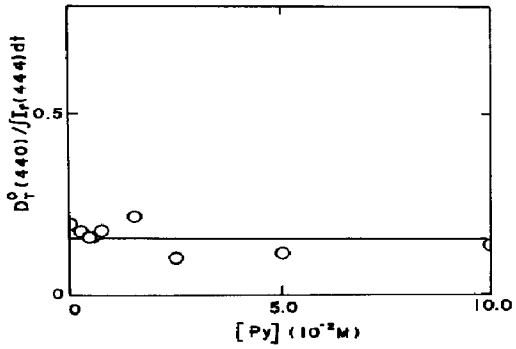
440 nm immediately after flashing, $D_T^0(440)$, were measured at various pyridine concentrations. The results are given in Fig. 7. Above 1*M* pyridine, both $\int I_f(444)dt$ and $D_T^0(440)$ become nil. Since in this concentration range of pyridine, the hydrogen bond formation in the ground state seems to be almost complete, it is clear that the singlet excited state of the hydrogen bonded 1-A does not undergo the fluorescence, the intersystem crossing and the reaction by direct excitation. Such situation is the same for the systems of 1-A–quinoline, 2-naphthol–pyridine. For the 2-naphthol–pyridine pair it was found that 2-naphthoxyl radical is produced by the triplet energy transfer from triphenylene to the hydrogen bonded species [16], and it was reported that one-fifth of the dynamic quenching process of the fluorescence by pyridine is responsible for the radical production [7]. Accordingly, the singlet excited state of the hydrogen bonded species, DA^*, should not be the precursor of the radical and the triplet state. A non-relaxed encounter complex between the fluorescer and the quencher, $(D^* \cdots A)$, is thought to be the precursor. Then the following reaction scheme may be adequate:

$$D^* + A \xrightarrow{k_q} (D^* \ldots A) \begin{cases} \xrightarrow{k_r^s} R \\ \xrightarrow{k_h^s} DA^* \\ \xrightarrow{k_t^s} DA^T \end{cases} \qquad \text{(II)}$$

It is clear that k_r^s is negligibly small for the 1-A–pyridine pair because no transient absorption appears at all. Intersystem crossing of the encounter complex of 1-A and pyridine was examined with the aid of eqn. (3) derived from schemes (I) and (II) on the assumption that the molar extinction coefficients of D^T and DA^T are equal:

$$\frac{D_T^0(\lambda)}{\int I_f(\lambda')dt} = \frac{\epsilon_T(\lambda)d}{\alpha(\lambda')k_f}(k_{ST} + k_q \Phi_{Ts}[Py]) \qquad (3)$$

where $\alpha(\lambda')$ is a constant depending on the experimental conditions and $\Phi_{Ts} = k_t^s/(k_t^s + k_h^s + k_r^s)$. Since $D_T^0(\lambda')/\int I_f(\lambda')dt$ is independent of [Py] as shown in



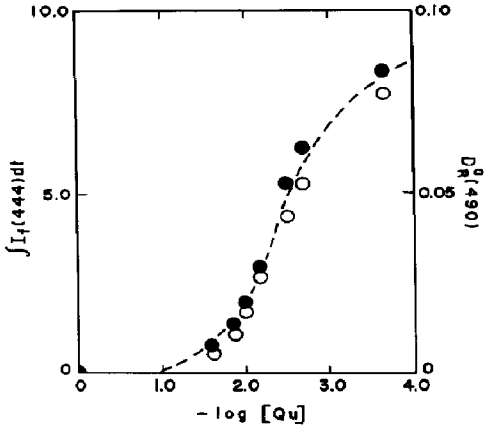


Fig. 8. Plot of $D_T^O(\lambda)/\int I_f(\lambda')dt$ *vs.* [Py].

Fig. 9. Plot of $\int I_f(444)dt$, $D_R^O(490)$ *vs.* log [Qu]. ○, $\int I_f(444)dt$; ●, $D_R^O(490)$.

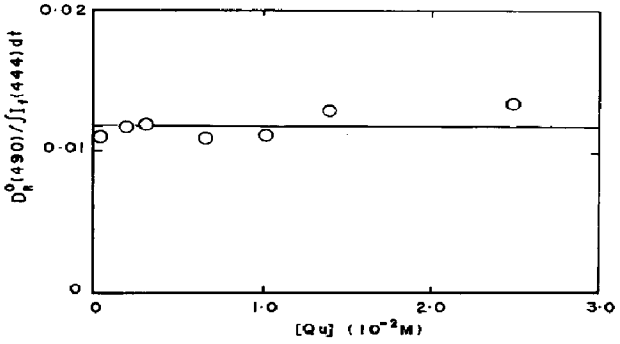


Fig. 10. Plot of $D_R^O(\lambda)/\int I_f(\lambda')dt$ *vs.* [Qu].

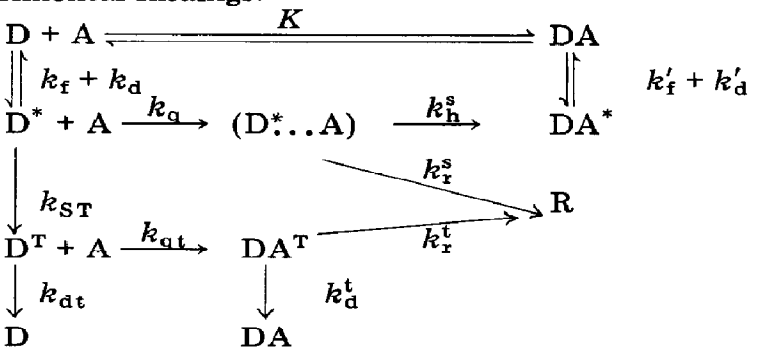
Fig. 8, intersystem crossing from the encounter complex is negligible. Therefore the relaxation process of the encounter complex is mainly the hydrogen bond formation.

In the case of the 1-A–quinoline pair, intersystem crossing and the radical production from the encounter complex are not distinguishable, because the intersystem crossing is followed by the rapid radical formation process. Equation (4) is derived in this case:

$$\frac{D_R^O(\lambda)}{\int I_f(\lambda')dt} = \frac{\epsilon_R(\lambda)d}{\alpha(\lambda')k_f}\left[k_{ST}\Phi_R + (\Phi_{Ts}\Phi_R + \Phi_{Rs})k_q[Qu]\right] \quad (4)$$

where $\Phi_{Rs} = k_r^s/(k_t^s + k_h^s + k_r^s)$. $\int I_f(444)dt$ and $D_R^O(490)$ measured at various quinoline concentrations are shown in Fig. 9. $D_R^O(\lambda)/\int I_f(\lambda')dt$ seems to increase slightly with increasing quinoline concentration as shown in Fig. 10. Owing to rather scattered data, we cannot conclude whether the intersystem crossing and the radical formation from the encounter complex occur or not. Anyhow, the contributions of these processes are small, *i.e.* $k_t^s + k_r^s \ll k_h^s$.

In the case of the 2-naphthol–pyridine pair, the radical formation from the encounter complex was confirmed; $(k_t^s + k_r^s)$ is one fourth of k_h^s. Since the hydrogen bonded triplet produces the radical, it is necessary to consider whether the radical is formed directly from the encounter complex or indirectly from the hydrogen bonded triplet produced through the intersystem crossing from the encounter complex. Both k_t^s and k_r^s are negligibly small compared with k_h^s in both cases of the 1-A–pyridine pair whose triplet is not reactive and the 1-A–quinoline pair whose triplet is reactive. Therefore, it seems that the probability of the intersystem crossing from the encounter complex is very small in general. Thus the radical formation seems to occur from the encounter complex directly. The following mechanism is consistent with the experimental findings:



The rate constants of elementary reactions involved in the deactivation of the excited 1-A were estimated in a similar manner to a previous paper [7] and summarized in Table 2 together with the previous results on 2-naphthol [7] for comparison. For the decay of DA^T, the radical production may be dominant when the reaction occurs; $k_r^t \gg k_d^t \simeq 10^4 s^{-1}$.

The reactivity of 1-A for pyridine differs from that of 2-naphthol in both the excited singlet and triplet states. The lower excitation energy may be one of several reasons for less reactivity of 1-A. However, the energy consideration alone does not explain the fact that the singlet excited 1-A is not reactive with quinoline but the lower lying triplet 1-A. The difference between the singlet excited states of 1-A and 2-naphthol is remarkable for the acid dissociation constants. Since the singlet excited 1-A is a much stronger proton donor compared with the singlet excited 2-naphthol, it seems probable that the encounter complex relaxes only to the hydrogen bonded state (DA^*) in the case of 1-A. The fact that the triplet 1-A reacts with quinoline and acridine but not with pyridine may be explained in terms of the difference in reduction potentials of quenchers, since the pK values of these quenchers are close to each other. Reduction potentials in DMF for pyridine, quinoline, and acridine are — 2.76, — 2.175, and — 1.62 V, respectively [17]. As regards the fate of DA^* there is no experimental clue. The view that the deactivation process is entirely due to direct internal conversion to DA, is not favourable because of the large energy gap. The transient hydrogen atom transfer reaction suggested in a previous paper [7] is a plausible process.

TABLE 2

Rate constants of elementary reactions involved in the deactivation of excited 1-A and 2-naphthol.

	2-Naphthol [7]	1-A
	Singlet state	
k_d	$<1.7 \times 10^7 s^{-1}$	$<10^7$
k_{ST}	$3.8 \sim 5.3 \times 10^7 s^{-1}$	$1.3 \times 10^8 s^{-1}$
k_f	$2.1 \times 10^7 s^{-1}$	$4.2 \times 10^7 s^{-1}$
$k_h^s \simeq 4k_r^s \gg k_t^s$		$k_h^s \gg k_r^s, k_t^s$
k_q	$1.2 - 1.4 \times 10^{10} M^{-1} s^{-1}$	$1.2 \times 10^{10} M^{-1} s^{-1}$ (pyridine) $1.3 \times 10^{10} M^{-1} s^{-1}$ (quinoline)
E_s [a]	$30{,}300\ cm^{-1}$	$25{,}200\ cm^{-1}$
k_d' [b]	$\gtrsim 2 \times 10^{10} s^{-1}$	$\gtrsim 4 \times 10^{10} s^{-1}$
k_{ST}'	$<10^7 \sim 10^8 s^{-1}$	$<10^7 \sim 10^8 s^{-1}$
k_f'	$\sim 2 \times 10^7 s^{-1}$	$\sim 4 \times 10^7 s^{-1}$
	Triplet state	
k_{dt}	$1.5 \times 10^4 s^{-1}$	$3.4 \times 10^3 s^{-1}$
k_{qt} [c]	$1.5 \sim 1.9 \times 10^9 M^{-1} s^{-1}$ (pyridine) $3.3 \times 10^9 M^{-1} s^{-1}$ (quinoline)	$\ll 1 \times 10^9 M^{-1} s^{-1}$ (pyridine) $1.1 \sim 1.4 \times 10^9 M^{-1} s^{-1}$ (quinoline)
E_T [d]	$21{,}100\ cm^{-1}$	$14{,}600\ cm^{-1}$
	Ground state	
K	$140\ M^{-1}$ (pyridine)	$142\ M^{-1}$ (pyridine) $200\ M^{-1}$ (quinoline)

[a] The energy level of the first excited singlet state.
[b] The prime means the rate constant of hydrogen bonded species.
[c] The rate constant of H-atom transfer reaction from 2-naphthol to triplet acridine is $2.9 \times 10^9\ M^{-1} s^{-1}$ [7], and that from triplet 1-A to acridine is $1.1 \times 10^9\ M^{-1} s^{-1}$.
[d] The energy level of the lowest triplet state.

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