Interaction between Excited β-Naphthol and Pyridine. Hydrogen-bond Formation in S* and H-Transfer Reaction in T

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The interaction between the excited β-naphthol and pyridine in cyclohexane has been investigated by an absorption-emission flash technique. The triplet naphthol has been found to be deactivated by pyridine with the rate constant of $1.5—1.9 \times 10^9$ M^{-1}sec^{-1}, yielding naphthoxyl radical. With 10^{-4} M pyridine the triplet naphthol is completely transformed into naphthoxyl radical. Above 10^{-1} M pyridine naphthol exists almost exclusively as a H-bonded species in the ground state, which is non-fluorescent and produces no transient species detectable by an ordinary flash apparatus. For 10^{-4}—10^{-1} M pyridine, the singlet excited naphthol undergoes collisional deactivation which most likely leads to a H-bonded species (rate constant, $1.2—1.4 \times 10^{10}$ M^{-1}sec^{-1}). At the same time naphthoxyl radical is also produced with about the same rate constant as that for the triplet state. The results strongly suggest that the mechanism for the internal conversion of the singlet excited state *via* H-bonding is a transient H-atom transfer.

An interesting feature of fluorescence of a hydrogen-bonded compound is that two π-electronic systems, fluorescer and quencher combined in conjugation *via* a hydrogen bond, such as naphthol–pyridine,[1c,5] carbazole–pyridine[4] and acridine dye–naphthol[1b] have no emissivity in general. This phenomenon was extensively studied in particular by Mataga and his coworkers,[1–4] and was attributed to the delocalization of π-electrons *via* H-bond, which may naturally involve charge transfer interaction as is expected from the mechanism proposed for hydrogen-bonding.[6] This was exemplified by one of the present authors (M.K.);[5] quinoline acting as an acceptor in C–T interaction quenches the fluorescence of β-naphthylmethylether (donor) in *n*-hexane although the quenching constant is about half that for β-naphthol which forms hydrogen bond with quinoline.

In the case of carbazole–pyridine in methylcyclohexane–isopentane at 77 K, Mataga *et al.* demonstrated that H-bonding significantly enhances internal conversion but not the intersystem crossing.[4] However, it is still unknown whether this conclusion generally holds or not.

On the other hand, Rehm and Weller[7] proposed on theoretical grounds that the mechanism of fluorescence quenching for naphthol–pyridine, benz(*c*)acridine–phenol is due to the transient hydrogen transfer. Thus it is desirable to study the effect of H-bonding on the two nonradiative processes in a more direct way at room temperature, and to study whether hydrogen transfer actually occurs and if so to study the correlation between H-bonding and H-transfer. In order to tackle these problems we have applied the absorption-emission flash technique[8] to the naphthol–pyridine system, measuring the triplet yield and the time-integrated fluorescence intensity of naphthol with one sample.

Experimental

Materials. β-Naphthol (G.R. grade, Wako Junyaku) was recrystallized twice from a mixed solvent of water and ethanol, and then sublimed twice *in vacuo*. β-Naphthylethylether synthesized by a standard method was recrystallized five times from ethanol and sublimed *in vacuo*. Cyclohexane and pyridine were purified by the standard method. Triethylamine (G.R. grade, Wako Junyaku) was used without further purification.

Apparatus and Procedure. Absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. The fluorescence intensity was measured with a specially constructed fluorometer. The flash apparatus was modified so that two or three phenomena could be observed simultaneously. The energy of a flash was usually about 130 Joule and its half duration was about 10 μsec. A Hoya-U2 filter was used for excitation. All the measurements were made in cyclohexane solutions at room temperature; the solutions were degassed by pump and thaw method unless otherwise stated. The peak heights in the fluorescence spectra were used as a measure of fluorescence intensity since fluorescence spectra of β-naphthol were not affected by the addition of pyridine. The methods of measuring transient absorption spectra and the time-integrated fluorescence intensities during flashing were essentially the same as reported.[8]

Outline of Method. In principle, the absorption-emission flash technique is expected to be applicable for studying quantitatively the responsibility of internal conversion and intersystem crossing to the nonradiative process.

The triplet yield $[\mathrm{T}]_0$ is related with the total quantity of light absorbed during one flash by

$$[\mathrm{T}]_0 = \tilde{\phi}_{\mathrm{ST}}\int I_{\mathrm{ab}}\mathrm{d}t \qquad (1)$$

and the time integrated fluorescence intensity (measured at λ') during a flash is given by

$$\int I_{\mathrm{f}}(\lambda')\mathrm{d}t = \alpha(\lambda')\tilde{\phi}_{\mathrm{f}}\int I_{\mathrm{ab}}\mathrm{d}t \qquad (2)$$

where $\tilde{\phi}_{\mathrm{f}}$ and $\tilde{\phi}_{\mathrm{ST}}$ are the eventual fluorescence quantum

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[1] a) N. Mataga, Y. Kaifu, and M. Koizumi, *Nature*, **175**, 731 (1955), This Bulletin, **29**, 115 (1956); b) N. Mataga and S. Tsuno, *ibid.*, **30**, 368, 711 (1957); c) N. Mataga, *ibid.*, **31**, 481 (1958).

[2] N. Mataga, Y. Torihashi, and Y. Kaifu, *Z. Physik. Chem. N.F.*, **34**, 379 (1962).

[3] N. Mataga and K. Ezumi, This Bulletin, **40**, 1350 (1967).

[4] N. Mataga, F. Tanaka, and M. Kato, *Acta. Phys. Polon.*, **34**, 733 (1968).

[5] T. Miwa and M. Koizumi, This Bulletin, **36**, 1619 (1963).

[6] S. Nagakura and M. Gouterman, *J. Chem. Phys.*, **26**, 881 (1957). H. Baba and S. Suzuki, *ibid.*, **35**, 1118 (1961).

[7] D. Rehm and A. Weller, *Israel J. Chem.*, **8**, 259 (1970).

[8] K. Kikuchi, H. Kokubun, and M. Koizumi, This Bulletin, **41**, 1545 (1968).

yield and intersystem crossing probability, respectively and $\alpha(\lambda')$ is a constant depending upon the setup of the apparatus and experimental conditions. It should be noted that $\tilde{\phi}_f$ and $\tilde{\phi}_{ST}$ are not constant but depend upon the composition of the solution. From (1) and (2) we have

$$[\mathrm{T}]_0/\int I_f(\lambda')\mathrm{d}t = \tilde{\phi}_{ST}/\alpha(\lambda')\tilde{\phi}_f \tag{3}$$

For the present system, the emitter of fluorescence is only the free naphthol molecule as verified experimentally. Thus, putting a fraction of light absorbed by free naphthol as δ and using the genuine ϕ_f, Eq. (2) can be rewritten as follows, where A is pyridine acting as a proton acceptor and k_q is the overall quenching constant.

$$\begin{aligned}\int I_f(\lambda')\mathrm{d}t &= \alpha(\lambda')\delta\phi_f\int I_{ab}\mathrm{d}t\\ \phi_f &= k_f/\{(k_d+k_f)+k_q[\mathrm{A}]\}\\ k_d &= k_i + k_c\end{aligned} \tag{4}$$

(i, internal conversion; c, intersystem crossing)

The intersystem crossing is in general involved in the collisional quenching for free species, occurring also for the H-bonded species. Thus Eq. (1) is most generally rewritten as follows.

$$\begin{aligned}[\mathrm{T}]_0 = {} & \delta\int I_{ab}\mathrm{d}t\times(k_{ST}+k_q{}^c[\mathrm{A}])/(k_d+k_f+k_q[\mathrm{A}])\\ & +(1-\delta)\frac{k_c'}{k_i'+k_c'}\int I_{ab}\mathrm{d}t\end{aligned} \tag{5}$$

where $k_q{}^c$ is the rate constant for the collision induced intersystem crossing, $k_c=k_{ST}$ and $'$ stands for hydrogen-bonded species. Hence

$$\frac{[\mathrm{T}]_0}{\int I_f(\lambda')\mathrm{d}t} = \frac{k_{ST}+k_q{}^c[\mathrm{A}]}{k_f\alpha(\lambda')} + \frac{(1-\delta)}{\delta}\,\frac{k_c'}{\alpha(\lambda')k_f}\gamma \tag{6}$$

or

$$\tilde{\phi}_{ST}/\tilde{\phi}_f = (k_{ST}+k_q{}^c[\mathrm{A}])/k_f + (1-\delta)k_c'\gamma/\delta k_f \tag{7}$$

where

$$\gamma = (k_d+k_f+k_q[\mathrm{A}])/(k_i'+k_c')$$

On the basis of the above equation, we may obtain information on the rate constants $k_q{}^c$, k_i', and k_c', if we know some fundamental constants for the solution of β-naphthol including ϕ_{ST} and if we measure $[\mathrm{T}]_0$ and $\int I_f(\lambda')$ dt at various pyridine concentrations.

Results and Discussion

First the ground state hydrogen bonding equilibrium of naphthol-pyridine in cyclohexane was investigated. The spectroscopic procedures and the method of evaluating the equilibrium constant K from them are similar to those in n-hexane.$^{5)}$

The value of K at 16°C was evaluated as $140\mathrm{M}^{-1}$. This is compared with $K=125$, 61 in n-hexane at 21 and at 42°C respectively.$^{5)}$

Quenching of Fluorescence by Pyridine. The fluorescence behavior of β-naphthol influenced by the addition of pyridine in cyclohexane is also similar to that in n-hexane.$^{5)}$ Thus the significant quenching occurs without any spectral change. Therefore, the same method of analysis can be applied if we assume the non-emissivity of hydrogen-bonded species. The equation$^{5)}$

$$\frac{F_0/F-1}{[\mathrm{A}]} = \left(k_q\tau_0+\frac{\varepsilon'}{\varepsilon}K\right) + k_q\tau_0\frac{\varepsilon'}{\varepsilon}K[\mathrm{A}] \tag{8}$$

can easily be derived from the scheme below. (In practice, the exciting wavelength was chosen so that $\varepsilon(\lambda)$ is equal to $\varepsilon'(\lambda)$. ε and ε' are the molar extinction coefficients of free naphthol and H-bonded species respectively.)

$$(\mathrm{I})\ \left\{\begin{array}{lll} \text{i)} & \mathrm{D}+\mathrm{A} \rightleftarrows \mathrm{DA} & K\ \text{(equilibrium constant)}\\ \text{ii)} & \mathrm{DA} \xrightarrow{h\nu} \mathrm{DA}^* & \\ \text{iii)} & \mathrm{DA}^* \longrightarrow \mathrm{DA} & (k_i'+k_c')\\ \text{iv)} & \mathrm{D} \xrightarrow{h\nu} \mathrm{D}^* & \\ \text{v)} & \mathrm{D}^* \longrightarrow \mathrm{D}+h\nu' & \\ \text{vi)} & \mathrm{D}^* \longrightarrow \mathrm{D} & k_d = k_i + k_c\\ \text{vii)} & \mathrm{D}^*+\mathrm{A} \longrightarrow \mathrm{D}+\mathrm{A} & k_q \end{array}\right.$$

Thus the collisional quenching vii) is superposed on the static quenching i) and iii). In a previous paper,$^{5)}$ it was assumed simply that process vii) consists of the formation of hydrogen bond in the excited state followed by a rapid degradation of electronic energy.

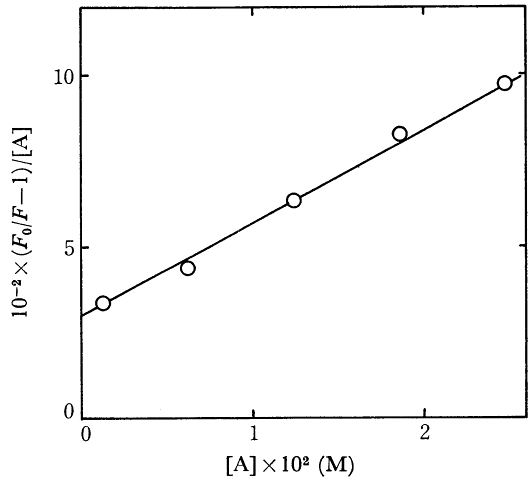

Fig. 1. The plot of $(F_0/F-1)/[\mathrm{A}]$ *vs.* [A].

Figure 1 shows the plot of $(F_0/F-1)/[\mathrm{A}]$ against [A]. By using $K=140\mathrm{M}^{-1}$, we evaluate the value of $k_q\tau_0$ as 160—$190\mathrm{M}^{-1}$. This is compared with the previous $k_q\tau_0$-value of 120 (21°C) in n-hexane. Putting $\tau_0=$ 13.3 nsec,$^{9)}$ we obtain $k_q=1.2$—$1.4\times10^{10}\mathrm{M}^{-1}\,\mathrm{sec}^{-1}$. Thus the collisional quenching occurs with the diffusion controlled rate constant.

Reaction between Triplet Naphthol and Pyridine. We first investigated the interaction between triplet naphthol and pyridine at low pyridine concentrations. Below 10^{-4}M of pyridine, the formation of H-bonded species in the ground state and the dynamic quenching of the singlet excited naphthol can be neglected as judged from the values of K, τ_0, and k_q obtained above.

Figure 2 gives a transient absorption spectrum obtained when the deaerated sloution of β-naphthol in cyclohexane is flashed; it does not appear in the aerated solution. This spectrum is attributed to the triplet-triplet absorption because of its close resemblance to the

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9) J. B. Barlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N.Y. (1965), p. 114.

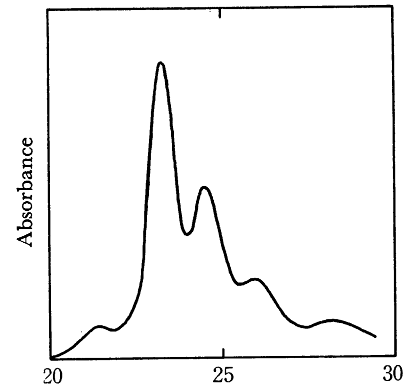

Fig. 2. T–T absorption spectrum of β-naphthol.

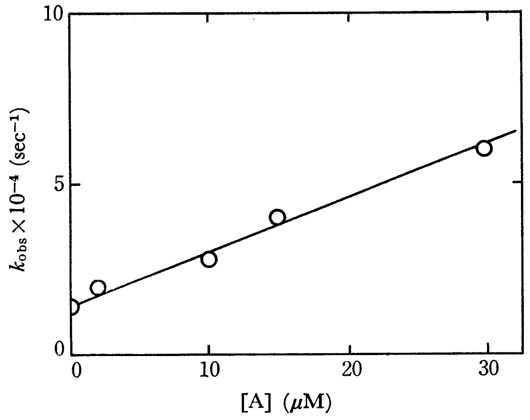

Fig. 3. The relation between the observed first order decay constant of β-naphthol triplet and pyridine concentration.

spectrum in literature.[10,11] For the sake of confirmation, T–T energy-transfer was ascertained to occur from β-naphthol to perylene. The decay was of first order with the rate constant 1.5×10^4 sec^{-1}.

The decay rate of triplet β-naphthol increased with increasing pyridine concentration. As shown in Fig. 3, the observed rate constant is satisfactorily linear with respect to [A].

$$k_{\mathrm{obs}} = k_{\mathrm{dt}} + k_{\mathrm{qt}}[\mathrm{A}]$$

where subscript t stands for triplet. From the intercept and inclination of the plot, we obtain

$$k_{\mathrm{qt}} = 1.5\times10^9\,\mathrm{M}^{-1}\,\mathrm{sec}^{-1} \qquad k_{\mathrm{dt}} = 1.5\times10^4\,\mathrm{sec}^{-1}$$

For pyridine concentrations higher than 10^{-4}M, quite a different spectrum as shown in Fig. 4 completely replaces the T–T absorption spectrum. The spectrum decays as a second order process with the rate constant k/ε—1.9×10^6 cm sec^{-1} (at 470 nm). The yield measured at the end of flashing increases with increasing pyridine concentrations up to 10^{-4}M. Since in this concentration region of pyridine, neither the formation of H-bond species in the ground state nor the collisional quenching of singlet excited naphthol by pyridine scarcely occurs, there is no doubt that this species (R) is produced by the reaction between triplet naphthol and pyridine. In fact it was confirmed that at 10^{-4}M of pyridine, the decay of triplet is accompanied by the build-up of R. Assuming the scheme

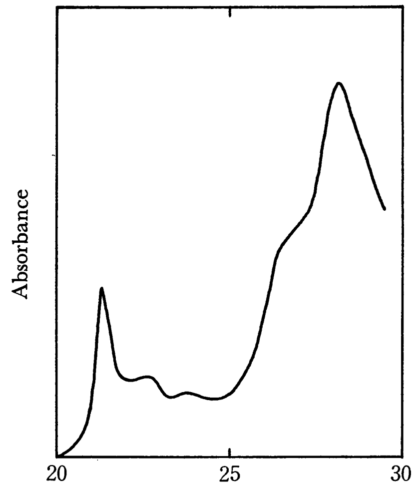

Fig. 4. The absorption spectrum of β-naphthoxyl radical.

$$(\mathrm{II})\left\{\begin{array}{l}\left.\begin{array}{l}\text{v)}\ \mathrm{D}\xrightarrow{h\nu}\mathrm{D}^*\\ \text{viii)}\ \mathrm{D}^*\longrightarrow\mathrm{D}^{\mathrm{T}}\end{array}\right\}\phi_{\mathrm{ST}}I_{\mathrm{ab}}\\ \text{ix)}\ \mathrm{D}^{\mathrm{T}}\xrightarrow{k_{\mathrm{dt}}}\mathrm{D}\\ \left.\begin{array}{l}\text{x)}\ \mathrm{D}^{\mathrm{T}}\xrightarrow{\mathrm{A}}\mathrm{R}\quad k^{\mathrm{r}}_{\mathrm{qt}}\\ \qquad\searrow\xrightarrow{\mathrm{A}}\mathrm{D}+\mathrm{A}\end{array}\right\}k_{\mathrm{qt}}\end{array}\right.$$

the yield of R at the end of a flash is given as follows ($I_{\mathrm{ab}}{}^0=\int I_{\mathrm{ab}}\mathrm{d}t$. $D_{\mathrm{R}}{}^0$, optical density (at 470 nm) at the end of a flash).

$$[\mathrm{R}]_0 = \frac{D_{\mathrm{R}}{}^0}{\varepsilon_{\mathrm{R}}\mathrm{d}} = I^0_{\mathrm{ab}}\times\phi_{\mathrm{ST}}\left(\frac{k^{\mathrm{r}}_{\mathrm{qt}}[\mathrm{A}]}{k_{\mathrm{qt}}[\mathrm{A}]+k_{\mathrm{dt}}}\right) \tag{9}$$

Hence

$$\frac{1}{D_{\mathrm{R}}{}^0} = \frac{1}{\varepsilon_{\mathrm{R}}\mathrm{d}\phi_{\mathrm{ST}}I^0_{\mathrm{ab}}}\left(\frac{k_{\mathrm{qt}}}{k^{\mathrm{r}}_{\mathrm{qt}}}+\frac{k_{\mathrm{dt}}}{k^{\mathrm{r}}_{\mathrm{qt}}[\mathrm{A}]}\right) \tag{10}$$

Figure 5 gives the $1/D_{\mathrm{R}}{}^0$ *vs.* $1/[\mathrm{A}]$ plot from which we obtain $k_{\mathrm{dt}}/k_{\mathrm{qt}}=7.9\times10^{-6}$ M. Inserting the value of $k_{\mathrm{dt}}=1.5\times10^4$ sec^{-1}, we get $k_{\mathrm{qt}}=1.9\times10^9$ M^{-1} sec^{-1} which agrees with the value of k_{qt} obtained from the effect of pyridine concentration on the triplet decay.

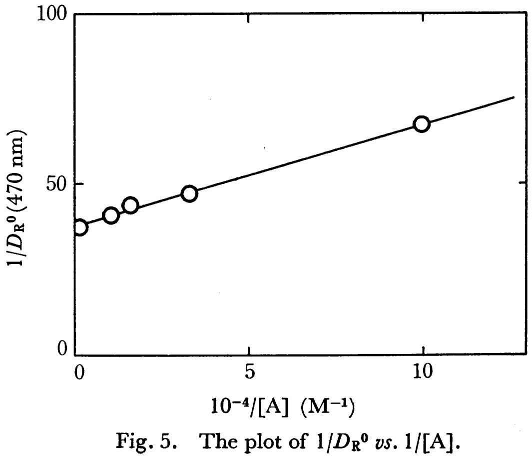

Fig. 5. The plot of $1/D_{\mathrm{R}}{}^0$ *vs.* $1/[\mathrm{A}]$.

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[10] G. Jackson and G. Porter, *Proc. Roy. Soc. Ser. A.*, **260** 13 (1961).

[11] E. J. Land, G. Porter, and E. Strachan, *Trans. Faraday Soc.*, **57**, 1885 (1961).

It might be concluded that the interaction between triplet naphthol and pyridine mainly leads to the formation of R. R was identified to be a neutral naphthoxyl radical for the following reasons. Porter and Jackson reported the formation of this species upon flashing the solution of naphthol in liquid paraffin.[10] The peak position they observed was 465 nm which agrees with the present result. Further it was found that a similar reaction occurs between triplet acridine[12] and β-naphthol in cyclohexane and benzene. In this case the transient spectra are the superposition of that of acridine C-radical and that of β-naphthoxyl radical. Figure 6 shows the plot of the observed decay rate of acridine triplet state against naphthol concentration from which we obtain $k_q=2.9\times10^9\text{M}^{-1}\text{sec}^{-1}$. An analogous reaction is known to occur between phenol and eosin yielding phenoxy radical and semiquinone of dye.[13]

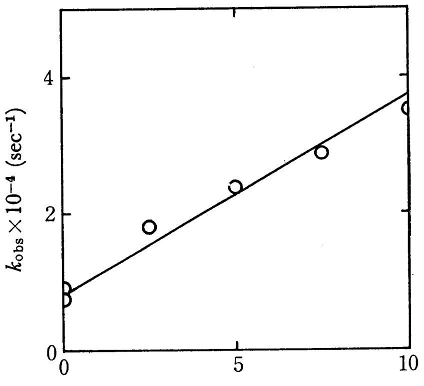
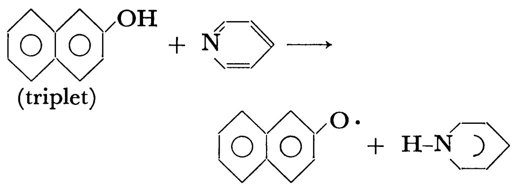


Fig. 6. The relation between the observed first order decay constant of acridine triplet and β-naphthol concentration.

Hence the reaction giving rise to this intermediate may be written as follows,[14]

xi)


It is interesting that the same reaction occurs even in the aerated solution although the yield of the intermediate is less on account of the quenching action of oxygen upon triplet naphthol. The effect of oxygen concentration on the yield of naphthoxyl radical can be treated by adding the following reaction to shceme (II).

$$\text{xii)}\quad D^T + O_2 \xrightarrow{k_q'} D + O_2$$

However, since the concentration of pyridine is moderately high, we should use Eq. (6) instead of (9), $[T]_0$ being replaced by $[R]_0$. Under the present conditions, the second term and $k_q{}^c[A]$ on the right hand side of (6) are neglected for the reason described later. Since the condition $k_{dt}\ll k_q{}^r[A]$ is satisfied, Eq. (10) can be modified as follows.

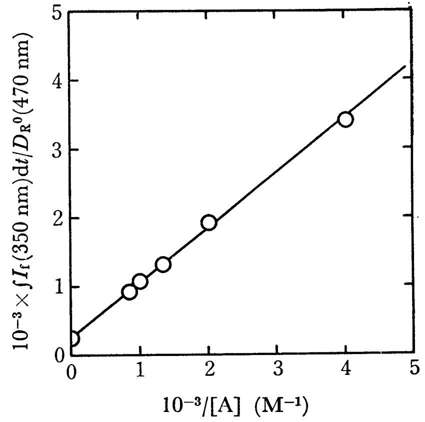


Fig. 7. The plot of $\int I_f(\lambda')dt/D_R{}^0$ *vs.* 1/[A].

$$\frac{\int I_f(\lambda')dt}{D_R{}^0} = \frac{\alpha(\lambda')k_f}{\varepsilon_R d k_{ST}}\left(\frac{k_{qt}}{k_{qt}^r}+\frac{k_q'[O_2]}{k_{qt}^r[A]}\right) \tag{11}$$

Figure 7 gives the plot of $\int I_f(\lambda')dt/D_R{}^0$ against 1/[A]. The datum for 1/[A]=0 was taken from the result in the deaerated solution and is exactly on the line drawn through other experimental data for the aerated solution. From the slope and intercept we obtain

$$k_q'[O_2]/k_{qt} = 3.3\times10^{-3}\text{M}$$

Inserting the value of $k_{qt}=(1.5\text{—}1.9)\times10^9\text{M}^{-1}\text{sec}^{-1}$ and $[O_2]=2.4\times10^{-3}$M (from the soubility of oxygen in cyclohexane), we evaluated k'_q to be $2.6\times10^9\text{M}^{-1}\text{sec}^{-1}$. This is a reasonable value which supports scheme (II).

TABLE 1. THE EFFECT OF ADDITION OF TEA ON THE DECAY RATE OF TRIPLET NAPHTHOL

$[\text{TEA}]_\text{M}$	k_{dt}(sec^{-1})	D_T(432 nm)
0	1.5×10^4	0.212
3×10^{-5}	2.2×10^4	0.189
3×10^{-4}	2.2×10^4	0.189
2×10^{-2}	2.6×10^4	0.072

In contrast to pyridine, triethylamine (TEA) which cannot act as a hydrogen atom acceptor scarcely affects the decay of triplet naphthol below 3×10^{-4}M as shown in Table 1. At 2×10^{-2}M of TEA, the yield of triplet naphthol decreases to some extent. This might be due to the increase in the rate of internal conversion of H-bonded species as in carbazole-TEA.[4] For naphthylmethylether which is incapable of hydrogen bonding with pyridine, the decay rate of triplet state is scarcely affected by the addition of pyridine. To sum up, scheme (II) holds only for the system consisting of H-atom donor and acceptor.

Quenching Action of Pyridine on the Singlet Excited State of Naphthol. Since it has been established that triplet naphthol is converted into neutral radical at pyridine concentrations $\gtrsim10^{-4}$M, $D_R{}^0$ should be used instead of $D_T{}^0$ in order to investigate the quenching action of pyridine on the fluorescence of naphthol. $\int I_f(350)$

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[12] It is interesting that the lowest T(π-π*) of acridine is involved in this photoreduction.

[13] L. I. Grossweiner and E. F. Zwicker, *J. Chem. Phys.*, **34**, 1411 (1961).

[14] It should be noted that another peak observed in the near ultraviolet region is also attributed to the same radical, since its decay feature is quite the same as that of the 470 nm peak both in deaerated and aerated solutions.

Table 2. Time integrated fluorescence intensity of naphthol and the yield of naphthoxyl radical

$[A]_o$, M	$\int I_f(350)dt$	$D_R{}^0(470)$	$\frac{D_R{}^0(470)}{\int I_f(350)dt}$
2.48×10^{-4}	1.97	0.051_3	0.026_2
2.48×10^{-3}	0.94_5	0.031_8	0.033_6
6.20×10^{-3}	0.48_5	0.018_7	0.038_6
1.24×10^{-2}	0.20_0	0.008_7	0.043_5
1.86×10^{-2}	0.08_5	0.004_8	0.056_5
2.48×10^{-2}	0.05_7	0.003_4	0.059_6
above 1×10^{-1}	0	0	

dt and $D_R{}^0$ (470 nm) were measured at various pyridine concentrations. The results are given in Table 2. It is seen that for $[A]_0 \gtrsim 10^{-1}$M, both $\int I_f(350)$ dt and $D_R{}^0(470)$ become zero. Since more than 90% of naphthol exists as hydrogen-bonded species, the remaining free naphhthol being almost completely quenched by pyridine in this concentration region of pyridine, it could be concluded that β-naphthol hydrogen bonded with pyridine scarcely undergoes intersystem crossing nor the reaction yielding naphthoxyl radical. Therefore the second term on the right hand side of Eqs. (6) and (5) can be neglected. However, there is a possibility of the formation of radical taking part in the collisional quenching of fluorescence, which may be discerned in the region of somewhat smaller pyridine concentrations. For this purpose, an analysis of the data in Table 2 was made by dividing process vii) in scheme (I) into three processes as follows.

$$\text{xv)}\quad D^* + A \xrightarrow{k_q{}^r} R$$

$$\text{xvi)}\quad D^* + A \xrightarrow{k_q{}^h} (D\cdots A)^* \text{ (H-bonded species)}$$

$$\text{xvii)}\quad D^* + A \xrightarrow{k_q{}^c} D^T + A$$

In other words, k_q in scheme (I) was assumed to be composed of three terms, $k_q = k_q{}^c + k_q{}^r + k_q{}^h$. However, since triplet naphthol if formed is quickly converted in to R under the present conditions, $k_q{}^r$ and $k_q{}^c$ cannot be discriminated experimentally. Therefore representing $(k_q{}^c + k_q{}^r)$ by $k_q{}^r$ and replacing $[T]_0$ by $[R]_0$, we get from (6)

$$\frac{D_R{}^0(\lambda)}{\int I_f(\lambda')dt} = \frac{\varepsilon_R(\lambda)d}{\alpha(\lambda')k_f}(k_{ST} + k_q{}^r[A]) \qquad (12)$$

It is assumed that the triplet naphthol is converted into R completely.

The left hand side of Eq. (12) is plotted against pyridine concentration in Fig. 8. We see that the radical formation reaction takes part in the quenching process. From the plot we obtain $k_q{}^r/k_{ST} = 5.6\times 10$M^{-1}. Using the value of (τ_0) of the singlet excited naphthol, we obtain $(\tau_0)^{-1} = k_f + k_d + k_{ST} = 7.5_2\times10^7$ sec^{-1}, our preliminary result for ϕ_{ST} being 0.5—0.7. Therefore k_{ST} is 3.8—5.3×10^7, and $k_q{}^r$ is evaluated as 2.1—3.0×10^9 M^{-1} sec^{-1}. Thus it is concluded that the formation of naphthoxyl radical occurs through the collisional interaction between singlet excited naphthol and pyridine, its rate constant being about the same as that in the triplet state. It is noteworthy that the value is significantly smaller than that of k_q, 1.2—1.4×10^{10}M^{-1}sec^{-1}, which was evaluated from the quenching of naphthol fluorescence by pyridine.

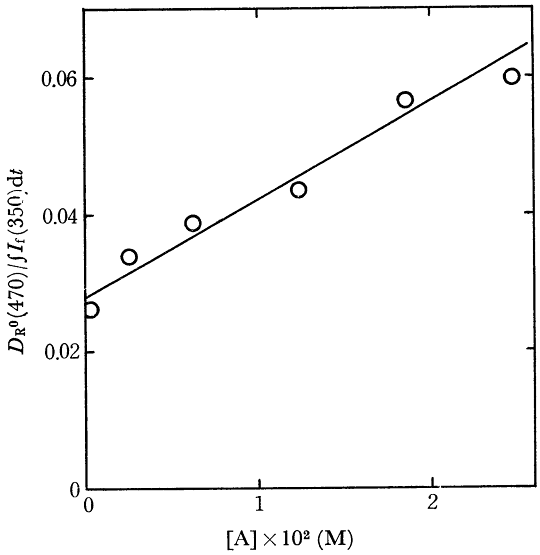

Fig. 8. The plot of $D_R{}^0$ $(\lambda)/\int I_f(\lambda')dt$ *vs.* [A].

Critical Consideration

The rate constants of various elementary reactions pertaining to the singlet excited and triplet states of naphthol are listed in Table 3. Comments will be given on some of them, in particular $k_q{}^h$ for excited free naphthol. k_i' and k_c' for the hydrogen-bond species were estimated as follows; k_i' from k_f[15] of free species multiplied by 10^3 on the basis of non-occurrence of fluorescence and intersystem crossing, and k_c' from the non-appearance of naphthoxyl radical.

Table 3. Rate constants of elementary reactions pertaining to the excited naphthol molecule in cyclohexane

	Singlet state		Triplet state
	free species	H-bonded species	
k_d	$k_i < 1.7\times10^7$ sec^{-1}	$k'_i \gtrsim 2\times10^{10}$ sec^{-1}	k_{dt} 1.5×10^4 sec^{-1}
	k_c 3.8—5.3×10^7 sec^{-1}	$k'_c < 10^7$—10^8 sec^{-1}	
	k_f 2.04×10^7 sec^{-1}	$k'_f \sim 2\times10^7$ sec^{-1}	
	k_h 9—12×10^9 M^{-1} sec^{-1}		k_{qt}^r 1.5—1.9×10^9 M^{-1} sec^{-1}
	$k_q{}^r$ 2.1—3.0×10^9 M^{-1} sec^{-1}		
	1.2—1.4×10^{10} M^{-1} sec^{-1}		

The present results demonstrate, that internal conversion is greatly enhanced by the formation of a hydrogen bond in the ground state. This is why the hydrogen-bonded species does not practically undergo intersystem crossing. The conclusion is essentially the same as that made by Mataga *et al.* on the carbazole–pyridine system.[4)]

Next will be discussed the nature of $k_q{}^r$ and $k_q{}^h$ and the smaller value of $k_q{}^r$ than that of $k_q{}^h$. There is no direct evidence for $k_q{}^h$ being connected with the forma-

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[15] 15) The absorption spectrum of the H-species dose not appreciably differ from that of the free species, and thus k_f' is equated to k_f.

tion of a H-bonded species, but this is highly plausible. According to Jackson and Porter,[10] acidity constants of β-naphthol in the ground, singlet excited and triplet states are respectively $pK_G=9.5$, $pK_{S*}=3.1$, and $pK_T=8.1—8.3$ (at 25°C). Since the strength of a hydrogen bond of an acid with a given base increases with the acidity, it is reasonable that hydrogen bond formation occurs much more easily in the singlet excited state[16] than in the ground and triplet states.

As regards $k_q{}^r$, it very likely occurs in the singlet excited state, although there is no direct experimental evidence, since if it connected with the reaction in the triplet state produced by the intersystem crossing of the excited H-bonded species, the value of $k_q{}^r$ should be more than one order less than the observed value, as judged from the values of k_i' and k_c'.

Thus, such a model can be rejected, and we may conclude that the singlet excited and triplet states of naphthol have about equal reactivity toward hydrogen atom transfer, as demonstrated by the same values of $k_q{}^r$ and k_{qt}. Further we may conclude that the significantly larger quenching constant of pyridine to naphthol fluorescence is mainly due to the formation of a H-bonded species, which does not occur in the triplet state. Perhaps radical formation and hydrogen bonding in the singlet excited state occur as competitive reactions and the latter overwhelms the former.

The above conclusions can be summarized by the scheme

$$\begin{tikzcd}
D + A \arrow[r, shift left, "K"] \arrow[d, shift right] & DA \arrow[l, shift left] \\
{}^1D^* + A \arrow[u, shift right, "{k_f + k_d \atop (k_d = k_i + k_c)}"'] \arrow[r] \arrow[d] \arrow[dr, "k_q{}^r"] & DA^* \arrow[u, "k_i'"'] \\
{}^3D + A \arrow[r] \arrow[d, "k_{dt}"] & R \\
{} &
\end{tikzcd}$$

where the reaction between D* and pyridine is mainly the formation of a H-bonded species, whereas that of triplet naphthol is only a radical formation.

Such situations might exist in general, since acidity and basicity for the singlet excited state differ greatly from those for the ground state but not so for the triplet state. As is well-known, acridine in the singlet excited state abstracts a hydrogen atom from alcohol (a poor proton donor), playing a role in the quenching of fluorescence. However, if we use a stronger proton donor such as naphthol or phenol, it might be expected also for acridine that a hydrogen-bond formation participates in the quenching of fluorescence whereas radical formation is dominant in the triplet state.

As regards the mechanism of internal conversion *via* H-bonding, it has been attributed in the past to the delocalization of π electron which usually induces C–T interaction.[1–4] This is true in some systems[5] but in the present case H-atom transfer is more plausible. Since the occurrence of H-transfer has been established both in the singlet excited and triplet states, it seems natural to assume that in the hydrogen-bonded species a transient H-transfer is also occurring *via* charge transfer interaction followed by proton transfer, producing a certain kind of radical pair. The pair, being unstable without doubt, will quickly be reconverted into the initial compound. This is likely to be the cause of internal conversion *via* H-bonding in the present system and similar ones. The results support the theoretical argument of Rehm and Weller[7] who concluded the hydrogen transfer mechanism of quenching for naphtholpyridine, benz(*c*)acridine–phenol *etc.* It is to be noted, however, that the eventual hydrogen transfer occurs not *via* excited hydrogen-bonded species but as a one act bimolecular process which plays only a small role in the quenching action of pyridine on naphthol.

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[16] When the H-bonded species is fluoroscent as TEA–carbazole, the rate constant for its formation is known to be diffusion controlled. (Ref. 4).