Deactivation of Triplet 2-Naphthol and 1-Anthrol by Aromatic *N*-Heterocycles

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A flash-photolytic investigation was carried out on the hydrogen bonding interaction of triplet 2-naphthol and 1-anthrol with aromatic *N*-heterocycles such as 4-methylpyridine, quinoline, and benzo[*h*]quinoline. The deactivation of triplet 2-naphthol and 1-anthrol by aromatic *N*-heterocycles was found to be due to the hydrogen atom transfer reaction. The relationship between the reactivity and the reduction potential of aromatic *N*-heterocycles suggests that the electron transfer from the triplet to the quencher is the primary process of the hydrogen atom transfer reaction.

Previously, we studied the hydrogen bonding interaction of the π-electronic system such as 2-naphthol–pyridine, 1-anthrol–pyridine, and 1-anthrol–quinoline in the ground, the triplet and the excited singlet states.1) On the basis of the results obtained, it was concluded that the hydrogen atom transfer reaction plays an important role in the dynamic deactivation through the hydrogen bonding interaction in the excited states and that the efficiency of the hydrogen atom transfer reaction in the excited state is affected by the acidity of the proton donor. In addition, the investigation of the triplet-triplet energy transfer from a suitable sensitizer to the hydrogen bonded species revealed that the triplet state of the hydrogen bonded species (^{3}DH–A) and the non-relaxed encounter complex (^{1}DH*···A) in the excited singlet state are the reaction state.2)

$$^1\mathrm{DH^*} + \mathrm{A} \rightleftarrows {}^1\mathrm{DH^*}\cdots\mathrm{A} \longrightarrow \dot{\mathrm{D}} + \mathrm{H\dot{A}}$$

$$^3\mathrm{DH} + \mathrm{A} \rightleftarrows {}^3\mathrm{DH\text{–}A} \longrightarrow \dot{\mathrm{D}} + \mathrm{H\dot{A}}$$

However, the difference in the reactivity between the excited singlet state and the triplet state is still not fully elucidated.

To clarify the reaction mechanism, it is of prime importance to find out the factors which govern the reactivity. In the present paper, we have investigated the effect of the reduction potential of the quenchers on the reactivity by a conventional flash apparatus.

Experimental

Materials. 2-Naphthol (G. R. grade, Tokyo Kasei) was recrystallized twice from the water–ethanol mixture, and sublimed twice *in vacuo.* 1-Anthrol used was the same as described before.1) Benzo[*h*]quinoline (G. R. grade, Tokyo Kasei) was recrystallized three times from the water–ethanol mixture, treated by thin-layer chromatography and sublimed *in vacuo.* 4-Methylpyridine (G. R. grade, Tokyo Kasei) was dried over barium oxide, distilled under reduced pressure and stored *in vacuo.* Quinoline (G. R. grade Tokyo Kasei) was distilled under reduced pressure and stored *in vacuo.* Cyclohexane was purified by the standard method.

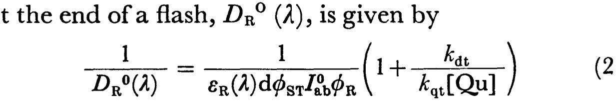
Apparatus and Procedure. Absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. The input energy of flash lamps was 65—130 J and its FWHM was about 10 μs. The combination of a Toshiba V-V40 and two plastic filters (cut off ≈380 nm) for the excitation of 1-anthrol and the combination of a Toshiba UV-D25 and a photographic plate glass for the excitation of 2-naphthol were used. Cyclohexane solutions were degassed by freeze-pump-thaw cycles. All measurements were made at about 25 °C.

Results and Discussion

A flashing of the deaerated cyclohexane solution of 2-naphthol gives the triplet-triplet absorption.3) Both the decay rate of the triplet 2-naphthol and the yield of the 2-naphthoxyl radical ($\dot{\mathrm{D}}$) increase with increasing quinoline concentration [Qu] up to 10^{-4} M, where neither the formation of hydrogen bond in the ground state nor the interaction of the excited singlet 2-naphthol with quinoline occurs. Since the triplet level of quinoline (21800 cm^{-1})4) is higher than that of 2-naphthol (21100 cm^{-1}), the deactivation of the triplet 2-naphthol is not due to the energy transfer but the hydrogen atom transfer reaction. The observed first order decay rate constant k_{obsd} is linear with respect to [Qu].

$$k_{\mathrm{obsd}} = k_{\mathrm{dt}} + k_{\mathrm{qt}}[\mathrm{Qu}] \tag{1}$$

From the slope, the quenching rate constant k_{qt} was obtained as $3.3\times10^9\ \mathrm{M^{-1}\,s^{-1}}$. The reaction scheme is described as follows.



$$\begin{tikzcd} \mathrm{DH} \arrow[r, "I_{\mathrm{ab}}"] & \mathrm{DH^*} \arrow[r, "\phi_{\mathrm{st}}"] & {}^3\mathrm{DH} \arrow[r, shift left, "k_1{}^{\mathrm{t}}{[\mathrm{A}]}"] \arrow[d, "k_{\mathrm{dt}}"'] & {}^3\mathrm{DH\text{–}A} \arrow[l, shift left, "k^{\mathrm{t}}_{-1}"] \arrow[r, "k_{\mathrm{r}}{}^{\mathrm{t}}"] \arrow[d, "k_{\mathrm{dt}}{}^{\mathrm{t}}"] & \dot{\mathrm{D}} + \mathrm{H\dot{A}} \\ & & \mathrm{DH} & \mathrm{DH\text{–}A} & \end{tikzcd}$$

Reaction scheme 1.

where DH and A stand for the proton donor and acceptor, respectively.

The absorbance of the 2-naphthoxyl radical measured at the end of a flash, $D_{\mathrm{R}}{}^{0}\ (\lambda)$, is given by

$$\frac{1}{D_{\mathrm{R}}{}^{0}(\lambda)} = \frac{1}{\varepsilon_{\mathrm{R}}(\lambda)\mathrm{d}\phi_{\mathrm{ST}}I^{0}_{\mathrm{ab}}\phi_{\mathrm{R}}}\left(1+\frac{k_{\mathrm{dt}}}{k_{\mathrm{qt}}[\mathrm{Qu}]}\right) \tag{2}$$

where $\phi_{\mathrm{R}}=k_{\mathrm{r}}{}^{\mathrm{t}}/(k_{\mathrm{r}}{}^{\mathrm{t}}+k_{\mathrm{dt}}{}^{\mathrm{t}})$ and $k_{\mathrm{qt}}=(k_{\mathrm{r}}{}^{\mathrm{t}}+k_{\mathrm{dt}}{}^{\mathrm{t}})\cdot k_1{}^{\mathrm{t}}/(k_{\mathrm{dt}}{}^{\mathrm{t}}+k_{\mathrm{r}}{}^{\mathrm{t}}+k_{-1}{}^{\mathrm{t}})$. The plot of $1/D_{\mathrm{R}}{}^{0}$ (470 nm) *vs.* 1/[Qu] is linear, from which the ratio $k_{\mathrm{qt}}/k_{\mathrm{dt}}$ was found to be $2.0\times10^5\ \mathrm{M^{-1}}$. Since $k_{\mathrm{dt}}=1.5\times10^4\ \mathrm{s^{-1}}$ is known,3) k_{qt} was determined to be $3.0\times10^9\ \mathrm{M^{-1}\,s^{-1}}$, which agrees well with $k_{\mathrm{qt}}=3.3\times10^9\ \mathrm{M^{-1}\,s^{-1}}$ obtained from the effect of quinoline concentration on the triplet decay. The reaction of the triplet 2-naphthol with quinoline yielding the 2-naphthoxyl radical occurs at one forth of the diffusion controlled rate; $1.1\times10^{10}\ \mathrm{M^{-1}\,s^{-1}}$ in cyclohexane.5)

The triplet 2-naphthol also reacts with 4-methylpyri-

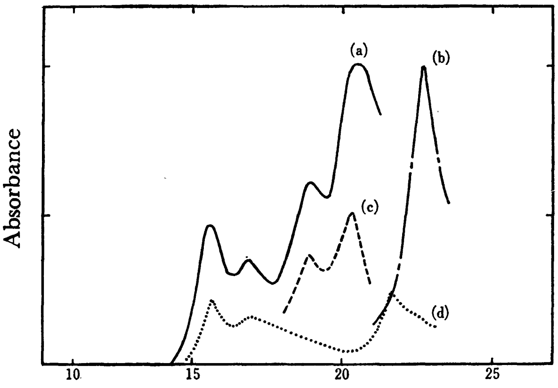


Fig. 1. Transient absorption spectra of 1-anthrol in cyclohexane. (a) [1-anthrol] = 1.0×10^{-4} M, [benzo[*h*]quinoline] = 1.0×10^{-3} M. (b) T-T absorption spectrum of 1-anthrol. (c) The spectrum of 1-anthroxyl radical. (d) The spectrum of benzo[*h*]quinoline radical.

Table 1. Quenohing rate constants of triplet 1-anthrol and 2-naphthol

Quencher	pK_a	k_{qt}/M^{-1} s^{-1}	Reduction potential in DMF$^{c)}$/V
		1-Anthrol	
Pyridine	$5.23^{a)}$	—	−2.76
Benzo[*h*] quinoline	$4.25^{a)}$	1.6×10^7	−2.23
Quinoline	$4.94^{a)}$	$(1.1—1.4)\times10^{9\ 1)}$	−2.175
Acridine	$5.5^{a)}$	$3.4\times10^{9\ 1)}$	−1.62
		2-Naphthol	
4-Methylpyridine	$6.02^{b)}$	4.0×10^8	−2.86
Pyridine	$5.23^{a)}$	$(1.5—1.9)\times10^{9\ 3)}$	−2.76
Quinoline	$4.94^{a)}$	$(3.0—3.3)\times10^{9)}$	−2.175

a) A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, **1948**, 2240. b) H.C. Brown and X. Mihm, *J. Am. Chem. Soc.*, **77**, 1723 (1955). c) B. J. Tabner and J. R. Yandle, *J. Chem. Soc., A*, **1968**, 381.

dine to produce the 2-naphthoxyl radical. The value of k_{qt} was determined as 4.0×10^8 M^{-1} s^{-1} from both the 4-methylpyridine concentration effect on the triplet decay and the yield of the 2-naphthoxyl radical. This value is smaller than that for the 2-naphthol–quinoline pair by about one order of magnitude.

The investigation was extended to the triplet 1-anthrol and benzo[*h*]quinoline (BQ) pair. With the addition of BQ, the decay rate of the triplet 1-anthrol increases and the transient absorption spectrum shown in Fig. 1(a) appears. This spectrum seems to be the superposition of the spectrum of the 1-anthroxyl radical[1] and that of the BQ radical[6] (Fig. 1(c), (d)). The observed first order decay rate constant of the triplet 1-anthrol is linear with respect to BQ concentration (*cf.* Eq. 1) and the quenching rate constant was found to be 1.6×10^7 M^{-1} s^{-1}. It is obvious that the hydrogen atom transfer reaction occurs between the triplet 1-anthrol and BQ. However the rate constant is smaller by about three orders of magnitude than the diffusion controlled rate constant.

In Table 1 are collected the quenching rate constants for the triplet 1-anthrol and the triplet 2-naphthol, together with reduction potentials and acid dissociation constants of the proton acceptors.

In a previous paper, the difference in the reactivity of 1-anthrol and 2-naphthol in the excited singlet state was explained by the difference of their acidities;[1] the hydrogen atom transfer is suppressed in the systems where the proton transfer is considered to occur easier. In the triplet state, however, the reaction rate constant has no correlation with the acidity of the proton acceptor. But reduction potential is associated with the quenching rate constant, which increases with the lowering of reduction potential. The reaction rate seems to be dependent on the easiness of the electron transfer in the encounter complex.

Therefore it seems plausible that the hydrogen atom transfer reaction occurs initially by the electron transfer followed by the proton transfer.

$$^3\mathrm{DH}\cdots\mathrm{A}\longrightarrow{}^3\overset{+}{\mathrm{D}}\mathrm{H}\cdots\overset{-}{\mathrm{A}}\longrightarrow\overset{\bullet}{\mathrm{D}}+\mathrm{H}\overset{\bullet}{\mathrm{A}}$$

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