

MECHANISMS OF DEACTIVATION OF TRIPLET 1-ANTHROL AND 2-NAPHTHOL BY AROMATIC N-HETEROCYCLES

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(Received December 6, 1976; in revised form February 26, 1977)

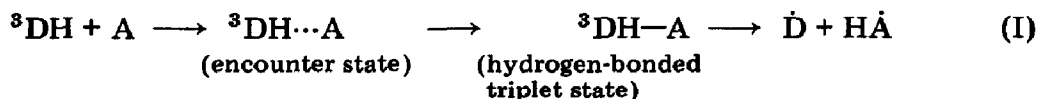
Summary

A flash photolytic investigation to determine the efficiency of the hydrogen atom transfer reaction in the triplet state was carried out for the systems of 1-anthrol-quinoline and 2-naphthol-pyridine in cyclohexane. The triplet states of 2-naphthol and 1-anthrol react respectively with pyridine and quinoline at a reaction efficiency of unity. In contrast, the reaction efficiency of the triplet 1-anthrol hydrogen bonded with quinoline is 0.59 and that of the triplet 2-naphthol hydrogen bonded with pyridine is 0.80. The difference in reaction efficiencies between the free and the hydrogen-bonded species implies that the hydrogen atom transfer reaction of the free species does not occur in the hydrogen-bonded triplet state following the encounter state but directly in the encounter state.

Introduction

We have previously studied the hydrogen bonding interaction of the π -electronic systems such as 2-naphthol-pyridine (2-N-Py), 1-anthrol-pyridine (1-A-Py) and 1-anthrol-quinoline (1-A-Q) in the ground, triplet and excited singlet states [1, 2]. It was found that the hydrogen (H) atom transfer reaction plays an important role in the deactivation of the excited state, and that the H atom transfer reaction occurs initially by electron transfer followed by proton transfer [3].

Moreover, investigation of the triplet-triplet (T-T) energy transfer from a suitable sensitizer to the hydrogen-bonded species DH-A [4] (where DH and A mean the aromatic hydroxy and the aromatic N-heterocyclic compound) revealed that the triplet state $^3\text{DH-A}$ of the hydrogen-bonded species is a reactive state of the H atom transfer reaction. Therefore, the following scheme was proposed for the reaction of the free species in the triplet state (^3DH):



where $\dot{\text{D}}$ and $\text{H}\dot{\text{A}}$ are the radicals corresponding to DH and A and ${}^3\text{DH}\cdots\text{A}$ is the encounter state in the triplet state which should be distinguished from ${}^3\text{DH}-\text{A}$. However, the T-T energy transfer experiment cannot exclude the possibility that the radicals are formed directly from the encounter state as in the case of the excited singlet state of 2-N [1].



In this paper we attempt to determine the efficiencies of the H atom transfer reaction in the triplet states of the free and in the hydrogen-bonded species in order to answer the question whether the reaction of the free species in the triplet state occurs by reaction schemes (I) or (II).

Experimental

2-Naphthol (GR grade, Tokyo Kasei) was recrystallized twice from a water-ethanol mixture and sublimed three times *in vacuo*. 1-Anthrol was synthesized according to the method of Schmidt [5], recrystallized from a water-ethanol mixture, treated by thin-layer chromatography on silica gel G and sublimed *in vacuo*. Specially purified anthracene was supplied by Prof. S. Kato, Tokyo University. Phenanthrene (zone refined, Tokyo Kasei) containing a trace of anthracene was treated by the Diels-Alder reaction, recrystallized from ethanol and sublimed *in vacuo*. The phenanthrene thus obtained was free from anthracene. Perylene (GR grade, Tokyo Kasei) was recrystallized from toluene. Quinoline (GR grade, Tokyo Kasei) was dried over barium oxide and distilled under reduced pressure. Pyridine (GR grade, Wako Junyaku) was dried over barium oxide and distilled (b.p. 105 °C). Cyclohexane (EP grade, Wako Junyaku) was purified by the standard method.

Absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. The flash energy was in the range 65 - 130 J; its FWHM was about 10 μs . The transmittances of the filter systems used for excitation are shown in Fig. 1. Cyclohexane solutions were degassed by freeze-pump-thaw cycles. All measurements were made at about 25 °C.

Results and discussion

When the hydrogen bond formation in the ground and the excited singlet state is neglected, the processes concerned with the triplet state are given as [5]



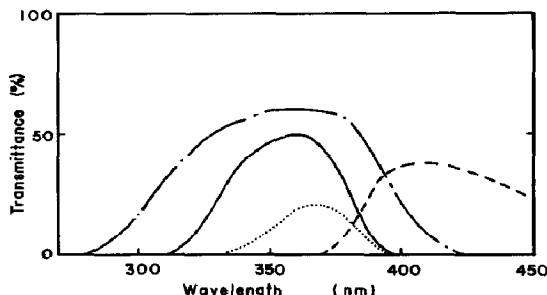


Fig. 1. The transmittance of the filters used for excitation: 1, — UV-P; 2, - . - UV-D25 + U-V31; 3, - - - V-V40 + plastic filter (cut-off 380 nm); 4, V-V40 + UV-P.



According to scheme (III) the efficiency of the H atom transfer reaction of the free species, $k_r/(k_r + k_d)$, can be estimated as follows [6]. The yield of $\dot{\text{D}}$ at the end of a flash is related to the total quantity of light absorbed during one flash, $\int I_{ab} dt$, by

$$\int d[\text{D}] \equiv [\dot{\text{D}}]_0 = \phi_{ST} \frac{k_r [\text{A}]}{k_{dt} + (k_r + k_d) [\text{A}]} \int I_{ab} dt \quad (1)$$

where the subscript zero stands for the quantity immediately after flashing. The time-integrated fluorescence intensity $\int I_f(\lambda') dt$ measured at λ' during a flash is given by

$$\int I_f(\lambda') dt = \alpha(\lambda') \phi_f \int I_{ab} dt \quad (2)$$

where ϕ_f is the fluorescence quantum yield and $\alpha(\lambda')$ is a constant depending on the set-up of the apparatus and experimental conditions. Thus, from eqns. (1), (2) and the relation

$$D_0^R(\lambda) = \epsilon_R(\lambda) [\dot{\text{D}}]_0 d \quad (3)$$

we obtain

$$\frac{\int I_f(\lambda') dt}{D_0^R(\lambda)} = \frac{\alpha(\lambda') \phi_f}{\epsilon_R(\lambda) d \phi_{ST}} \frac{k_r + k_d}{k_r} \left(1 + \frac{k_{dt}}{k_r + k_d} \frac{1}{[\text{A}]} \right) \quad (4)$$

where $D_0^R(\lambda)$ and $\epsilon_R(\lambda)$ are the absorbance at the end of a flash and the molar extinction coefficient of $\dot{\text{D}}$ at wavelength λ respectively and d is the optical path length (10 cm). In the present case k_{dt} is $3.4 \times 10^3 \text{ s}^{-1}$ for 1-A and $1.5 \times 10^4 \text{ s}^{-1}$ for 2-N, and $(k_r + k_d)$ is $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for 1-A-Q and $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for 2-N-Py [2]. Accordingly the condition $(k_r + k_d) [\text{A}] \gg k_{dt}$ is satisfied when $[\text{A}] > 10^{-5} \text{ M}$, and eqn. (4) is safely approximated to be

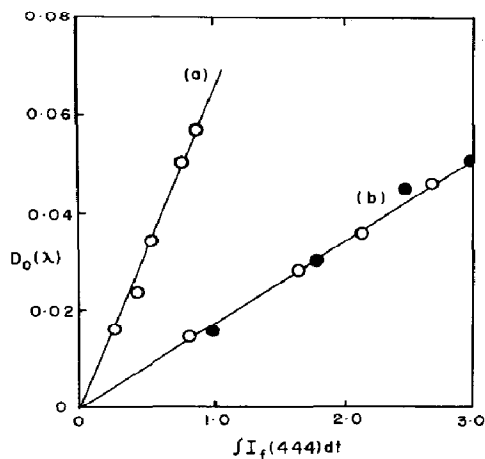


Fig. 2. The plot of $D_0^R(\lambda)$ and $D_0^T(\lambda)$ vs. $\int I_f(\lambda')dt$: (a) $D_0^T(440)$, $[1-A] = 1 \times 10^{-4}$ M; (b) $D_0^R(490)$ -●- $[1-A] = 1 \times 10^{-4}$ M, $[Q] = 8.4 \times 10^{-5}$ M, -○- $[1-A] = 1 \times 10^{-4}$ M, $[Q] = 1.2 \times 10^{-3}$ M. Filter system, 3.

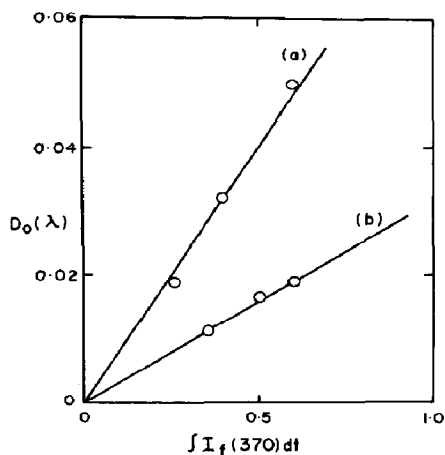


Fig. 3. The plot of $D_0^R(\lambda)$ and $D_0^T(\lambda)$ vs. $\int I_f(\lambda')dt$: (a) $D_0^T(435)$, $[2-N] = 3 \times 10^{-4}$ M; (b) $D_0^R(470)$, $[2-N] = 3 \times 10^{-4}$ M, $[Py] = 3 \times 10^{-4}$ M. Filter system, 2.

$$\frac{\int I_f(\lambda')dt}{D_0^R(\lambda)} = \frac{\alpha(\lambda)\phi_f}{\epsilon_R(\lambda)d\phi_{ST}} \frac{k_r + k_d}{k_r} \quad (4a)$$

Since the triplet lifetime is much longer than the flash duration at $[A] = 0$ M, the absorbance $D_0^T(\lambda)$ of the T-T absorption immediately after flashing is expressed as

$$\frac{D_0^T(\lambda)}{\int I_f(\lambda')dt} = \epsilon_T(\lambda)d \frac{\phi_{ST}}{\alpha(\lambda)\phi_f} \quad (5)$$

where $\epsilon_T(\lambda)$ is the molar extinction coefficient of the T-T absorption. The plots of $D_0^R(\lambda)$ and $D_0^T(\lambda)$ against $\int I_f(\lambda')dt$ are given in Figs. 2 and 3. From the slopes of these plots the values of $D_0^R(\lambda)/\int I_f(\lambda')dt$ and $D_0^T(\lambda)/\int I_f(\lambda')dt$ were evaluated and are cited in Table 1. From eqns. (4a) and (5) we obtain

$$\frac{k_r}{k_r + k_d} = \frac{D_0^R(\lambda)/\int I_f(\lambda')dt}{D_0^T(\lambda)/\int I_f(\lambda')dt} \frac{\epsilon_T(\lambda)}{\epsilon_R(\lambda)} \quad (6)$$

The molar extinction coefficients of the T-T absorption of 1-A and 2-N were determined by means of the energy transfer method [7] from 1-A and 2-N to perylene. The molar extinction coefficient of the T-T absorption of perylene was determined as $\epsilon_T = 13\,000 \text{ cm}^{-1} \text{ M}^{-1}$ at 480 nm by using anthracene ($\epsilon_T = 64\,700 \text{ cm}^{-1} \text{ M}^{-1}$ at 425 nm [8]) as an energy donor.

The molar extinction coefficients of the 1-anthroxyl and 2-naphthoxyl radicals were determined as follows. The triplet 1-anthrol reacts with acridine to produce the 1-anthroxyl radical and the acridine C-radical [2]. The triplet acridine reacts with 2-naphthol to yield the acridine C-radical and the 2-naphthoxyl radical [1]. As the concentration of the 1-anthroxyl or

TABLE 1

The values of the reaction efficiency and necessary values for its evaluation

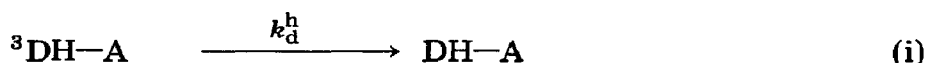
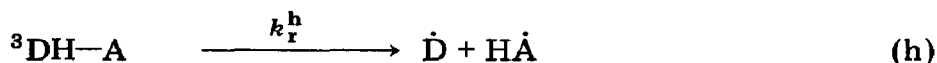
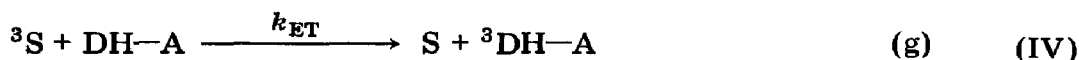
1-anthrol-quinoline; triplet sensitizer anthracene							
$D_0^R(490)$	$D_0^T(440)$	$D_0^R(490)$	$D_0^{T,S}(425)$	$\epsilon_T^{1-A}(440)$	$\epsilon_R(490)$	k_T	$\frac{k_T^h}{k_T^h + k_d^h}$
$\frac{\int I_f(444)dt}{\int I_f(444)dt}$	$\frac{\int I_f(444)dt}{\int I_f(444)dt}$	$\frac{\int I_f^S(450)dt}{\int I_f^S(450)dt}$	$\frac{\int I_f^S(450)dt}{\int I_f^S(450)dt}$	$(\text{cm}^{-1} \text{M}^{-1})$	$(\text{cm}^{-1} \text{M}^{-1})$	$\frac{k_T}{k_T + k_d}$	$\frac{k_T^h}{k_T^h + k_d^h}$
0.018	0.067	0.031	0.44	28 300	7600	1	0.59
2-naphthol-pyridine; triplet sensitizer phenanthrene							
$D_0^R(470)$	$D_0^T(435)$	$D_0^R(470)$	$D_0^{T,S}(482.5)$	$\epsilon_T^{2-N}(435)$	$\epsilon_R(470)$	k_T	$\frac{k_T^h}{k_T^h + k_d^h}$
$\frac{\int I_f(370)dt}{\int I_f(370)dt}$	$\frac{\int I_f(370)dt}{\int I_f(370)dt}$	$\frac{\int I_f^S(365)dt}{\int I_f^S(365)dt}$	$\frac{\int I_f^S(365)dt}{\int I_f^S(365)dt}$	$(\text{cm}^{-1} \text{M}^{-1})$	$(\text{cm}^{-1} \text{M}^{-1})$	$\frac{k_T}{k_T + k_d}$	$\frac{k_T^h}{k_T^h + k_d^h}$
0.032	0.08	0.023	0.20	6500	2600	1	0.80

2-naphthoxyl radical produced by the above reactions is equal to that of the acridine C-radical, we have

$$\begin{aligned} D_0^R(\lambda) &= \{\epsilon_R(\lambda)[\dot{D}]_0 + \epsilon'(\lambda)[\dot{A}c]_0\}d \\ &= \{\epsilon_R(\lambda) + \epsilon'(\lambda)\}[\dot{A}c]_0d \end{aligned}$$

where $\dot{A}c$ stands for the acridine C-radical. As the molar extinction coefficient $\epsilon'(\lambda)$ of the acridine C-radical is known to be $4100 \text{ cm}^{-1} \text{ M}^{-1}$ at 510 nm [8], the concentration $[\dot{A}c]_0$ of the acridine C-radical immediately after flashing can be evaluated and then the molar extinction coefficient of 1-anthroxyl or 2-naphthoxyl radical is obtained (see Table 1). All experimental parameters necessary to evaluate eqn. (6) become available, and an efficiency of unity for the H atom transfer reaction was obtained for both 1-A-Q and 2-N-Py.

When the hydrogen bond formation is complete in the ground state, a suitable triplet sensitizer is necessary to excite the hydrogen-bonded species into the triplet state, because both the yields of the fluorescence and the intersystem crossing of the hydrogen-bonded species are nil. Anthracene was used as a triplet sensitizer for the 1-A-Q system. Phenanthrene ($\epsilon_T = 18\,000 \text{ cm}^{-1} \text{ M}^{-1}$ at 482.5 nm) was a sensitizer for 2-N-Py. Then the following scheme seems to be adequate [4]:



where S means the triplet sensitizer. Since k_{ET} is of the order of the diffusion controlled rate constant and k_{dt}^s is $1 \times 10^3 \text{ s}^{-1}$ for anthracene and $3 \times 10^3 \text{ s}^{-1}$ for phenanthrene, $k_{ET}[\text{DH-A}] \gg k_{dt}^s$ when $[\text{DH-A}] > 10^{-5} \text{ M}$. Then the yield of \dot{D} at the end of a flash is

$$[\dot{D}]_0 = \frac{k_r^h}{k_r^h + k_d^h} [{}^3S]_0 \quad (7)$$

The yield $[{}^3S]_0$ of 3S immediately after flashing is related to the time-integrated fluorescence intensity $\int I_f^S(\lambda') dt$:

$$[{}^3S]_0 = \frac{\phi_{ST}^S}{\alpha(\lambda')\phi_f^S} \int I_f^S(\lambda') dt \quad (8)$$

where the superscript S stands for the triplet sensitizer. From eqns. (7) and (8) the following relation is obtained:

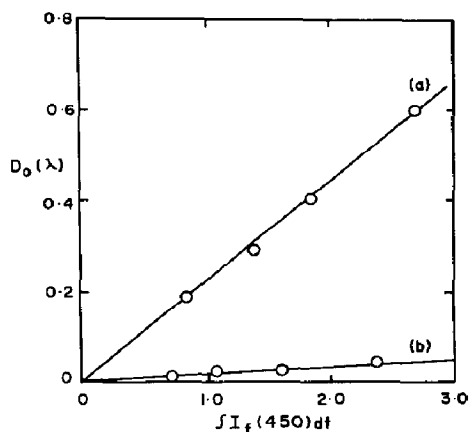


Fig. 4. The plot of $D_0^R(\lambda)$ and $D_0^{T\cdot S}(\lambda)dt$ vs. $\int I_f^S(\lambda')dt$: (a) $D_0^{T\cdot S}(425)$, [anthracene] = 3×10^{-4} M; (b) $D_0^R(490)$, [anthracene] = 3×10^{-4} M, [1-A] = 2.5×10^{-5} M, [Q] = 1×10^{-1} M. Filter system, 4.

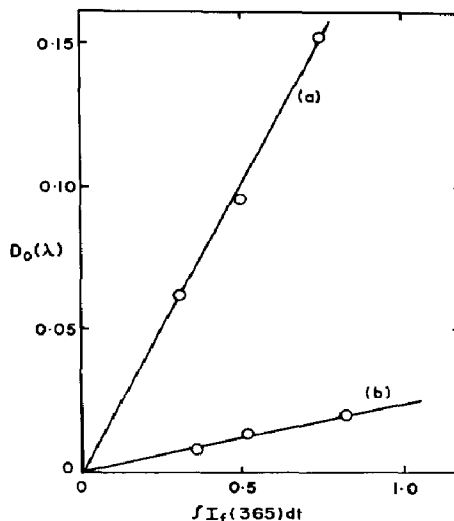


Fig. 5. The plot of $D_0^R(\lambda)$ and $D_0^{T\cdot S}(\lambda)$ vs. $\int I_f^S(\lambda')dt$: (a) $D_0^{T\cdot S}(482.5)$, [phenanthrene] = 2×10^{-3} M; (b) $D_0^R(470)$, [phenanthrene] = 2×10^{-3} M, [2-N] = 6×10^{-5} M, [Py] = 1×10^{-1} M. Filter system, 1.

$$\frac{k_r^h}{k_r^h + k_d^h} = \frac{D_0^R(\lambda) / \int I_f^S(\lambda') dt \epsilon_T^S(\lambda)}{D_0^{T\cdot S}(\lambda) / \int I_f^S(\lambda') dt \epsilon_R(\lambda)} \quad (9)$$

where ϵ_T^S and $D_0^{T\cdot S}$ are the molar extinction coefficient and the absorbance of the T-T absorption of the sensitizer. The plots of $D_0^R(\lambda)$ and $D_0^{T\cdot S}(\lambda)$ against $\int I_f^S(\lambda') dt$ are given in Figs. 4 and 5. From the slopes of these plots the values of $D_0^R(\lambda) / \int I_f^S(\lambda') dt$ and $D_0^{T\cdot S}(\lambda) / \int I_f^S(\lambda') dt$ were obtained and are cited in Table 1.

By the use of the values summarized in Table 1 and of eqn. (9) the values of $k_r^h / (k_d^h + k_r^h)$ were calculated and are listed in Table 1. The efficiencies of the H atom transfer reaction of $^3\text{DH-A}$ are significantly less than unity.

The present result, *i.e.* that the efficiency $k_r^h / (k_d^h + k_r^h)$ of the H atom transfer reaction of $^3\text{DH-A}$ is less than unity, indicates that the triplet state of the hydrogen-bonded species decays not only by the H atom transfer reaction ((h) in scheme (IV)) but also by the other radiationless pathway ((i) in scheme (IV)). Therefore the efficiency of the H atom transfer reaction of free species in the triplet state, $k_r / (k_r + k_d)$ (scheme (III)), will be less than unity if all of the H atom transfer reaction occurs from the hydrogen-bonded triplet state following the encounter state (scheme (I)). The fact that the reaction efficiency of the free species, $k_r / (k_r + k_d)$, is unity for both systems studied implies that almost all of the H atom transfer reaction occurs from the encounter state (scheme (II)).

