HYDROGEN-ATOM TRANSFER REACTION FROM PHENOL TO EXCITED 7,8-BENZOQUINOLINE

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Summary

The hydrogen-bonding interaction between excited 7,8-benzoquinoline and phenol was investigated in cyclohexane by an emission—absorption flash technique. The dynamic quenching of the excited singlet and triplet 7,8-benzoquinoline with phenol gives rise to a hydrogen-atom transfer reaction with efficiencies of 0.25 and 1.0 respectively. Independent of whether the excited state is a hydrogen-bond donor or an acceptor, the efficiency for the excited singlet state changes considerably among hydrogen-bonding systems of the type $\geqslant$N---H—O$\lessdot$, whereas the efficiency for the triplet state is unity for all the reacting systems. For these reactions the dynamic quenching is regarded as resulting from the competitive reactions of hydrogen-atom transfer and hydrogen-bond formation.

1. Introduction

From the standpoint of the hydrogen-atom transfer reaction, we have hitherto studied the hydrogen-bonding interaction of two-conjugate π-electronic systems in the excited singlet and triplet states by an emission—absorption flash technique [1 - 7]. From the difference in reaction yields between the excited singlet and triplet states for free and hydrogen-bonded species, it was concluded that (i) in the excited singlet state the hydrogen-atom transfer reaction occurs only in the non-relaxed encounter state prior to hydrogen-bond formation and that (ii) in the triplet state the hydrogen-atom transfer reaction occurs in both the non-relaxed encounter state and the hydrogen-bonded state. This conclusion is based on the results obtained for the hydrogen-bonding systems $\geqslant$—O—H---N$\lessgtr$ and $\geqslant$N—H---N$\lessgtr$ in which the hydrogen-bond donor is excited. It proves interesting to investigate a system in which the hydrogen-bond acceptor is excited.

In the present work we studied the hydrogen-bonding interaction in the excited singlet and triplet states for the 7,8-benzoquinoline–phenol (BQ–PhOH) system in cyclohexane. In this system the value for $\Delta pK_a = pK_a(\text{donor}) - pK_a(\text{acceptor})$, which is a measure of the facility of hydrogen-bond formation, is close to zero even in the excited singlet state, because the pK_a for BQ in the excited singlet state and that for PhOH in the ground state are 11.0 [8] and 10.0 respectively. Therefore, the hydrogen-bond formation in the excited singlet state might not be particularly advantageous compared with that in the triplet state, and a high reaction yield is expected for the hydrogen-atom transfer reaction in the excited singlet state as well as in the triplet state if the reaction yield depends only on ΔpK_a.

2. Experimental details

BQ (Guaranteed Reagent grade, Tokyo-Kasei) was treated by thin-layer chromatography and sublimed under vacuum. PhOH (Guaranteed Reagent grade, Wako-Junyaku) was dried over calcium chloride, distilled under reduced pressure and then stored in vacuum. Pyrene (Extra Pure grade, Tokyo-Kasei) was zone refined and recrystallized from ethanol. 2-Naphthol (Guaranteed Reagent grade, Tokyo-Kasei) was recrystallized twice from an ethanol–water mixture and sublimed twice under vacuum. The procedure for the purification of cyclohexane (Extra Pure grade, Wako-Junyaku) has been reported previously [7]. Sample solutions were degassed by freeze–pump–thaw cycles.

Absorption spectra were recorded using a Hitachi 330 spectrophotometer. Fluorescence spectra were measured using a spectrophotometer built in our laboratory. The fluorescence lifetime was measured using a phase fluorometer modulated at 10.7 MHz. The method of measuring the transient absorption and the time-integrated fluorescence intensity during a flash has been reported previously [1]. A xenon flash lamp (32 - 200 J; full width at half-maximum, 10 - 20 μs) was used for excitation with a combination of Toshiba UVD 25 and UV 31 filters, which transmits light in the range 300 - 400 nm. All measurements were made at 296 K unless noted otherwise.

3. Results and discussion

BQ forms a hydrogen-bonded complex with PhOH in the ground state. Absorption spectra of BQ in cyclohexane containing various amounts of PhOH are shown in Fig. 1. Isosbestic points appear at 31 850, 31 550, 30 490, 30 120, 29 070 and 28 780 cm^{-1}. The hydrogen-bond equilibrium constant K_g in the ground state was determined to be 14 M^{-1} at 298 K.

The fluorescence yield $\Phi_F = 0.11$ in cyclohexane at 296 K was determined using a 1 N H_2SO_4 aqueous solution of quinine sulphate as the stan-
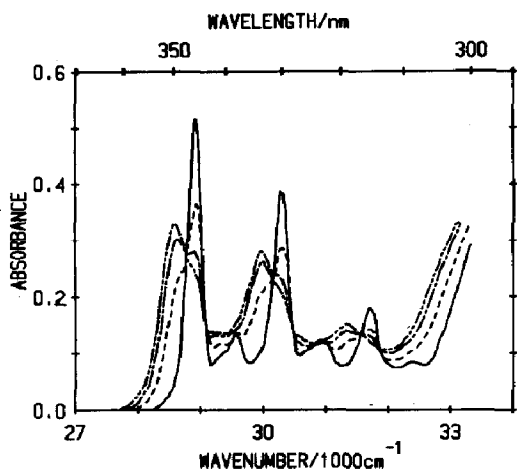
Fig. 1. Absorption spectra of 0.1 mM BQ in cyclohexane containing various amounts of PhOH: ——, 0 M; — — —, 50 mM; — · —, 144 mM; — ·· —, 263 mM.
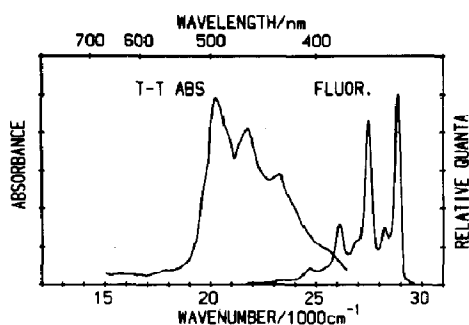
Fig. 2. T–T absorption and fluorescence spectra of BQ in cyclohexane.

dard [9]. With the addition of PhOH, the fluorescence of BQ is quenched without any change in the fluorescence spectrum (shown in Fig. 2). This finding shows that the observed fluorescence comes from free BQ and that the hydrogen-bonded BQ does not fluoresce. The fluorescence quenching is described by the equation

$$\frac{F^0}{F} = (1 + K_g[\text{PhOH}])(1 + k_q \tau_0[\text{PhOH}]) \tag{1}$$

for excitation at an isosbestic point. Using the measured fluorescence lifetime $\tau_0 = 4.0$ ns, we obtained $k_q = 1.2 \times 10^{10}$ M^{-1} s^{-1} for the bimolecular quenching rate constant.

Flashing of the deaerated solution of BQ gives a transient absorption (shown in Fig. 2) whose spectral shape does not change throughout its decay. It was assigned to the T–T absorption of BQ by investigating the triplet-energy transfer from BQ (triplet energy, $21\,800$ cm^{-1} [10, 11]) to pyrene (triplet energy, $16\,800$ cm^{-1} [12]). The decay was the superposition of first- and second-order processes: $k_1 = (1 - 2) \times 10^3$ s^{-1} and $k_2 = 2.8 \times 10^9$ M^{-1} s^{-1}.

The quantum yield Φ_{isc} of intersystem crossing was determined using an emission–absorption flash technique [13]. The equation

$$\frac{\Phi_{isc}^B}{\Phi_{isc}^A} \frac{\epsilon_T^B(\lambda^B)}{\epsilon_T^A(\lambda^A)} = \frac{\{\alpha(\lambda')\Phi_F\}^B}{\{\alpha(\lambda')\Phi_F\}^A} \frac{D^B(\lambda^B)/\int I_F^B(\lambda')\,dt}{D^A(\lambda^A)/\int I_F^A(\lambda')\,dt} \tag{2}$$

was used, where $\alpha(\lambda')$ is a constant depending upon the experimental conditions, $D(\lambda)$ is the absorbance of the T–T absorption at the end of a flash, $\int I_F(\lambda')\,dt$ is the time-integrated fluorescence intensity at λ' during the flash excitation, and the superscripts B and A denote BQ and anthracene (used as a reference) respectively. The molar extinction coefficient $\epsilon_T^B(\lambda^B)$ of the

T–T absorption for BQ was determined to be $6.3 \times 10^3 \, M^{-1} \, cm^{-1}$ at 495 nm by the triplet-energy transfer from BQ to anthracene (triplet energy, 14 900 cm^{-1} [14]). The molar extinction coefficient $\epsilon_T^A(\lambda^A)$ for the T–T absorption of anthracene was reported to be 64 700 $M^{-1} \, cm^{-1}$ at 422 nm [15]. The values of Φ_F and Φ_{isc} for anthracene in cyclohexane were reported to be 0.30 [16] and 0.71 [17] respectively. Using the results listed in Table 1, Φ_{isc}^B was determined to be 0.88. It is noteworthy that the sum of Φ_F and Φ_{isc} is close to unity.

TABLE 1

Triplet yield of BQ and the quantities necessary for its evaluation

$\dfrac{\epsilon_T^B(495)}{\epsilon_T^A(422)}$	$\dfrac{\{\alpha(385)\Phi_F\}^B}{\{\alpha(385)\Phi_F\}^A}$	$\dfrac{D^B(495)/\int I_F^B(385)\,dt}{D^A(422)/\int I_F^A(385)\,dt}$	Φ_{isc}^A	Φ_{isc}^B
0.097	0.45	0.27	0.71	0.88

The decay rate of triplet BQ increases on increasing the PhOH concentration. The observed first-order rate constant k_{obs} is linear with respect to the PhOH concentration:

$$k_{obs} = k_{dt} + k_{qt}[PhOH] \tag{3}$$

The quenching rate constant was determined to be $k_{qt} = 1.2 \times 10^9 \, M^{-1} \, s^{-1}$.

Flashing of the solution containing 0.1 mM BQ and 1 mM PhOH gives another transient absorption (Fig. 3, spectrum a) which was measured immediately after flashing. The decay is second order with a rate constant of $6.8 \times 10^9 \, M^{-1} \, s^{-1}$. If a hydrogen-atom transfer reaction occurs between BQ and PhOH as in the case of the excited 2-naphthol–pyridine system [1], the transient absorption (Fig. 3, spectrum a) can be attributed to the semi-quinone radical of BQ (BQH·) because the counter-radical, i.e. the phenoxy radical PhO·, has no absorption in the visible region [18]. To confirm this
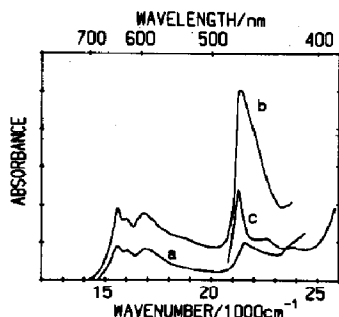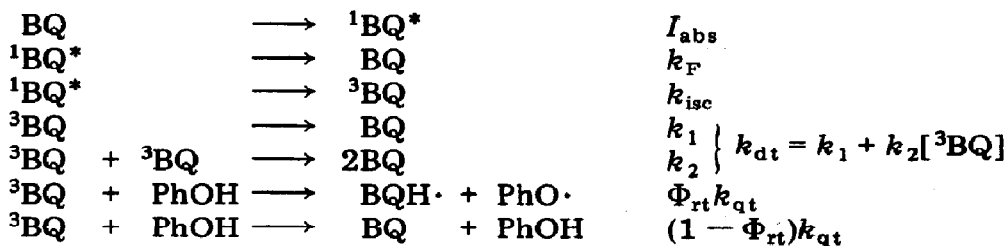

Fig. 3. Transient absorption spectra observed immediately after flashing for the cyclohexane solutions containing 0.1 mM BQ and 1 mM PhOH (curve a) or 0.1 mM BQ and 0.5 mM 2-naphthol (curve b). Curve c, absorption spectrum of the 2-naphthoxyl radical (see ref. 1).

assignment we measured the transient absorption spectrum (Fig. 3, spectrum b) for a solution containing 0.1 mM BQ and 0.5 mM 2-naphthol. Figure 3, spectrum b, is regarded as the superposition of Fig. 3, spectrum a, and the spectrum of the 2-naphthoxyl radical (Fig. 3, spectrum c). Therefore it is obvious that the hydrogen-atom transfer from PhOH to excited BQ occurs to yield BQH· and PhO·. The reaction giving rise to these radicals may be written as

BQ   PhOH   BQH·   PhO·
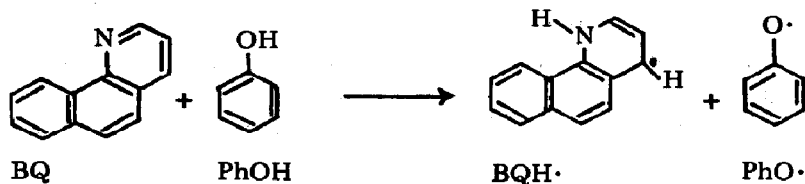
The molar extinction coefficient ϵ_{BQH} of BQH· was determined to be 1.5 × 10^3 M^{-1} cm^{-1} at λ_{max} = 590 nm using the molar extinction coefficient of the 2-naphthoxyl radical (2.6 × 10^3 M^{-1} cm^{-1} at λ_{max} = 470 nm) [5].

The yield of BQH· also increases on increasing the PhOH concentration up to about 1 mM, for which both hydrogen-bond formation and fluorescence quenching are negligible. Therefore there is no doubt that BQH· is produced from the reaction between triplet BQ and PhOH, and the formation of BQH· can be explained by the following mechanism:

$$
\begin{array}{lll}
BQ & \longrightarrow {}^1BQ^* & I_{abs} \\
{}^1BQ^* & \longrightarrow BQ & k_F \\
{}^1BQ^* & \longrightarrow {}^3BQ & k_{isc} \\
{}^3BQ & \longrightarrow BQ & k_1 \\
{}^3BQ + {}^3BQ & \longrightarrow 2BQ & k_2 \\
{}^3BQ + PhOH & \longrightarrow BQH· + PhO· & \Phi_{rt}k_{qt} \\
{}^3BQ + PhOH & \longrightarrow BQ + PhOH & (1 - \Phi_{rt})k_{qt}
\end{array}
$$

$\left. \begin{array}{l} k_1 \\ k_2 \end{array} \right\} k_{dt} = k_1 + k_2[{}^3BQ]$

At a sufficiently high concentration of PhOH, for which $k_{dt} \ll k_{qt}[PhOH]$, the BQH· concentration at the end of a flash is related to the total quantity $\int I_{abs}\, dt$ of light absorbed by BQ during a flash by the equation

$$[BQH·] = \Phi_{isc}\Phi_{rt}\int I_{abs}\, dt \tag{4}$$

where Φ_{rt} is the reaction yield for dynamic triplet quenching. In the absence of PhOH the concentration of triplet BQ at the end of a flash is given by

$$[{}^3BQ] = \Phi_{isc}\int I_{abs}\, dt \tag{5}$$

Furthermore, the time-integrated fluorescence intensity during a flash is given by

$$\int I_F(\lambda')\, dt = \alpha(\lambda')\Phi_F\int I_{abs}\, dt \tag{6}$$

From eqns. (4) - (6) and the relation

$$D_{BQH}(\lambda) = \epsilon_{BQH}(\lambda)[BQH\cdot]d \tag{7}$$

we obtain

$$\Phi_{rt} = \frac{D_{BQH}(\lambda)/\int I_F(\lambda') \, dt}{D^B(\lambda'')/\int I_F(\lambda') \, dt} \frac{\epsilon_T^B(\lambda'')}{\epsilon_{BQH}(\lambda)} \tag{8}$$

where $D_{BQH}(\lambda)$ is the absorbance of BQH· immediately after flashing and $d = 10$ cm is the optical path length of the sample cell. From the slopes of the plots shown in Fig. 4, and $\epsilon_T^B(425)/\epsilon_{BQH}(590) = 4.2$, we obtained $\Phi_{rt} = 1.0$. This result, that the dynamic quenching of triplet BQ by PhOH is entirely due to the hydrogen-atom transfer reaction, is the same as the result for the systems 2-naphthol–pyridine and 1-anthrol–quinoline [5] (see Table 2).

At PhOH concentrations above 1 mM, fluorescence quenching occurs and the triplet decay is entirely due to the radical-formation reaction. Furthermore, it was confirmed that excitation of the hydrogen-bonded species gives no emission and no transient absorption. Thus the formation of BQH· is satisfactorily described by the following mechanism:

$$
\begin{array}{lll}
BQ & \longrightarrow \quad {}^1BQ^* & I_{abs} \\
{}^1BQ^* & \longrightarrow \quad BQ & k_F \\
{}^1BQ^* & \longrightarrow \quad {}^3BQ & k_{isc} \\
{}^1BQ^* + PhOH & \longrightarrow \quad BQH\cdot + PhO\cdot & \Phi_r k_q \\
{}^1BQ^* + PhOH & \longrightarrow \quad BQ \quad + PhOH & (1 - \Phi_r)k_q \\
{}^3BQ \quad + PhOH & \longrightarrow \quad BQH\cdot + PhO\cdot & k_{qt}
\end{array}
$$
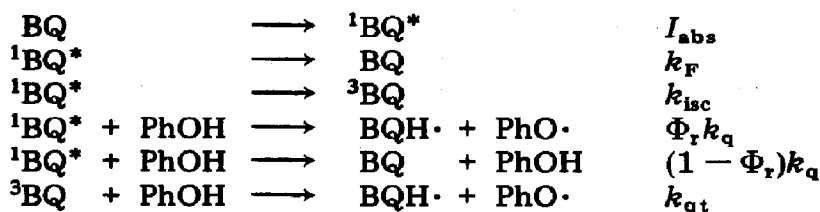
According to this scheme, we obtain

$$\frac{D_{BQH}(\lambda)}{\int I_F(\lambda') \, dt} = \frac{\epsilon_{BQH}(\lambda)d}{\alpha(\lambda')k_F}(k_{isc} + \Phi_r k_q [PhOH]) \tag{9}$$

Figure 5 shows the plot of $D_{BQH}(\lambda)/\int I_F(\lambda') \, dt$ versus [PhOH]. From the slope and the intercept we obtained $\Phi_r k_q/k_{isc} = 13.5$ M^{-1}. With $k_q = 1.2 \times 10^{10}$ M^{-1} s^{-1} and $k_{isc} = 2.2 \times 10^8$ s^{-1}, we obtain $\Phi_r = 0.25$. This is larger than
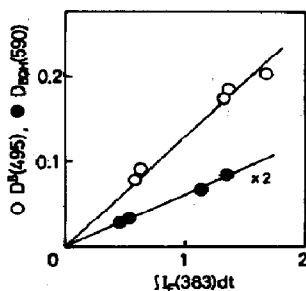

Fig. 4. Plots of $D^B(\lambda'')$ and $D_{BQH}(\lambda)$ vs. $\int I_F(\lambda') \, dt$ ($\lambda = 590$ nm; $\lambda' = 383$ nm; $\lambda'' = 495$ nm): $\bigcirc$, 0 M PhOH; $\bullet$, 0.7 mM PhOH.

TABLE 2

Summary of the hydrogen-atom transfer reaction in the excited singlet and triplet states

System	Triplet state			Excited singlet state		
	k_{qt} ($\times 10^9$ M^{-1} s^{-1})	Φ_{rt}	ΔpK_a	k_q ($\times 10^{10}$ M^{-1} s^{-1})	Φ_r	ΔpK_a
I 1-Anthrol*–pyridine[a]	—	0	4.8	1.2	0	−5.3
II 1-Anthrol*–quinoline[b]	1.1 - 1.4	1.0	5.1	1.3	<0.1	−5.0
III 2-Naphthol*–pyridine[c]	1.5 - 1.9	1.0	3.0	1.2 - 1.4	0.20	−2.4
IV 7,8-Benzoquinoline*–phenol	1.2	1.0	4.3	1.2	0.25	−1.0

[a]See ref. 3.
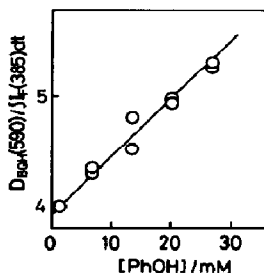[b]See refs. 3 and 5.
[c]See refs. 1 and 5.

Fig. 5. Plot of $D_{BQH}(\lambda)/\int I_F(\lambda')\,dt$ vs. [PhOH] (λ = 590 nm; λ' = 385 nm).

the result for the system 1-anthrol–quinoline but is close to that for the system 2-naphthol–pyridine. One of the reasons why the value of Φ_r for the system investigated in this study is not as large as predicted in Section 1 may be the occurrence of geminate radical recombination. The recombination is spin allowed for the reaction in the excited singlet state but is spin forbidden for the reaction in the triplet state.

The results for the hydrogen-atom transfer reaction for excited singlet and triplet states are summarized in Table 2. The non-reactivity of triplet 1-anthrol with pyridine is attributed to the deficient excitation energy, because the reduction potential of pyridine is 0.5 V smaller than that of quinoline [19]. For systems II - IV the k_{qt} are nearly identical and the Φ_{rt} are unity. For systems I - IV the k_q are in the diffusion-controlled limit in each case and the difference in Φ_r is considerable. It is clear that Φ_r increases with increasing ΔpK_a. Judging from the energy gap $\Delta E(S_1-T_1)$ between the excited singlet and triplet states of the fluorescer, the hydrogen-atom transfer reaction in the excited singlet state is energetically possible for all these systems. Since the excited singlet state of the hydrogen-bonded species deactivates instantaneously without giving rise to emission and reaction, the decrease in Φ_r with decreasing ΔpK_a is attributed to the hydrogen-bond formation in the encounter state. As the ΔpK_a are negative in the excited singlet state but positive in the triplet state and the orbital character in the excited states is π,π^* in each case, the difference between Φ_r and Φ_{rt} is considered to be due to the remarkable difference in ability between the excited singlet state and the triplet state to form hydrogen bonds.

Both in the present study and in previous work it has been established that in two-conjugate π-electronic systems of the type $\geqslant$N---H—O—$\lessgtr$ the dynamic quenching can be regarded as resulting from the competitive reactions in the encounter state of hydrogen-atom transfer and hydrogen-bond formation, whether the excited species is the hydrogen-bond donor or the acceptor.

Acknowledgment

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