Laser Flash Photolysis Studies on Proton-Enhanced Hydrogen Atom Transfer Reaction from Triplet Naphthol to Benzophenone via a Triplet Exciplex^{1a}

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The laser flash photolysis study at 355 nm in the 1-naphthol (ROH) and benzophenone (BP) system with and without H₂SO₄ has been carried out in acetonitrile-water (4:1 v/v) or methanol at 290 K. For the ROH (3.0×10^{-3} M)-BP (6.7×10^{-3} M) system containing $[H_2SO_4] = 0$ or 0.5 M in acetonitrile-water (4:1 v/v), triplet benzophenone (³BP*) produced by fast intersystem crossing of singlet benzophenone (¹BP*) excited at 355 nm is quenched by ROH with almost diffusion processes $(8.4 \times 10^9 \text{ or } 9.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively). Triplet naphthol (³ROH⁺) is produced in the nanosecond region by triplet energy transfer from ³BP* to ROH with efficiencies of 0.73 for $[H_2SO_4] = 0$ M and 0.39 for $[H_2SO_4] = 0.5$ M. Subsequently, in the microsecond region, the hydrogen atom transfer (HT) reaction from ³ROH^{*} to BP occurs to produce the 1-naphthoxy radical (RO) and the benzophenone kethyl radical (>COH) with efficiencies 0.73 for $[H_2SO_4] = 0$ M and 0.85 for $[H_2SO_4]$ = 0.5 M. The rate constant for the decay of ${}^{3}ROH^{*}$ (k_{obst}) linearly increases with an increase of H₂SO₄ concentration. As for an increase of BP concentration, the k_{obsd} value increases not linearly, which shows a negative curve in both systems with and without H_2SO_4 . Especially for the methanol solution with $[H_2SO_4] = 0$ M, a leveling off is clearly observed at higher BP concentrations ([BP] ≥ 0.5 M). In the absence of H₂SO₄, the mechanism for the HT reaction from ³ROH^{*} to BP can be explained by the intraexciplex HT reaction of the triplet exciplex 3(ROH...>CO)* established with an equilibrium constant of $K_1 = 6.7 \text{ M}^{-1}$ in acetonitrile-water (4:1 v/v) or 4.2 M⁻¹ in methanol. The mechanism of the proton-enhanced HT reaction is suggested that the protonated triplet exciplex ³(ROH...>+COH)* formed in a prototropic equilibrium with ³(ROH···>CO)^{*} undergoes the intraexciplex electron-transfer reaction to give the triplet radical pair ³(ROH⁺⁺···>COH) which rapidly decomposes into $R\dot{O} + \dot{C}OH + H^+$.

Introduction

Hydrogen atom transfer reactions in the triplet state of carbonyl compounds from a variety of substrates such as alcohols, hydrocarbons, and amines are well-known. The reaction proceeds by either hydrogen atom transfer or electron transfer followed by proton transfer. A large number of studies on intermolecular and intramolecular hydrogen atom transfer reactions of carbonyl triplets have been reported.²⁻¹⁵ However, until recently, little attention has been paid to the hydrogen atom transfer reaction from triplet aromatic compounds produced by triplet sensitization of carbonyl compounds to carbonyl compounds.^{16,17}

On the other hand, acid-base reactions in the excited state of aromatic compounds are elementary processes in both chemistry and biochemistry.¹⁸⁻²⁵ Recently, there has been considerable interest in the photophysical and photochemical properties of aromatic compounds in the presence of protons:²⁶ proton transfer reactions in the excited state and proton-induced quenching,²⁷⁻²⁹ a one-way proton-transfer reaction in the excited state of hydrogen-bonded complexes,^{30,31} examples for the absence of excited-state prototropic equilibrium.³² These are photochemical and photophysical phenomena upon direct excitation.

In a previous paper,¹⁷ it has been found by means of laser flash photolysis that the hydrogen atom transfer (HT) reaction occurs from the triplet naphthol (3ROH*) to benzophenone (BP) in methanol. We concluded that the HT reaction from ³ROH* to BP proceeds via the triplet exciplex ³(ROH--->CO)^{*.17} However, Gorman et al. reported that no evidence for exciplex intermediacy was given by the result of linear plots of the rate constant for the triplet naphthol decay vs [BP] ([BP] $\leq 3.0 \times 10^{-2}$ M).³³ For the case of the HT reaction from the triplet naphthylammonium ion $({}^{3}RNH_{3}^{+*})$ to BP ([BP] ≤ 0.22 M), the formation of the triplet exciplex $(RNH_3^+ \rightarrow CO)^*$ was concluded on the basis of the fact that the plots of the rate constant for the triplet naphthylammonium ion decay vs [BP] showed a negative curve.34 Therefore, to make clear the ambiguity in the mechanism of the HT reaction from ³ROH^{*} to BP, kinetic measurements at higher concentrations $(\geq 0.1 \text{ M})$ of BP should be performed.

In the present paper, we carried out laser flash photolysis at 355 nm of the ROH-BP system in the [BP] range 0-1.0 M in a mixed solvent of acetonitrile-water (4:1 v/v) or methanol, and evidence for the triplet exciplex formation was given from kinetic studies. The proton-enhanced HT reaction from ${}^{3}ROH^{*}$ to BP was found to be in contrast to that of ${}^{3}RNH_{3}^{+*}$ to BP, for which

the HT rate constant markedly decreased with an increase of acid concentration.³⁴ The effect of protons on the triplet exciplex was discussed in detail for the ROH-BP system.

Experimental Section

1-Naphthol and benzophenone (G.R. grade, Wako) were recrystallized twice from ethanol-water mixtures (1:1 v/v). Methanol, acetonitrile (Spectrosol, Wako) and H₂SO₄ (97%, Wako) were used as supplied. H₂SO₄ was used as the proton source since it is known that the counterion (SO₄²⁻) does not quench the triplet molecules.³⁵ Deionized water was distilled.

The concentration of 1-naphthol (ROH) was usually 3.0×10^{-3} M. Benzophenone (BP) was used as a triplet sensitizer in the concentration range 0–1.0 M. All samples in quartz cells with 1- or 10-mm path length were degassed by freeze-pump-thaw cycles on a high-vacuum line. Spectral data regarding transients were obtained by a fresh sample to avoid excessive exposure to the laser pulse.

Absorption spectra were recorded on a Hitachi 200-10 spectrophotometer.

Laser flash photolysis was carried out at 290 K by using third harmonics (355 nm) of a Nd³⁺:YAG laser from J. K. Lasers (HY 500); the pulse duration and energy were 8 ns and 70 mJ/pulse, respectively. The detection system of transient absorption spectra has been reported elsewhere.³⁴

Results

Absorption Spectra in the Ground State. The absorption spectrum of the ROH-BP system in an acetonitrile-water mixture (4:1 v/v) showed the same as a superposition of those of ROH and BP at 290 K. Since ROH has no absorbance at 355 nm, only BP in the ROH-BP system can be excited upon a 355-nm laser pulse. In the presence of protons ($[H_2SO_4] = 0.5$ M), the absorption spectrum of the ROH-BP system had no difference from that in the absence of protons. Therefore, it is regarded that neither protonation to BP nor ROH occurs in the ground state.

Primary Process for Production of ³**ROH**^{*} **by Triplet Energy Transfer of** ³**BP**^{*}. After the excited singlet state of **BP** (¹**BP**^{*}) is produced upon a 355-nm laser pulse in the ROH-BP system, triplet benzophenone (³**BP**^{*}) is formed within a picosecond time scale via fast intersystem crossing.^{36,37} As reported previously,¹⁷ in the presence of ROH, ³**BP**^{*} is quenched by the following three processes: triplet energy transfer to ROH, hydrogen abstraction



from ROH, and deactivation induced by ROH. To elucidate the processes to quench ³BP^{*}, time-resolved transient absorption spectra upon laser excitation for the ROH ((0–5.0) × 10⁻³ M)–BP (6.7 × 10⁻³ M) systems containing [H₂SO₄] = 0 and 0.5 M were analyzed in a nanosecond region at 290 K.

The $T_n \leftarrow T_1$ absorption band of ³BP* shows its peak at 525 nm at 10 ns after a laser pulse.¹⁷ The transient absorption of ³BP* decays according to first-order kinetics with the rate constant τ_{BP}^{-1} . Since plots of τ_{BP}^{-1} vs [ROH] ($\leq 5.0 \times 10^{-3}$ M) made a straight line, quenching of ³BP* by ROH was found to follow a Stern-Volmer relationship. Therefore, the decay rate constant (τ_{BP}^{-1}) is expressed as follows:

$$\tau_{\rm BP}^{-1} = (\tau^0_{\rm BP})^{-1} + k_{\rm g}[\rm ROH]$$
(1)

where $\tau_{BP}^{0}^{-1}$ and k_q are the lifetime of ${}^{3}BP^{*}$ in the absence of ROH and the rate constant for quenching of ${}^{3}BP^{*}$ by ROH, respectively. From the slopes and the intercepts of the lines, the values of k_q and $\tau_{BP}^{0}^{-1}$ were obtained as $8.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $2.5 \times 10^4 \text{ s}^{-1}$ for $[H_2SO_4] = 0 \text{ M}$ and $9.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $2.2 \times 10^6 \text{ s}^{-1}$ for $[H_2SO_4] = 0.5 \text{ M}$, respectively. The obtained values of k_q are close to those of a diffusion-controlled process. The value of $\tau_{BP}^{0}^{-1}$ in the presence of $[H_2SO_4] = 0.5 \text{ M}$ was greater than that in the absence of H_2SO_4 . This result can be explained by considering the small lifetime (ca. 13 ns) of the protonated ${}^{3}BP^{*}$ (${}^{3}BPH^{+*}$) formed due to the pK^{*}_{a} value of ${}^{3}BP^{*}$ (0.18).^{38,39}

As the intensity of the 525-nm band for the T-T absorption of ³BP* decreased, the 430-nm band with vibrational structures appeared within 200 ns after laser pulsing in the ROH-BP system. The latter band is ascribed to the $T_n \leftarrow T_1$ absorption of the 1-naphthol triplet (³ROH*) produced by triplet energy transfer of ³BP*.¹⁷ The triplet energies of BP and ROH are known to be 69.2 and 58.6 kcal mol⁻¹, respectively, in a polar solvent.⁴⁰ The efficiency of triplet-triplet energy transfer from ³BP* to ROH (ϕ_{ET}) can be obtained as the concentration ratio ([³ROH*]_{max}/[³BP*]_{max}). The concentrations of ³BP* and ³ROH* were determined by the use of the molar absorption coefficients, $\epsilon = 7800 \text{ M}^{-1} \text{ cm}^{-1}$ at 525 nm and $\epsilon = 9000 \text{ M}^{-1} \text{ cm}^{-1}$ at 430 nm, respectively, in methanol.¹⁷ We obtained the ϕ_{ET} values as 0.73 ± 0.05 and 0.39 ± 0.03 for ROH (3.0 × 10⁻³ M)-BP (6.7 × 10⁻³ M) systems with [H₂SO₄] = 0 and 0.5 M, respectively. It is clear that the efficiency of triplet-triplet energy transfer is reduced by the addition of protons to the ROH-BP system.

The deactivation processes of ³BP^{*} in the presence of ROH are expressed in Scheme I, where $k_{\rm ET}$, $k_{\rm HA}$, $k'_{\rm HA}$, and $k'_{\rm q}$ are the rate constants for the triplet energy transfer reaction from ³BP^{*} to ROH, the hydrogen atom abstraction of ³BP^{*} from solvent molecules (MH), the hydrogen atom abstraction of ³BP^{*} from ROH, and the ROH-induced quenching of ³BP^{*}, respectively. Judging from the small value of $\tau^0_{\rm BP}^{-1}$ (2.5 × 10⁴ s⁻¹) compared with that (5 × 10⁶ s⁻¹) in methanol,¹⁷ the usual hydrogen atom abstraction of ³BP^{*} from solvent molecules (MH) was negligible in acetonitrile-water (4:1 v/v). Therefore, we have

$$k_{\rm g} = k_{\rm ET} + k'_{\rm HA} + k'_{\rm g} \tag{2}$$

The value of $k_{\rm ET}$ can be evaluated by

$$k_{\rm ET} = \phi_{\rm ET} k_{\rm q} \tag{3}$$

TABLE I: Experimental Data of the Decay of ³BP⁺ at [BP] = 6.7×10^{-3} M in Acetonitrile–Water (4:1 v/v) at 290 K: Quenching Rate Constant (k_q), Decay Rate Constant of ³BP⁺ in the Absence of ROH $(\tau^{0}_{BP})^{-1}$, and Efficiencies of the Triplet Energy Transfer (ϕ_{ET}), the Usual Hydrogen Abstraction of ³BP⁺ from ROH (ϕ'_{HA}) and the ROH-Induced Quenching ($\phi'_{e})^{a,b}$



^a For details, see text. ^b Errors $\pm 10\%$. ^c [ROH] = 3.0×10^{-3} M.



Figure 1. Time-resolved transient absorption spectra of the ROH (3.0 $\times 10^{-3}$ M)-BP (6.7 $\times 10^{-3}$ M) system in acetonitrile-water (4:1 v/v) in a microsecond region for [H₂SO₄] = 0 M (a) and 0.5 M (b) observed after 355-nm laser pulsing at 290 K.

By the use of eq 3 and the obtained values of both $\phi_{\rm ET}$ and $k_{\rm q}$, the values of $k_{\rm ET}$ were determined to be 6.1×10^9 and 3.6×10^9 M^{-1} s⁻¹ in the ROH-BP system with [H₂SO₄] = 0 and 0.5 M, respectively. The latter value is smaller than that of the former. This reduction may be derived from the shorter lifetime of ³BPH^{+*} associated with the presence of protons and an increase of viscosity in the presence of H₂SO₄.³⁴ For the hydrogen atom abstraction of ³BP^{*} from ROH in the absence of acid, the efficiency ($\phi'_{\rm HA}$) was determined as 0.09. The efficiency of ROH-induced quenching ($\phi'_{\rm q}$) was calculated as 0.18 ($\phi'_{\rm q} = 1 - \phi_{\rm ET} - \phi'_{\rm HA}$). The experimental data obtained are listed in Table I.

HT Reaction from ³ROH^{*} to BP. The triplet energy-transfer reaction from ³BP^{*} to ROH is accomplished within 200 ns after 355-nm laser pulsing. To elucidate the deactivation processes of ³ROH^{*} in the ROH-BP systems with $[H_2SO_4] = 0$ and 0.5 M, transient absorption spectra were analyzed in a microsecond time scale.

Figure 1 shows the typical transient absorption spectra observed 0.2–7 μ s after laser pulsing in the ROH (3.0 × 10⁻³ M)-BP (6.7 × 10⁻³ M) systems containing (a) [H₂SO₄] = 0 and (b) 0.5 M in acetonitrile-water (4:1 v/v) at 290 K. In both spectra a and b, the 430-nm band for ³ROH* decreases with an isosbestic point at 490 nm, accompanying an increase in intensities of the 545-and the 400-nm bands for the benzophenone kethyl radical (>ĊOH) and the 1-naphthoxy radical (RO), respectively.¹⁷

Figure 2 shows the time traces of the transient absorbance changes observed at 430 nm (a and c) for ${}^{3}ROH^{*}$ and 545 nm (b and d) for >COH after laser pulsing in the ROH (3.0 × 10⁻³



Figure 2. Time traces of the absorbance changes for transient species observed at 430 nm (a) and 545 nm (b) for $[H_2SO_4] = 0$ M and at 430 nm (c) and 545 nm (d) for $[H_2SO_4] = 0.5$ M after a 355-nm laser pulse in the ROH (3.0 × 10⁻³ M)-BP (6.7 × 10⁻³ M) system in acetonitrile-water (4:1 v/v) at 290 K.

M)-BP (6.7 × 10⁻³ M) systems with $[H_2SO_4] = 0$ (a and b) and 0.5 M (c and d) in acetonitrile-water (4:1 v/v) at 290 K. The rate constants (k_{obsd}) of the decay for ³ROH* and the rise for >COH were obtained with the method described previously.³⁴ The values of k_{obsd} were determined as (2.8 ± 0.2) × 10⁵ s⁻¹ for $[H_2SO_4] = 0$ M and (7.4 ± 0.3) × 10⁵ s⁻¹ for $[H_2SO_4] = 0.5$ M, respectively. The rate constant for the decay of ³ROH* was almost identical with that for the rise of >COH within experimental error (10%), showing that the HT reaction took place from ³ROH* to BP. On the other hand, the k_{obsd} value at 430 or 545 nm in the system with $[H_2SO_4] = 0.5$ M is 2.6 times greater than that in the system without H_2SO_4 . This indicates that k_{obsd} at 430 or 545 nm is obviously enhanced by protons.

The efficiency (ϕ_{HT}) for the HT reaction from ³ROH* to BP can be obtained according to

$$\phi_{\text{HT}} = [>COH]_{\text{HT}} / [^{2}\text{ROH}^{*}]_{\text{max}} = (OD_{\text{max}}^{545} - OD_{7=0}^{545})(OD_{\text{max}}^{430})^{-1}(\epsilon(>\dot{C}OH) + \epsilon(\dot{R}OH))^{-1}\epsilon(^{3}\text{ROH}^{*})$$
(4)

Here, $[>\dot{C}OH]_{HT}$ and $[{}^{3}ROH^{*}]_{max}$ are the net concentrations of $>\dot{C}OH$ produced by the HT reaction and of ${}^{3}ROH^{*}$ by energy transfer from ${}^{3}BP^{*}$, respectively. The terms of OD^{545} and OD^{430} are the absorbances at 545 and 430 nm, respectively, as shown in Figure 2. The molar absorption coefficients $\epsilon({}^{3}ROH^{*})$, $\epsilon(>\dot{C}OH)$, and $\epsilon(RO)$ of ${}^{3}ROH^{*}$, $>\dot{C}OH$, and RO are, respectively, 9000 M⁻¹ cm⁻¹ at 430 nm, 3220 M⁻¹ cm⁻¹ at 545 nm, and 830 M⁻¹ cm⁻¹ at 545 nm.¹⁷ By the use of eq 4, the values of ϕ_{HT} were determined as 0.73 ± 0.05 and 0.85 ± 0.05 in the ROH (3.0 $\times 10^{-3}$ M)-BP (6.7×10^{-3} M) system with [H₂SO₄] = 0 and 0.5 M, respectively. It is obvious that the addition of protons to the ROH-BP system enhances both the rate constant and the efficiency of the HT reaction.

Proton Effect on the HT Reaction. We have found by kinetic studies on the transient species that the addition of protons to the ROH-BP system significantly enhances the rate constant for the decay of ${}^{3}ROH^{*}$ or the formation of >COH. This finding implies that the HT reaction from ${}^{3}ROH^{*}$ to BP is affected by protons. To elucidate the effect of protons on the HT reaction, laser photolysis at 355 nm was carried out in the ROH-BP system with various concentrations of H₂SO₄.

Figure 3 shows the plots of the decay rate constant (k_{obsd}) of ${}^{3}ROH^{*}$ at 430 nm vs [H₂SO₄] (≤ 1.0 M) obtained upon a laser



Figure 3. Plots of the decay rate constant (k_{obsd}) of ³ROH^{*} as a function of $[H_2SO_4]$ observed at 430 nm after laser pulsing at 355 nm in the ROH $(3.0 \times 10^{-3} \text{ M})$ -BP (0.1 M) system in acetonitrile-water (4:1 v/v) at 290 K.



Figure 4. Plots of the decay rate constant (k_{obsd}) of ³ROH^{*} as a function of [BP] observed at 430 nm after laser pulsing in the ROH $(3.0 \times 10^{-3} \text{ M})$ -BP system with $[H_2SO_4] = 0$ (O), 0.5 (Δ), and 1.0 M (\Box) in acetonitrile-water (4:1 v/v) at 290 K. The solid curves are calculated from eq 9'. See text for details.

pulse in the ROH $(3.0 \times 10^{-3} \text{ M})$ -BP (0.1 M) system containing various [H₂SO₄] in acetonitrile-water (4:1 v/v) at 290 K. The k_{obsd} value linearly increases with an increase of [H₂SO₄]. Therefore, k_{obsd} is formulated as

$$k_{\text{obsd}} = k_{\text{d}} + k_{\text{s}}[\text{H}_2\text{SO}_4]$$
(5)

where k_s and k_d are the quenching rate constant by H₂SO₄ and the decay rate constant of ³ROH* for the ROH (3.0 × 10⁻³ M)-BP (0.1 M) system without H₂SO₄, respectively. From the slope and intercept of the line, we had $k_s = 4.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_d = 3.5 \times 10^6 \text{ s}^{-1}$. It will be discussed in the following section what the k_s value means.

On the next stage, the relationship between k_{obsd} and [BP] was investigated.

Figure 4 shows the plots of k_{obsd} at 430 nm as a function of [BP] ($\leq 2.0 \times 10^{-1}$ M) obtained by laser photolysis at 355 nm in the ROH (3.0×10^{-3} M)-BP systems containing [H₂SO₄] = 0, 0.5, and 1.0 M in acetonitrile-water (4:1 v/v) at 290 K. The value of k_{obsd} considerably increases with an increase of [BP] at each [H₂SO₄], but not linearly. Especially, in the system with [H₂SO₄] = 0 M, a leveling off at higher [BP] (>0.2 M) may be expected. However, we had difficulty with the solubility of BP ([BP] > 0.2 M) in a mixed solvent of acetonitrile and water (4:1 v/v) at 290 K. Therefore, we performed laser photolysis in the ROH-BP system without H₂SO₄ in methanol at higher [BP] (>0.2 M).

Figure 5 shows the plots of k_{obsd} at 430 nm as a function of [BP] (≤ 0.5 M) obtained by laser photolysis at 355 nm in the ROH (3.0×10^{-3} M)-BP systems without H₂SO₄ in methanol at 290 K. The values of k_{obsd} increase with an increase of [BP], showing a negative curve. This result cannot be explained as a simple



Figure 5. Plots of the decay rate constant (k_{obsd}) for ³ROH^{*} as a function of [BP] observed at 430 nm after laser pulsing in the ROH $(3.0 \times 10^{-3} \text{ M})$ -BP system with $[H_2SO_4] = 0$ M in methanol at 290 K. The solid curve is calculated from eq 9'. For details, see text.

SCHEME II



quenching mechanism of ³ROH^{*} by BP as reported by Gorman et al.³³

We have two candidates to explain this nonlinear quenching: (1) triplet-triplet annihilation of ³ROH^{*}, whose concentration increases with an increase of [BP]; (2) exciplex formation between ³ROH^{*} and BP. In the studied range of [BP], the transient peak at 430 nm of ³ROH^{*} decays according to first-order kinetics. Therefore, the nonlinear behavior shown in Figures 4 and 5 is not caused by triplet-triplet annihilation of ³ROH^{*}. Furthermore, ³ROH^{*} is not quenched by protons appreciably considering the following reason: as [BP] approaches 0 M, the value of k_{obsd} at each [H₂SO₄] in Figure 4 becomes close to the same.

The solid lines in Figures 4 and 5 are calculated with the rate equation derived from the proposed mechanism as discussed in the next section.

Discussion

Mechanism for the HT Reaction in the Absence of Protons. In a previous paper,¹⁷ we suggested that the HT reaction from ³ROH* to BP in the absence of protons occurs via the triplet exciplex ³(ROH--->CO)* shown in Scheme II and concluded that the triplet exciplex is a locally excited triplet state of ROH having a weak charge-transfer structure.¹⁷ A mechanism similar to Scheme II has been shown for the ³RNH₃^{+*}-BP system very recently.³⁴ In Scheme II, we denote that k_0 , k'_0 , and $k_{\rm HT}$ are the decay rate constants for ${}^{3}ROH^{*}$ in the absence of BP, 3 -(ROH...>CO)* to ROH plus BP in the ground state and 3 -(ROH...>CO)* to the production of >COH and RO (i.e., the HT rate constant), respectively. Here, k_1 and k_{-1} are the rate constants for the formation and the dissociation of ³(ROH--->CO)*, respectively. A fast equilibrium between (3ROH* + >CO) and ${}^{3}(ROH \rightarrow CO)^{*}$ with an equilibrium constant (K_{1}) is supposed. According to Scheme II, the observed rate constant (k_{obsd}) for the decay of ³ROH^{*} is formulated as follows:

$$k_{\text{obsd}} = (k_0 + k_{\text{ex}} K_1 [\text{BP}])(1 + K_1 [\text{BP}])^{-1}$$
 (6)

where
$$k_{ex} = k'_0 + k_{HT}$$
, $K_1 = k_1/k_{-1}$, and $k_{ex} = k'_0 + k_{HT}$. On

TABLE II: Kinetic Parameters of the HT Reaction in the ROH-BP System at 290 $K^{a,b}$

solvent		$k_{\rm ex}^{\rm c}/{\rm s}^{-1}$	$\frac{K_1}{M^{-1}}$	$\frac{k_{\rm p}{\rm K'_2}^{d,e}}{{ m M}^{-1}~{ m s}^{-1}}$
acetonitrile-water (4:1 v/v)	without protons	9.1 × 10 ⁶	6.7	
methanol	with protons without protons	9.1×10^{6} 1.1×10^{7}	6.7 4.2	1.2×10^{7}

^aExperimental errors within 10%. ^b $k_0 = 1.4 \times 10^5 \text{ s}^{-1}$. See ref 17. ^c $k_{ex} = k'_0 + k_{HT} \simeq k_{HT}$. ^dFor K'₂, see text. ^c $k_p = k''_0 + k_{el} \simeq k_{el}$.

SCHEME III



the assumption that the value of k_0 is negligible compared to those of the competitive processes, i.e., $k_0 \ll k_{ex}K_1[BP]$, eq 6 can be transformed as

$$k_{\text{obsd}}^{-1} = k_{\text{ex}}^{-1} + (k_{\text{ex}}K_1)^{-1}[\text{BP}]^{-1}$$
 (7)

By the use of the experimental values of k_{obsd} obtained in methanol, plots of k_{obsd}^{-1} vs [BP]⁻¹ gave a straight line. From the slope and the intercept of the line, we obtained $k_{ex} = 1.1 \times 10^7 \text{ s}^{-1}$ and K_1 = 4.2 M⁻¹. Since $k_0 = 1.4 \times 10^5 \text{ s}^{-1}$,¹⁷ the assumption of $k_0 \ll$ $k_{er}K_1[BP]$ is proper in the range [BP] > 0.02 M. The solid curve in Figure 5 was calculated by eq 6 using the determined values of k_{ex} and K_1 . In the same way, the values of k_{ex} and K_1 in acetonitrile-water (4:1 v/v) at 290 K were obtained as 9.1×10^6 s^{-1} and 6.7 M⁻¹, respectively. The solid curve for [H₂SO₄] = 0 M in Figure 4 was calculated by eq 6 using the determined values of k_{ex} and K_1 in acetonitrile-water (4:1 v/v) at 290 K. Since the experimental values of k_{obsd} are in a good agreement with those calculated in both acetonitrile-water (4:1 v/v) and methanol, the proposed mechanism is appropriate for the HT reaction from ³ROH* to BP without acid. The kinetic parameters obtained are listed in Table II.

For the ROH $(3.0 \times 10^{-3} \text{ M})$ -BP $(6.7 \times 10^{-3} \text{ M})$ system without acid, the efficiency of the HT reaction (ϕ^0_{HT}) was obtained to be 0.73 in acetonitrile-water (4:1 v/v) at 290 K. According to Scheme II, ϕ^0_{HT} can be expressed as

$$\phi^{0}_{HT} = k_{HT} K_{1} [BP] (k_{0} + k_{ex} K_{1} [BP])^{-1}$$
(8)

By use of $k_0 = 1.4 \times 10^5 \text{ s}^{-1}$ and the determined values of k_{ex} and K_1 , we obtained $k_{\text{HT}} = 8.9 \times 10^6 \text{ s}^{-1}$. From the value of k_{HT} , we have estimated the ratio of the HT reaction to the deactivation processes of the triplet exciplex ${}^3(\text{ROH}{--}\text{CO})^*$ to be $k_{\text{HT}}/k_{\text{ex}} = 0.98$. Therefore, once ${}^3(\text{ROH}{--}\text{CO})^*$ is produced, it is fated to undergo the HT reaction very effectively.

Mechanism for the HT Reaction in the Presence of Protons. Laser flash photolysis studies on the ROH-BP system in the presence of protons revealed that the rate constant for the decay of ${}^{3}\text{ROH}^{*}$ (k_{obsd}) significantly increases with an increase of [H₂SO₄] and [BP]. Plots of k_{obsd} vs [H₂SO₄] in Figure 3 and of k_{obsd} vs [BP] in Figure 4 showed a straight line and a negative curve, respectively. To explain these experimental results, we propose the reaction mechanism for the ROH-BP system in the

presence of protons as shown in Scheme III. In the presence of protons, ³(ROH...>CO)* forms the protonated triplet exciplex ³(ROH···>+COH)* with an equilibrium constant K_2 . Here, k_2 and k_{-2} are the rate constants for protonation of ³(ROH--->CO)* and deprotonation of ³(ROH-->+COH)*, respectively. Therefore, we have $K_2 = k_2/k_{-2}$. As stated above, the triplet exciplex ³(ROH--->CO)* has a weak charge-transfer structure from ROH to BP. Accordingly, the protonation to the benzophenone site (>CO) of ³(ROH···>CO)* may occur to produce ³(ROH··· >+COH)*. It should be noted that there is no protonation to BP in the ground-state since the pK_a (S₀) of BP in the ground state is known to be very negative $(-5.7)^{40}$ under the experimental condition. The protonated triplet exciplex ³(ROH...>+COH)* decays to ROH + >CO + H^+ in the ground state with the rate constant (k''_0) or undergoes the intraexciplex electron-transfer reaction with the rate constant (k_{el}) to produce the triplet radical pair ³(ROH^{•+}···>COH). The radical pair rapidly transforms RO + >COH + H⁺. We write the decay rate constant of ³(ROH····>+COH)* as k_p (= $k''_0 + k_{el}$). According to Scheme III, k_{obsd} is formulated as

$$k_{\text{obsd}} = (k_0 + k_{\text{ex}}K_1[\text{BP}] + k_pK_1K_2[\text{BP}][\text{H}^+]) \times (1 + K_1[\text{BP}] + K_1K_2[\text{BP}][\text{H}^+])^{-1}$$
(9)

Since the activity of H_2SO_4 in acetonitrile-water (4:1 v/v) is unknown, we denote K'_2 and $[H_2SO_4]$ for K_2 and $[H^+]$, respectively. Thus, we obtain

$$k_{\text{obsd}} = (k_0 + k_{\text{ex}}K_1[\text{BP}] + k_pK_1K_2'[\text{BP}][\text{H}_2\text{SO}_4]) \times (1 + K_1[\text{BP}] + K_1K_2'[\text{BP}][\text{H}_2\text{SO}_4])^{-1} (9')$$

If it is assumed that $1 + K_1[BP] \gg K_1 K'_2[BP][H_2SO_4]$, eq 9' is rewritten as

$$k_{\text{obsd}} = (k_0 + k_{\text{ex}}K_1[\text{BP}])(1 + K_1[\text{BP}])^{-1} + (k_pK_1K'_2[\text{BP}])(1 + K_1[\text{BP}])^{-1}[\text{H}_2\text{SO}_4] (10)$$

Comparing eq 5 with eq 10, we have

$$k_{\rm s} = (k_{\rm p}K_1K_2'[{\rm BP}])(1 + K_1[{\rm BP}])^{-1} = 4.8 \times 10^6 \,{\rm s}^{-1}$$
 (11)

$$k_{\rm d} = (k_0 + k_{\rm ex} K_1 [BP])(1 + K_1 [BP])^{-1}$$
 (12)

When [BP] = 0.1 M and $K_1 = 6.7 \text{ M}^{-1}$ are substituted into eq 11, we obtain $k_p K'_2 = 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. We calculated the values of k_d with the obtained values of k_0 , k_{ex} , K_1 , and [BP] = 0.1 M to be $3.7 \times 10^6 \text{ s}^{-1}$. This value agrees well with the experimental value ($3.5 \times 10^6 \text{ s}^{-1}$ for [BP] = 0.1 M obtained in Figure 3) within an experimental error (10%).

The solid curves for $[H_2SO_4] = 0.5$ and 1.0 M in Figure 4 are calculated from eq 9' by using the determined values of k_0 , k_{ex} , K_1 , and $k_pK'_2$. The calculated values are consistent with experimental ones. The kinetic parameters in the presence of protons are also summarized in Table II.

For the ROH $(3.0 \times 10^{-3} \text{ M})$ -BP $(6.7 \times 10^{-3} \text{ M})$ system with $[H_2SO_4] = 0.5 \text{ M}$, the total efficiency (ϕ^p_{HT}) of the HT reaction in the presence of protons was obtained as 0.85. According to Scheme III, ϕ^p_{HT} is formulated as

$$\phi_{\text{HT}}^{p} = (k_{\text{HT}}K_{1}[\text{BP}] + k_{\text{el}}K_{1}K'_{2}[\text{BP}][\text{H}_{2}\text{SO}_{4}]) \times (k_{0} + k_{\text{ex}}K_{1}[\text{BP}] + k_{p}K_{1}K'_{2}[\text{BP}][\text{H}_{2}\text{SO}_{4}])^{-1} (13)$$

When we introduce into eq 13 the ratio of γ , which is defined as $\gamma = k_{\rm el}/k_{\rm p}$, and use the determined values of k_0 , $k_{\rm HT}$ ($\simeq k_{\rm ex}$), $k_p K'_2$, [BP] = 6.7 × 10⁻³ M, and [H₂SO₄] = 0.5 M, we have $\gamma = 1.1$. Considering an experimental error (10%) in determining $\phi^{\rm p}_{\rm HT}$, $k_{\rm p}$ can be regarded as $k_{\rm el}$ (i.e., $k_{\rm el} \gg k''_0$). Therefore, ³(ROH⁺⁺...>COH) produced by the intraexciplex electron-transfer reaction dissociates into ROH⁺⁺ and >COH effectively without the back-electron-transfer reaction. In the present ROH-BP system, the naphthoxy cation radical (ROH⁺⁺) could not be detected. However, in a previous report on the proton-assisted electron-transfer reaction from the triplet 1-methoxynaphthalene (³ROMe⁺) to BP in the presence of H₂SO₄, the 1-methoxynaphthalene cation radical (ROMe⁺⁺) was observed as a transient



Figure 6. Calculated values of the efficiencies of the HT reaction as a function of $[H_2SO_4]$ in the ROH $(3.0 \times 10^{-3} \text{ M})$ -BP $(6.7 \times 10^{-3} \text{ M})$ system; the total HT efficiency $\phi^p_{HT} (=\phi^0_{HT} + \phi^H_{HT})$ (a) and the net one ϕ^0_{HT} contributed from ³(ROH-->CO)^{*} (b) and the proton-enhanced one ϕ^H_{HT} via ³(ROH-->⁺COH)^{*} (c). See text for details.

species.⁴¹ The protonated BP has a relatively large electron affinity, resulting in the occurrence of the intraexciplex electron-transfer reaction.¹³ Considering that the electronic structure of ³ROH* is very similar to that of ³ROMe*, it is reasonable to suppose the intermediate ROH*+ produced by the intraexciplex electron-transfer reaction in the ROH-BP system.

The proton effect on the HT reaction from the triplet naphthylammonium ion (${}^{3}RNH_{3}^{+*}$) to BP has been investigated, and it has been shown that the rate constant for the HT reaction via the triplet exciplex ${}^{3}(RNH_{3}^{+**}>CO)^{*}$ markedly decreases with an increase of acid concentration.³⁴ The proton effect is accounted for by assuming that at higher acid concentrations the protonated triplet exciplex ${}^{3}(RNH_{3}^{+**}>^{+}COH)^{*}$ rapidly decomposes into ${}^{3}RNH_{3}^{+*} + >CO + H^{+}$ due to the Coulombic repulsion. In the RNH_{3}^{+} -BP system, protons behave to reduce the rate constant of the HT reaction. In contrast, for the ROH-BP system with protons, the rate constant for the HT reaction is enhanced by the formation of the protonated triplet exciplex ${}^{3}(ROH_{**}>^{+}COH)^{*}$.

For the ROH-BP system in the presence of protons, the net efficiencies of the HT reaction ϕ^0_{HT} and ϕ^H_{HT} via ³(ROH-->CO)^{*} and ³(ROH-->CO)^{*} are expressed by eqs 14 and 15, respectively, since the total HT efficiency (ϕ^p_{HT}) is equal to ϕ^0_{HT} plus ϕ^H_{HT} :

$$\phi^{0}_{HT} = (k_{HT}K_{1}[BP]) \times (k_{0} + k_{ex}K_{1}[BP] + k_{r}K_{1}K'_{2}[BP][H_{2}SO_{4}])^{-1} (14)$$

$$\phi^{H}_{HT} = k_{el}K_{1}K'_{2}[BP][H_{2}SO_{4}] \times (k_{0} + k_{ex}K_{1}[BP] + k_{p}K_{1}K'_{2}[BP][H_{2}SO_{4}])^{-1} (15)$$

Figure 6 shows the calculated values of $\phi_{\rm HT}^{\rm p}$, $\phi_{\rm HT}^{\rm 0}$, $and \phi_{\rm HT}^{\rm H}$ for [BP] = 6.7 × 10⁻³ M as a function of [H₂SO₄] by eqs 13-15, respectively, using the obtained values of k_0 , $k_{\rm HT}$ ($\simeq k_{\rm ex}$), K_1 , and $k_{\rm p}K'_2$ ($\simeq k_{\rm el}K'_2$). With an increase of [H₂SO₄], the value of $\phi_{\rm PHT}^{\rm p}$ ($=\phi_{\rm HT}^{\rm 0} + \phi_{\rm HT}^{\rm H}$) gradually increases and approaches unity at an infinite value of [H₂SO₄]. The value of $\phi_{\rm HT}^{\rm H}$ increases considerably while $\phi_{\rm HT}^{\rm 0}$ decreases with an increase of [H₂SO₄]. This demonstrates that in the presence of protons, the protonated exciplex plays an important role in the efficiency of the HT reaction.

Conclusion

It has been shown by means of laser flash photolysis at 355 nm that the HT reaction from ${}^{3}ROH^{*}$ (produced by the triplet sensitization of BP) to BP occurs via the triplet exciplex ${}^{3}(ROH \dots > CO)^{*}$ having a weak CT structure. That is, the intraexciplex HT reaction of ${}^{3}(ROH \dots > CO)^{*}$ effectively produces RO and >COH in a microsecond region. For the ROH-BP

system without protons, the HT mechanism is shown by Scheme II. It is found that in the presence of protons (H_2SO_4) , the HT reaction is considerably enhanced, in contrast to the case of the RNH₃⁺-BP system.³⁴ The proton effect on the HT reaction can be accounted for by Scheme III. The kinetic parameters for the ROH-BP system with and without protons are given in Table II. The protonated exciplex ³(ROH...>+COH)* is formed by the protonation to ${}^{3}(ROH \rightarrow CO)^{*}$, and subsequently the intraexciplex electron-transfer reaction of ${}^{3}(ROH \rightarrow ^{+}COH)^{*}$ occurs to give ROH⁺⁺ and >COH. The cation radical (ROH⁺⁺) rapidly dissociates into RO and H⁺.

Registry No. Benzophenone, 119-61-9; naphthol, 1321-67-1; sulfuric acid, 7664-93-9; hydrogen, 1333-74-0.

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