Hydrogen-atom and proton-induced electron transfer reactions via triplet exciplexes

HARUO SHIZUKA* and MINORU YAMAJI

Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

Abstract. It has been shown by means of laser flash photolysis at 355 nm that (1) hydrogen atom transfer (HT) from triplet naphthalene derivatives (produced by the triplet sensitization of benzophenone (BP)) to BP occurs via a triplet exciplex having a weak charge-transfer structure; (2) in the presence of protons, HT is enhanced in the naphthol–BP system via a protonated triplet exciplex whereas in the naphthylammonium ion–BP system, markedly reduced; (3) in the methoxynaphthalene–BP system, proton-induced electron transfer (ET) takes place via a protonated triplet exciplex, and (4) these triplet exciplexes have sandwich-like structures on the basis of experiments for intramolecular HT and ET of the methylene bridged compounds.

Keywords. Laser flash photolysis; hydrogen-atom transfer; proton-induced electron transfer; triplet exciplexes; triplet naphthalene derivatives.

1. Introduction

Acid–base reactions in the excited states of aromatic compounds have been extensively studied since they are elementary processes in both chemistry and biochemistry (Förster 1950; Weller 1952, 1956, 1961; Beens *et al* 1965; Wehry and Rogers 1966; Van der Donckt 1970; Ireland and Wyatt 1976; Schulman 1976, 1977; Klopffer 1977). In this decade, there has been considerable interest in photochemical and photophysical properties of aromatic compounds in the presence of protons (Shizuka 1985): proton transfer reactions in the excited state and proton-induced quenching (Tsutsumi and Shizuka 1977, 1978; Shizuka and Tobita 1982; Shizuka *et al* 1988), a one-way proton transfer reaction in the excited state of hydrogen-bonded complexes (Shizuka *et al* 1985, 1986; Shizuka and Serizawa 1986) and examples for the absence of excited-state prototropic equilibrium (Shizuka *et al* 1985d).

On the other hand, 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 upon direct excitation (Wagner and Hammond 1968; Dalton and Turro 1970; Wagner 1971, 1976; Turro *et al* 1972; Cohen *et al* 1973; Scaiano 1973/1974; Formosinho 1976, 1978; Arimitsu *et al* 1975; Turro 1978; Okada *et al* 1980, 1982; Peters *et al* 1980, 1982; Simon and Peters 1981, 1982, 1984; Manring and Peters 1983;

*For correspondence

Hoshino *et al* 1986; Wagner *et al* 1986; Hoshino and Shizuka 1987, 1988, 1993; Devadoss and Fessenden 1990, 1991; Miyasaka *et al* 1991). However, until recently, little attention has been paid to hydrogen-atom and electron-transfer reactions from triplet aromatic compounds produced by triplet sensitization of carbonyl compounds to carbonyl compounds (Shizuka and Fukushima 1983; Shizuka *et al* 1985a, b; Kohno *et al* 1991; Yamaji *et al* 1992; Kaneko *et al* 1993; Sekiguchi *et al* 1993).

By means of laser flash photolysis with third harmonics (355 nm) from a nanosecond Nd³⁺:YAG laser, kinetic studies on the hydrogen atom (HT) and proton-induced electron transfer ($p - eT$) reactions from triplet naphthalene derivatives (produced by the triplet sensitization of benzophenone) to benzophenone have been carried out. It is revealed that the HT and $p - eT$ reactions proceed via the triplet exciplexes having a sandwich-like structure with weak charge-transfer interaction. The proton effects on the rate constants for the HT and $p - eT$ reactions have been also investigated. The reaction mechanisms are illustrated.

2. Results and discussion

2.1 The hydrogen atom transfer reaction of triplet naphthylammonium ion to benzophenone (Kohno *et al* 1991)

The excited singlet state of benzophenone (¹BP*) is initially produced upon 355-nm laser excitation in the naphthylammonium ion (RNH₃⁺)-benzophenone (BP) system since only BP has absorbance at 355 nm in the present system. According to the El-Sayed rule (1962–1964), the triplet benzophenone (³BP*) was formed via fast intersystem crossing at picosecond time scale (Anderson *et al* 1974; Damschen *et al* 1978).

Since the triplet energies of BP and RNH₃⁺ are 69.2 (Murov 1973) and 60.9 kcal/mol (Shizuka and Fukushima 1983), respectively, the ET reaction occurs from ³BP* to RNH₃⁺ in the nanosecond time scale, competing with hydrogen abstraction of ³BP* from RNH₃⁺ or solvent molecules.

Figure 1 shows the time-resolved transient absorption spectra obtained after a 355-nm laser pulse in the RNH₃⁺ (3.0 × 10⁻³ M)–BP (1.12 × 10⁻² M) system in the presence of [H₂SO₄] = 0.015 M (a) and 0.5 M (b) in methanol–water (9:1 v/v) at 290 K. The absorption band at 410 nm in figure 1a or 415 nm in figure 2b is the triplet–triplet ($T - T$) absorption of RNH₃⁺ produced by triplet energy transfer (ET) from triplet benzophenone (³BP*). On the microsecond time scale, the $T - T$ absorption of RNH₃⁺ decreases, and absorption bands with peaks at 510 and 545 nm appear in intensity with an isosbestic point at 455 nm. The 510- and 545-nm bands correspond to the absorption spectra of the naphthylamine cation radical (RNH₂^{•+}) and the benzophenone ketyl radical (>C•OH) (Land 1968) respectively. The first-order rate constants (k_{obsd}) for the decay of triplet naphthylammonium ion (³RNH₃⁺*) observed at 410 nm and 415 nm are 2.4 × 10⁶ s⁻¹ and 2.0 × 10⁵ s⁻¹ for the present systems with [H₂SO₄] = 0.015 M and 0.5 M, respectively. On the other hand, both the rate constants for the rises of RNH₂^{•+} at 510 and >C•OH at 545 nm are consistent with those for the decay of ³RNH₃⁺ in both cases. Therefore, it is concluded that the hydrogen atom transfer (HT) reaction from ³RNH₃⁺ to BP occurs effectively to yield RNH₂^{•+} and >C•OH regardless of the concentration of the acid used. However, the k_{obsd} value for the HT of ³RNH₃⁺ is strongly affected and is reduced by the acid

Figure 1. Time-resolved transient absorption spectra of the RNH_3^+ ($3.0 \times 10^{-3}\text{ M}$)-BP ($1.12 \times 10^{-2}\text{ M}$) systems on the microsecond time scale in the presence of $[H_2SO_4] = 0.015\text{ M}$ (a) and 0.5 M (b) in MeOH-water (9:1 v/v) at 290 K obtained after laser photolysis at 355 nm (Kohno *et al* 1991).

concentration. The efficiencies (ϕ_{HT}) of the HT reaction from $^3RNH_3^{+*}$ to BP are 0.95 and 0.31 for the present systems with $[H_2SO_4] = 0.015\text{ M}$ and 0.5 M , respectively. It is obvious that the ϕ_{HT} value as well as that of k_{obsd} is affected considerably by addition of acids.

In order to study the reaction mechanism for the HT reaction from $^3RNH_3^{+*}$ to BP in the presence of protons, the concentration effects of BP and acids are investigated by nanosecond laser flash photolysis.

Figure 2 shows the plots of k_{obsd} vs $[BP]$ in the presence of $[H_2SO_4] = 0.015\text{ M}$ (a), 0.05 M (b) and 0.5 M (c). The value of k_{obsd} increases with increase of $[BP]$, while it decreases with increase of $[H_2SO_4]$. However, there is a leveling off at higher $[BP]$, especially at lower $[H_2SO_4]$ ($\leq 0.05\text{ M}$), which indicates an equilibrium in the excited state such as a triplet exciplex. On the other hand, figure 3 shows the plots of k_{obsd} vs $[acid]$ in order to study the proton effect on the HT reaction of RNH_3^+ -BP systems at various $[acid]$ with H_2SO_4 and $HClO_4$ as proton sources. The value of

Figure 2. Plots of the decay rate constant (k_{obsd}) of $^3\text{RNH}_3^{+*}$ as a function of $[\text{BP}]$ monitored at 410 nm in the presence of $[\text{H}_2\text{SO}_4] = 0.015 \text{ M}$ (a), 0.05 M (b) and 0.2 M (c). The solid curve denotes the calculated value of k_{obsd} by using (1) (Kohno *et al* 1991).

Figure 3. Plots of the decay rate constant (k_{obsd}) of $^3\text{RNH}_3^{+*}$ as a function of acid $[\text{H}_2\text{SO}_4]$ (○), HClO_4 (●) in the presence of $[\text{BP}] = 1.12 \times 10^{-2} \text{ M}$. The solid curve denotes the calculated values of k_{obsd} by using (1) (Kohno *et al* 1991).

k_{obsd} drastically decreases with an increase of $[\text{acid}]$. The k_{obsd} value obtained in the HClO_4 system agrees with that in the H_2SO_4 system as shown in figure 3. H_2SO_4 is known to behave almost as a monoprotic acid even in dilute solution (Cox and Yates 1978).

Scheme 1.

From the above results, the mechanism of the HT reaction is accounted for by scheme 1, where the triplet exciplex, $^3(\text{RNH}_3^+ \cdots >\text{CO})^*$ formed between $^3\text{RNH}_3^{+\ast}$ and BP with 1:1 ratio, k_1 and k_{-1} are the rate constants for formation and decomposition of $^3(\text{RNH}_3^+ \cdots >\text{CO})^*$, respectively, k_0 and k'_0 the decay rate constants of $^3\text{RNH}_3^{+\ast}$ and $^3(\text{RNH}_3^+ \cdots >\text{CO})^*$ to the ground state ($\text{RNH}_3^+ + \text{BP}$), respectively, k_{HT} the rate constant for HT via $^3(\text{RNH}_3^+ \cdots >\text{CO})^*$ and k_a denotes the decay rate constant of $^3(\text{RNH}_3^+ \cdots >\text{COH})^*$ by protonation, resulting in the reproduction of $^3\text{RNH}_3^{+\ast} + \text{BP}$ due to the Coulombic repulsion in the protonated triplet exciplex, $^3(\text{RNH}_3^+ \cdots >\text{COH})^*$. That is, the concentration of free $^3\text{RNH}_3^{+\ast}$ increases with increase of $[\text{H}_2\text{SO}_4]$. Therefore, the vibrational structures of the T - T absorption spectrum of $^3\text{RNH}_3^{+\ast}$ at 415 nm with $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$ are sharper than that of $^3(\text{RNH}_3^+ \cdots >\text{CO})^*$ at 410 nm with $[\text{H}_2\text{SO}_4] = 0.015 \text{ M}$ as shown in figure 1.

According to scheme 1, k_{obsd} is expressed by

$$k_{\text{obsd}} = \{k_0 + K_1 \cdot [\text{BP}] \cdot k_{\text{ex}} \cdot (1 + [\text{H}_2\text{SO}_4] \cdot k'_2/k_{-1})^{-1}\} \cdot \{1 + K_1 \cdot [\text{BP}] \cdot (1 + [\text{H}_2\text{SO}_4] \cdot k'_2/k_{-1})^{-1}\}^{-1}, \quad (1)$$

where we use $k'_2 \cdot [\text{H}_2\text{SO}_4]$ instead of $k_2 \cdot [\text{H}^+]$. When the kinetic parameters in scheme 1 are $K_1 (= k_1/k_{-1}) = 110 \text{ M}^{-1}$, $k'_2/k_{-1} = 40 \text{ M}^{-1}$, $k_0 = 1 \times 10^4 \text{ s}^{-1}$ and $k_{\text{ex}} (= k'_0 + k_{\text{HT}}) = 5 \times 10^6 \text{ s}^{-1}$, the calculated values of k_{obsd} from (1) shown as solid curves in figures 2 and 3 are in good agreement with the experimental ones.

2.2 The hydrogen atom transfer reaction from triplet naphthol to BP

When the naphthol (ROH)-BP system is employed under 355-nm laser pulsing, the ET reaction occurs in the nanosecond time scale from $^3\text{BP}^*$ to ROH competing with

Figure 4. Time-resolved transient absorption spectra of the ROH (3.0×10^{-3} M)-BP (6.7×10^{-3} M) system in acetonitrile-water (4:1 v/v) in a microsecond region for $[H_2SO_4] = 0$ M (a) and 0.5 M (b) observed after 355-nm laser pulsing at 290 K (Kaneko *et al* 1993).

hydrogen abstraction from ROH and deactivation of $^3BP^*$ by ROH. The triplet energies of BP and ROH are known to be 69.2 and 58.6 kcal mol $^{-1}$, respectively, in a polar solvent (Murov 1973).

In order to elucidate the HT reaction from $^3ROH^*$ to BP with $[H_2SO_4] = 0$ and 0.5 M, transient absorption spectra were analyzed on a microsecond time scale. Figure 4 shows the typical transient absorption spectra observed at 0.2–7 μs after laser pulsing in ROH (3.0×10^{-3} M)-BP (6.7×10^{-3} M) systems containing (a) $[H_2SO_4] = 0$ 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 triplet naphthol ($^3ROH^*$) decreases with an isosbestic point at 490 nm, accompanying an increase in intensities of the 545-nm and the 400-nm bands for the benzophenone ketyl radical ($>\dot{C}OH$) and the 1-naphthoxy radical ($\dot{R}O$), respectively.

Figure 5 shows the time traces of the transient absorbance changes observed at 430 nm ((a) and (c)) for $^3ROH^*$ and 545 nm ((b) and (d)) for $>\dot{C}OH$ after laser pulsing in ROH (3.0×10^{-3} 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 $^3ROH^*$ are $2.8 (\pm 0.2) \times 10^5$ s $^{-1}$ for $[H_2SO_4] = 0$ M and $7.4 (\pm 0.3) \times 10^5$ s $^{-1}$ for $[H_2SO_4] = 0.5$ M, respectively. The rate constant for the decay of $^3ROH^*$ is almost identical with that for the rise of $>\dot{C}OH$ within experimental error (10 %) showing that the HT reaction takes place from $^3ROH^*$ to BP. On the other hand, the k_{obsd} value at 430 or 545 nm in the system with

Figure 5. Time traces of the absorbance changes for transient species observed at 430 nm (a) and 545 nm (b) for $[\text{H}_2\text{SO}_4] = 0 \text{ M}$ and at 430 nm (c) and 545 nm (d) for $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$ after a 355-nm laser pulse in the ROH ($3.0 \times 10^{-3} \text{ M}$)–BP ($6.7 \times 10^{-3} \text{ M}$) system in acetonitrile–water (4:1 v/v) at 290 K (Kaneko *et al* 1993).

$[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$ 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 $^3\text{ROH}^*$ to BP are 0.73 and 0.85 for ROH ($3.0 \times 10^{-3} \text{ M}$)–BP ($6.7 \times 10^{-3} \text{ M}$) systems with $[\text{H}_2\text{SO}_4] = 0 \text{ M}$ and 0.5 M , respectively. These results show that the value of ϕ_{HT} is enhanced by protons as well as that of k_{obsd} . These findings imply that the HT reaction from $^3\text{ROH}^*$ to BP is enhanced by protons in contrast to the case of RNH_3^+ (Kohno *et al* 1991). In order to elucidate the effect of protons on the HT reaction, laser photolysis at 355 nm was carried out in the ROH–BP system at various concentrations of H_2SO_4 .

Figure 6 shows the plots of the decay rate constant (k_{obsd}) of $^3\text{ROH}^*$ at 430 nm vs $[\text{H}_2\text{SO}_4]$ ($\leq 1.0 \text{ M}$) obtained by laser photolysis in ROH ($3.0 \times 10^{-3} \text{ M}$)–BP (0.1 M) systems containing various $[\text{H}_2\text{SO}_4]$ in acetonitrile–water (4:1 v/v) at 290 K. The k_{obsd} value linearly increases with an increase of $[\text{H}_2\text{SO}_4]$. Therefore, k_{obsd} is formulated as

$$k_{\text{obsd}} = k_d + k_s \cdot [\text{H}_2\text{SO}_4], \quad (2)$$

where k_s and k_d are the quenching rate constant by H_2SO_4 and the decay rate constant of $^3\text{ROH}^*$ for the ROH ($3.0 \times 10^{-3} \text{ M}$)–BP (0.1 M) system without H_2SO_4 , respectively. From the slope and intercept of the line, we have $k_s = 4.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_d = 3.5 \times 10^6 \text{ s}^{-1}$.

Figure 7 shows the plots of k_{obsd} at 430 nm as a function of $[\text{BP}]$ ($\leq 2.0 \times 10^{-1} \text{ M}$) obtained by laser photolysis at 355 nm in ROH ($3.0 \times 10^{-3} \text{ M}$)–BP systems containing $[\text{H}_2\text{SO}_4] = 0, 0.5$ and 1.0 M in acetonitrile–water (4:1 v/v) at 290 K. The value of

Figure 6. Plots of the decay rate constant (k_{obsd}) of $^3\text{ROH}^*$ as a function of $[\text{H}_2\text{SO}_4]$ observed at 430 nm after laser pulsing at 355 nm in the ROH (3.0×10^{-3} M)–BP (0.1 M) system in acetonitrile–water (4:1 v/v) at 290 K (Kaneko *et al* 1993).

Figure 7. Plots of the decay rate constant (k_{obsd}) of $^3\text{ROH}^*$ as a function of $[\text{BP}]$ observed at 430 nm after laser pulsing in the ROH (3.0×10^{-3} M)–BP system with $[\text{H}_2\text{SO}_4] = 0$ ($\circ$), 0.5 ($\triangle$) and 1.0 M ($\times$) in acetonitrile–water (4:1 v/v) at 290 K. The solid curves are calculated by (7) (Kaneko *et al* 1993).

k_{obsd} increases considerably, though not linearly, with an increase of $[\text{BP}]$ at each $[\text{H}_2\text{SO}_4]$. These plots imply the formation of the triplet exciplex, $^3(\text{ROH} \cdots > \text{CO})^*$, which is considered to have a weak charge-transfer interaction from ROH to BP since no difference in the T – T absorption spectrum between $^3\text{ROH}^*$ and $^3(\text{ROH} \cdots > \text{CO})^*$ is observed.

In order to explain the above results, a reaction mechanism is suggested for the ROH–BP system without protons in scheme 2, where k_0 , k'_0 and k_{HT} are the decay rate constants for $^3\text{ROH}^*$ in the absence of BP, $^3(\text{ROH} \cdots > \text{CO})^*$ to ROH plus BP in the ground state and $^3(\text{ROH} \cdots > \text{CO})^*$ to the production of $> \dot{\text{C}}\text{OH}$ and $\text{R}\dot{\text{O}}$ (i.e., the HT rate constant), respectively, k_1 and k_{-1} the rate constants for the formation and the dissociation of $^3(\text{ROH} \cdots > \text{CO})^*$, respectively. A fast equilibrium between ($^3\text{ROH}^* + > \text{CO}$) and $^3(\text{ROH} \cdots > \text{CO})^*$ with an equilibrium constant (K_1) is supposed. According to scheme 2, the observed rate constant (k_{obsd}) for the decay of

Scheme 2.

$^3\text{ROH}^*$ is formulated as follows,

$$k_{\text{obsd}} = (k_0 + k_{\text{ex}} \cdot K_1 \cdot [\text{BP}]) \cdot (1 + K_1 \cdot [\text{BP}])^{-1}, \quad (3)$$

where $K_1 = k_1/k_{-1}$ and $k_{\text{ex}} = k'_0 + k_{\text{HT}}$. On the assumption that the value of k_0 is negligible compared to those of the competitive processes, i.e., $k_0 \ll k_{\text{ex}} \cdot K_1 \cdot [\text{BP}]$, (3) can be transformed as

$$k_{\text{obsd}}^{-1} = k_{\text{ex}}^{-1} + (k_{\text{ex}} \cdot K_1)^{-1} \cdot [\text{BP}]^{-1}. \quad (4)$$

By the use of the experimental values of k_{obsd} obtained in acetonitrile–water (4:1 v/v), plots of k_{obsd}^{-1} vs $[\text{BP}]^{-1}$ gave a straight line. From the slope and the intercept of the line, we obtained $k_{\text{ex}} = 9.1 \times 10^6 \text{ s}^{-1}$ and $K_1 = 6.7 \text{ M}^{-1}$. Since $k_0 = 1.4 \times 10^5 \text{ s}^{-1}$ (Shizuka *et al* 1985a) the assumption of $k_0 \ll k_{\text{ex}} \cdot K_1 \cdot [\text{BP}]$ is proper in the range $[\text{BP}] > 0.02 \text{ M}$. The solid curve for $[\text{H}_2\text{SO}_4] = 0 \text{ M}$ in figure 7 was calculated from (3) 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 good agreement with those calculated, the proposed mechanism is appropriate for the HT reaction from $^3\text{ROH}^*$ to BP without acid.

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_{HT}^0) was 0.73 in acetonitrile–water (4:1 v/v) at 290 K. According to scheme 2, ϕ_{HT}^0 can be expressed as

$$\phi_{\text{HT}}^0 = k_{\text{HT}} \cdot K_1 \cdot [\text{BP}] \cdot (k_0 + k_{\text{ex}} \cdot K_1 \cdot [\text{BP}])^{-1}. \quad (5)$$

By the use of $k_0 = 1.4 \times 10^5 \text{ s}^{-1}$ (Shizuka *et al* 1985a) 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 $^3(\text{ROH} \cdots > \text{CO})^*$ as $k_{\text{HT}}/k_{\text{ex}} = 0.98$. Therefore, once $^3(\text{ROH} \cdots > \text{CO})^*$ is produced, it is fated to undergo the HT reaction very effectively.

Scheme 3.

The mechanism in scheme 2 is extended to the ROH-BP system in the presence of protons as shown in scheme 3 considering the protonated triplet exciplex ${}^3(\text{ROH} \cdots >\dot{\text{C}}\text{OH})^*$. In the presence of protons, ${}^3(\text{ROH} \cdots >\text{CO})^*$ forms the protonated triplet exciplex ${}^3(\text{ROH} \cdots >\dot{\text{C}}\text{OH})^*$ with an equilibrium constant ($K_2 = k_2/k_{-2}$). Here, k_2 and k_{-2} are the rate constants for protonation of ${}^3(\text{ROH} \cdots >\text{CO})^*$ and deprotonation of ${}^3(\text{ROH} \cdots >\dot{\text{C}}\text{OH})^*$, respectively. The protonated triplet exciplex ${}^3(\text{ROH} \cdots >\dot{\text{C}}\text{OH})^*$ decays to $\text{ROH} + >\text{CO} + \text{H}^+$ 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 ${}^3(\text{ROH}^{+\cdot} \cdots >\dot{\text{C}}\text{OH})$. The radical pair rapidly transforms $\text{R}\dot{\text{O}} + >\dot{\text{C}}\text{OH} + \text{H}^+$. The decay rate constant of ${}^3(\text{ROH} \cdots >\dot{\text{C}}\text{OH})^*$ is denoted as $k_p (= k''_0 + k_{\text{el}})$. As stated above, the triplet exciplex ${}^3(\text{ROH} \cdots >\text{CO})^*$ has a weak charge transfer structure from ROH to BP. Accordingly, protonation of the benzophenone site ($>\text{CO}$) of ${}^3(\text{ROH} \cdots >\text{CO})^*$ may occur to produce ${}^3(\text{ROH} \cdots >\dot{\text{C}}\text{OH})^*$. According to scheme 3, k_{obsd} is formulated as

$$k_{\text{obsd}} = (k_0 + k_{\text{ex}} \cdot K_1 \cdot [\text{BP}] + k_p \cdot K_1 \cdot K_2 \cdot [\text{BP}] \cdot [\text{H}^+]) \cdot (1 + K_1 \cdot [\text{BP}] + K_1 \cdot K_2 \cdot [\text{BP}] \cdot [\text{H}^+])^{-1} \quad (6)$$

Since the activity of H_2SO_4 in acetonitrile-water (4:1 v/v) is unknown, we denote K'_2 and $[\text{H}_2\text{SO}_4]$ for K_2 and $[\text{H}^+]$, respectively. Thus, we obtain

$$k_{\text{obsd}} = (k_0 + k_{\text{ex}} \cdot K_1 \cdot [\text{BP}] + k_p \cdot K_1 \cdot K'_2 \cdot [\text{BP}] \cdot [\text{H}_2\text{SO}_4]) \cdot (1 + K_1 \cdot [\text{BP}] + K_1 \cdot K'_2 \cdot [\text{BP}] \cdot [\text{H}_2\text{SO}_4])^{-1} \quad (6')$$

If it is assumed that $1 + K_1 \cdot [\text{BP}] \gg K_1 \cdot K'_2 \cdot [\text{BP}] \cdot [\text{H}_2\text{SO}_4]$, (6') is rewritten as

$$k_{\text{obsd}} = (k_0 + k_{\text{ex}} \cdot K_1 \cdot [\text{BP}]) \cdot (1 + K_1 \cdot [\text{BP}])^{-1} + (k_p \cdot K_1 \cdot K'_2 \cdot [\text{BP}]) \cdot (1 + K_1 \cdot [\text{BP}])^{-1} \cdot [\text{H}_2\text{SO}_4]. \quad (7)$$

Comparing (2) with (7), we have

$$k_s = (k_p \cdot K_1 \cdot K'_2 \cdot [\text{BP}]) \cdot (1 + K_1 \cdot [\text{BP}])^{-1} = 4.8 \times 10^6 \text{ s}^{-1},$$

and

$$k_d = (k_0 + k_{\text{ex}} \cdot K_1 \cdot [\text{BP}]) \cdot (1 + K_1 \cdot [\text{BP}])^{-1}. \quad (9)$$

When $[\text{BP}] = 0.1 \text{ M}$ and $K_1 = 6.7 \text{ M}^{-1}$ are substituted into (8), we obtain $k_p \cdot K'_2 = 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. We calculated the values of k_d as $3.7 \times 10^6 \text{ s}^{-1}$, with the values obtained of k_0 , k_{ex} , K_1 and $[\text{BP}] = 0.1 \text{ M}$. This value agrees well with the experimental value ($3.5 \times 10^6 \text{ s}^{-1}$) for $[\text{BP}] = 0.1 \text{ M}$ obtained in figure 3 within experimental error (10%).

The solid curves for $[\text{H}_2\text{SO}_4] = 0.5$ and 1.0 M in figure 7 are calculated from (6') by using the determined values of k_0 , k_{ex} , K_1 and $k_p \cdot K'_2$. The calculated values are consistent with experimental ones.

For the ROH ($3.0 \times 10^{-3} \text{ M}$)–BP ($6.7 \times 10^{-3} \text{ M}$) system with $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$, the total efficiency (ϕ_{HT}^p) of the HT reaction in the presence of protons was obtained as 0.85. According to scheme 3, ϕ_{HT}^p is formulated as

$$\phi_{\text{HT}}^p = (k_{\text{HT}} \cdot K_1 \cdot [\text{BP}] + k_{\text{el}} \cdot K_1 \cdot K'_2 \cdot [\text{BP}] \cdot [\text{H}_2\text{SO}_4]) \cdot (k_0 + k_{\text{ex}} \cdot K_1 \cdot [\text{BP}] + k_p \cdot K_1 \cdot K'_2 \cdot [\text{BP}] \cdot [\text{H}_2\text{SO}_4])^{-1}. \quad (10)$$

When we introduce into (10) the ratio of γ which is defined as $\gamma = k_{\text{el}}/k_p$, and use the determined values of k_0 , k_{HT} ($\approx k_{\text{ex}}$), $k_p \cdot K'_2$, $[\text{BP}] = 6.7 \times 10^{-3} \text{ M}$ and $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$, we have $\gamma = 1.1$. Considering the experimental error (10%) in determining ϕ_{HT}^p , k_p can be regarded as k_{el} (i.e., $k_{\text{el}} \gg k_0$). Therefore, ${}^3(\text{ROH}^+ \cdots >\dot{\text{C}}\text{OH})$ produced by the intraexciplex electron transfer reaction dissociates into ROH^+ and $>\dot{\text{C}}\text{OH}$ effectively without the back-electron transfer reaction. The deprotonation of ROH^+ rapidly occurs to produce $\text{R}\dot{\text{O}}$ plus H^+ since ROH^+ seems to be very acidic.

2.3 Proton-induced electron transfer reaction from triplet methoxynaphthalene to BP (Yamaji *et al* 1992)

When the ROH of an ROH–BP system is replaced by methoxynaphthalene (ROME) in the absence of protons, no reaction occurs owing to the triplet methoxynaphthalene (${}^3\text{ROME}^*$) produced by triplet sensitization of BP. However, in the presence of protons in the ROME–BP system, proton-assisted photoionization (p -ion) reaction of ${}^3\text{ROME}^*$ produced by triplet sensitization of BP effectively occurs to produce the methoxynaphthalene cation radical ($\text{ROME}^{\cdot+}$) and $>\dot{\text{C}}\text{OH}$ (Shizuka *et al* 1985b).

Figure 8a shows the transient absorption spectra on a microsecond time scale for the 1 ROME ($3.0 \times 10^{-3} \text{ M}$)–BP ($6.7 \times 10^{-3} \text{ M}$)– H_2SO_4 (1.0 M) system in acetonitrile–water (4:1 v/v) at 290 K. The $T_n \leftarrow T_1$ absorption of BP at 525 nm disappears within 100 ns after laser pulsing, resulting in the formation of a transient peak at 435 nm.

The transient spectrum at 435 nm was assigned to the $T_n \leftarrow T_1$ absorption of 1 ROME. At 500 ns after laser pulsing, new transient peaks at 380, 545, and 650 nm appear with a decrease of the 435-nm peak for $^3\text{1 ROME}^*$ with an isosbestic point at 490 nm. The 545-nm transient is known as $>\dot{\text{C}}\text{OH}$ (Land 1968). Both transient peaks at 380 and 650 nm are ascribable to the 1-methoxynaphthalene cation radical, $1\text{ ROME}^{\cdot+}$. The reference spectra of $^3\text{1 ROME}^*$, $>\dot{\text{C}}\text{OH}$, and $1\text{ ROME}^{\cdot+}$ are depicted in figure 8b. The molar absorption coefficient of $1\text{ ROME}^{\cdot+}$ can be readily determined from spectral analysis since the rate constant for the formation of $1\text{ ROME}^{\cdot+}$ is the same as that of $>\dot{\text{C}}\text{OH}$. The rate constants for the rise of both transient peaks at 545 nm for $>\dot{\text{C}}\text{OH}$ and 650 nm for $1\text{ ROME}^{\cdot+}$ were the same as that for the decay, $k_{\text{obsd}} = 8.9 \times 10^5 \text{ s}^{-1}$ observed at 435 nm for $^3\text{1 ROME}^*$ within 5% experimental error, as shown in figure 8c. In the absence of protons, no photoionization takes place in the 1 ROME–BP system upon 355 nm excitation. These results show that the ionization of $^3\text{1 ROME}^*$ is assisted by both protons and BP, leading to the production of $1\text{ ROME}^{\cdot+}$ and $>\dot{\text{C}}\text{OH}$.

Figure 8. (a) & (b).

Figure 8. (a) Time-resolved transient absorption spectra in a microsecond time scale for the 1 ROME (3.0×10^{-3} M)–BP (6.7×10^{-3} M)– H_2SO_4 (1.0 M) system in acetonitrile–water (4:1 v/v) observed after 355-nm laser pulsing at 290 K (Yamaji *et al* 1992). (b) Reference absorption spectra for the transient species ($^3\text{1 ROME}^*$, $>\dot{\text{C}}\text{OH}$ and $1\text{ ROME}^{+\cdot}$) (Yamaji *et al* 1992). (c) Time traces of the absorbance changes for transient species monitored at 435 nm ($^3\text{1 ROME}^*$) (1), at 545 nm ($>\dot{\text{C}}\text{OH}$) (2) and at 650 nm ($1\text{ ROME}^{+\cdot}$) (3) after a 355-nm laser pulse to the 1 ROME (3.0×10^{-3} M)–BP (6.7×10^{-3} M)– H_2SO_4 (1.0 M) system in acetonitrile–water (4:1 v/v) at 290 K (Yamaji *et al* 1992).

Similar transient spectra of $^3\text{2 ROME}^*$ were obtained in the 2 ROME (3.0×10^{-3} M)–BP (6.7×10^{-3} M) system containing $[\text{H}_2\text{SO}_4] = 1.0$ M by laser flash photolysis at 355 nm as shown in figure 9a. The transient absorption at 430 nm for $^3\text{2 ROME}^*$ ($\epsilon = 14,700 \text{ M}^{-1} \text{ cm}^{-1}$) (Yamaji *et al* 1992) produced by triplet sensitization of BP decreases with increase of the new absorption peaks 545 nm for $>\dot{\text{C}}\text{OH}$ ($\epsilon = 3220 \text{ M}^{-1} \text{ cm}^{-1}$) (Land 1968), 380 and 600 nm ($\epsilon = 6500 \text{ M}^{-1} \text{ cm}^{-1}$) for $2\text{ ROME}^{+\cdot}$. The decay rate constant, $k_{\text{obsd}} = 1.0 \times 10^5 \text{ s}^{-1}$ at 290 K observed at 430 nm for $^3\text{2 ROME}^*$ was the same as the rise rate at 545 nm for $>\dot{\text{C}}\text{OH}$ or 600 nm for $2\text{ ROME}^{+\cdot}$. The reference spectra of the transients are also shown in figure 9b. These observations demonstrate that in the presence of protons, the ionization of $^3\text{2 ROME}^*$ occurs to produce the 2-methoxynaphthalene cation radical, $2\text{ ROME}^{+\cdot}$, and the

Figure 9. (a) Time-resolved transient absorption spectra in a microsecond time scale for the 2ROME ($3.0 \times 10^{-3} \text{ M}$)– BP ($6.7 \times 10^{-3} \text{ M}$)– H_2SO_4 (1.0 M) system in acetonitrile–water (4:1 v/v) observed after 355-nm laser pulsing at 290 K (Yamaji *et al* 1992). (b) Reference absorption spectra for the transient species ($^3\text{2ROME}^*$, $^{\cdot}\text{COH}$ and 2ROME^+) (Yamaji *et al* 1992).

benzophenone ketyl radical, $>\dot{\text{C}}\text{OH}$. No photoionization upon 355 nm excitation was observed for the 2 ROME–BP system in the absence of protons.

From these results, the ionization of $^3\text{ROME}^*$ can be expressed as

The ionization potentials of 1 ROME and 2 ROME are known to be 179.4 and 182.6 kcal mol⁻¹, respectively (Shizuka and Tobita 1982). However, the proton-assisted photoionization of ROME occurs with lower triplet energies (1 ROME: 59.7 kcal mol⁻¹, Murov 1973; 2 ROME: 61.9 kcal mol⁻¹, Yamaji *et al* 1992).

The efficiencies (ϕ_{ion}) for the ionization of ROME are evaluated as 0.84 for the 1 ROME (3.0×10^{-3} M)–BP (6.7×10^{-3} M)–H₂SO₄ (1.0 M) system and 0.29 for the 2 ROME (3.0×10^{-3} M)–BP (6.7×10^{-3} M)–H₂SO₄ (1.0 M) system.

The deactivation processes of $^3\text{ROME}^*$ produced by the triplet sensitization of BP have been studied in the ROME–BP–H₂SO₄ system under various concentrations of BP and H₂SO₄ at 290 K.

Upon laser excitation at 355 nm in the 1 ROME (3.0×10^{-3} M)–BP (≤ 0.2 M) systems with [H₂SO₄] = 0, 0.5 and 1.0 M at 290 K, the decay rate constants, k_{obsd} of $^3\text{1 ROME}^*$ at 435 nm were measured. The k_{obsd} value corresponds to the decay rate constant of $^3\text{ROME}^*$ which is equal to the rise rate constant of 1 ROME $^{\cdot+}$ or $>\dot{\text{C}}\text{OH}$ as described above. Figure 10 shows the plots of k_{obsd} vs [BP] obtained after laser pulsing to 1 ROME–BP–H₂SO₄ systems. The value of k_{obsd} increases with increase of [BP] and [H₂SO₄] though not linearly. Especially in the system with [H₂SO₄] = 0, a leveling-off is expected at higher [BP] (≥ 0.2 M). Similar results were obtained in the 2 ROME (3.0×10^{-3} M)–BP (≤ 0.2 M) systems with [H₂SO₄] = 0, 0.1 and 1.0 M at 290 K as

Figure 10. Plots of the decay rate constant (k_{obsd}) of $^3\text{1 ROME}^*$ as a function of [BP] observed at 435 nm after laser pulsing at 355 nm in the 1 ROME (3.0×10^{-3} M)–BP systems with [H₂SO₄] = 0 (○), 0.5 (△) and 1.0 M (×) in acetonitrile–water (4:1 v/v) at 290 K. The solid lines are calculated using (16) (Yamaji *et al* 1992).

Figure 11. Plots of the decay rate constant (k_{obsd}) of $^3\text{ROME}^*$ as a function of $[\text{BP}]$ observed at 430 nm after laser pulsing at 355 nm in the 2ROME ($3.0 \times 10^{-3}\text{ M}$)–BP systems with $[\text{H}_2\text{SO}_4] = 0$ (○), 0.1 (△) and 1.0 M (×) in acetonitrile–water (4:1 v/v) at 290 K. The solid lines are calculated using (16) (Yamaji *et al* 1992).

shown in figure 11. Such a nonlinear quenching of $^3\text{ROME}^*$, as shown in figures 10 and 11, cannot be explained by a simple quenching mechanism, and implies the existence of the triplet exciplex, $^3(\text{ROME} \cdots >\text{CO})^*$. In order to account for these experimental results, we propose the proton-assisted photoionization mechanism shown in scheme 4, where $^3\text{ROME}^*$, $^3(\text{ROME} \cdots >\text{CO})^*$ and $^3(\text{ROH} \cdots >\dot{\text{C}}\text{OH})^*$ denote the triplet ROME, the 1:1 triplet exciplex and the protonated triplet exciplex, respectively, k_0 , k_{ex} and k_0'' the decay rate constants of $^3\text{ROME}^*$, $^3(\text{ROME} \cdots >\text{CO})^*$

and $^3(\text{ROME} \cdots > \dot{\text{C}}\text{OH})^*$, respectively, to the ground state, K_1 and K_2 the corresponding equilibrium constants for complex formations, and k_{et} the rate constant for the intraexciplex electron transfer reaction of $^3(\text{ROME} \cdots > \dot{\text{C}}\text{OH})^*$. Spectral changes in the $T_n \leftarrow T_1$ absorptions among $^3\text{ROME}^*$, $^3(\text{ROME} \cdots > \text{CO})^*$ and $^3(\text{ROME} \cdots > \dot{\text{C}}\text{OH})^*$ were scarcely observed, suggesting that these triplet exciplexes have weak charge-transfer structures. The acid–base reactions of $^3\text{BP}^*$ are known to be very fast, their equilibria are established within 20 ns after laser pulsing (Hoshi and Shizuka 1986). In scheme 4, we neglected the proton-induced quenching of $^3\text{ROME}^*$ considering the following reason; as $[\text{BP}]$ approaches 0 M, the values of k_{obsd} at each $[\text{H}_2\text{SO}_4]$ in figures 10 and 11 become close to the same. On the assumption that both equilibria for the formation of $^3(\text{ROME} \cdots > \text{CO})^*$ and $^3(\text{ROME} \cdots > \dot{\text{C}}\text{OH})^*$ are attained within 200 ns, the following equation for the observed decay rate, k_{obsd} observed at 435 nm for $^3\text{1 ROME}^*$ and at 430 nm for $^3\text{2 ROME}^*$ can be derived,

$$k_{\text{obsd}} = (k_0 + K_1 \cdot [\text{BP}] \cdot k_{\text{ex}} + K_1 \cdot K_2 \cdot [\text{BP}] \cdot [\text{H}^+] \cdot k_p) \cdot (1 + K_1 \cdot [\text{BP}] + K_1 \cdot K_2 \cdot [\text{BP}] \cdot [\text{H}^+])^{-1}, \quad (12)$$

where $k_p = k_{et} + k_0''$. Since there is no information about the activity of H_2SO_4 in acetonitrile–water (4:1 v/v), we use K'_2 and $[\text{H}_2\text{SO}_4]$ instead of K_2 and $[\text{H}^+]$, respectively. Therefore, (12) is reformed as

$$k_{\text{obsd}} = (k_0 + K_1 \cdot [\text{BP}] \cdot k_{\text{ex}} + K_1 \cdot K'_2 \cdot [\text{BP}] \cdot [\text{H}_2\text{SO}_4] \cdot k_p) \cdot (1 + K_1 \cdot [\text{BP}] + K_1 \cdot K'_2 \cdot [\text{BP}] \cdot [\text{H}_2\text{SO}_4])^{-1}. \quad (12')$$

At first, we consider the simplest case of the 1 ROME (3.0×10^{-3} M)–BP (≤ 0.2 M) and the 2 ROME (3.0×10^{-3} M)–BP (≤ 0.2 M) systems in the absence of H_2SO_4 . For these cases, (12') can be simplified as

$$k_{\text{obsd}} = (k_0 + K_1 \cdot [\text{BP}] \cdot k_{\text{ex}}) \cdot (1 + K_1 \cdot [\text{BP}])^{-1}. \quad (13)$$

On the assumption that the value of k_0 is small enough to be negligible, i.e., $k_0 \ll K_1 \cdot [\text{BP}] \cdot k_{\text{ex}}$ in the $[\text{BP}]$ range studied (10^{-2} M $\leq [\text{BP}] \leq 0.2$ M), (13) can be transformed as

$$k_{\text{obsd}}^{-1} = k_{\text{ex}}^{-1} + (K_1 \cdot k_{\text{ex}})^{-1} \cdot [\text{BP}]^{-1}. \quad (14)$$

By the use of the experimental values of k_{obsd} obtained for 1 ROME and 2 ROME, plots of k_{obsd}^{-1} vs $[\text{BP}]^{-1}$ gave a straight line. From the slope and the intercept of the line, we obtained the values of k_{ex} and K_1 as $1.6 \times 10^6 \text{ s}^{-1}$ and 10.1 M^{-1} for 1 ROME, $2.5 \times 10^6 \text{ s}^{-1}$ and 4.0 M^{-1} for 2 ROME, respectively. Since we experimentally obtained the values of k_0 as $6.8 \times 10^4 \text{ s}^{-1}$ and $5.4 \times 10^4 \text{ s}^{-1}$ for 1 ROME and 2 ROME, respectively, upon 266-nm laser excitation to ROME in acetonitrile–water (4:1 v/v) at 290 K, the assumption of $k_0 \ll K_1 \cdot [\text{BP}] \cdot k_{\text{ex}}$ is proper in the range $[\text{BP}] \geq 10^{-2}$ M. The solid curves for $[\text{H}_2\text{SO}_4] = 0$ M in figures 10 and 11 are, respectively, calculated by (13) and the determined values of k_{ex} and K_1 . The calculated values are in good agreement with those measured in both 1 ROME–BP and 2 ROME–BP systems.

For the next step, in order to determine the values of k_p and K'_2 for the ROME–BP system in the presence of protons, we have measured the k_{obsd} values for the ROME–BP system with various $[\text{H}_2\text{SO}_4]$ in acetonitrile–water (4:1 v/v) at 290 K.

Figure 12. Plots of the decay rate constant (k_{obsd}) of $^3\text{1 ROME}^*$ as a function of $[\text{H}_2\text{SO}_4]$ observed at 435 nm after laser pulsing at 355 nm in the 1 ROME ($3.0 \times 10^{-3} \text{ M}$)–BP ($6.7 \times 10^{-3} \text{ M}$)– H_2SO_4 (1.0 M) system in acetonitrile–water (4:1 v/v) at 290 K (Yamaji *et al* 1992).

Figures 12 and 13 show the plots of k_{obsd} vs. $[\text{H}_2\text{SO}_4]$ observed for 1 ROME ($3.0 \times 10^{-3} \text{ M}$)–BP ($1.0 \times 10^{-1} \text{ M}$) and 2 ROME ($3.0 \times 10^{-3} \text{ M}$)–BP ($1.0 \times 10^{-1} \text{ M}$) systems, respectively. In both systems, plots show a straight line. Therefore, we can express k_{obsd} as a function of $[\text{H}_2\text{SO}_4]$ as follows

$$k_{\text{obsd}} = k_d + k_s \cdot [\text{H}_2\text{SO}_4]. \quad (15)$$

From the intercept and the slope of the line, we obtained the values of k_d and k_s as $8.0 \times 10^5 \text{ s}^{-1}$ and $3.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for 1 ROME, $7.5 \times 10^5 \text{ s}^{-1}$ and $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for 2 ROME, respectively. When we assume $1 + K_1 \cdot [\text{BP}] \gg K_1 \cdot K'_2 \cdot [\text{BP}] \cdot [\text{H}_2\text{SO}_4]$ in the range studied ($10^{-2} \text{ M} \leq [\text{BP}] \leq 0.2 \text{ M}$ and $[\text{H}_2\text{SO}_4] \leq 1.0 \text{ M}$), (12') is written as

$$k_{\text{obsd}} = (k_0 + K_1 \cdot [\text{BP}] \cdot k_{\text{ex}}) \cdot (1 + K_1 \cdot [\text{BP}])^{-1} + K_1 \cdot K'_2 \cdot [\text{BP}] \cdot k_p \cdot (1 + K_1 \cdot [\text{BP}])^{-1} \cdot [\text{H}_2\text{SO}_4]. \quad (16)$$

Comparing (15) with (16), we have

$$k_d = (k_0 + K_1 \cdot [\text{BP}] \cdot k_{\text{ex}}) \cdot (1 + K_1 \cdot [\text{BP}])^{-1}, \quad (17)$$

$$k_s = K_1 \cdot K'_2 \cdot [\text{BP}] \cdot k_p \cdot (1 + K_1 \cdot [\text{BP}])^{-1}. \quad (18)$$

When we use $[\text{BP}] = 0.1 \text{ M}$ and the determined values of K_1 and k_s in (18), the values of $K'_2 \cdot k_p$ are obtained as $6.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $4.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for 1 ROME–BP and 2 ROME–BP systems, respectively. According to (17), we calculated the values k_d with the determined values of k_0 , k_{ex} , K_1 and $[\text{BP}] = 0.1 \text{ M}$ to be $8.6 \times 10^5 \text{ s}^{-1}$ and $7.7 \times 10^5 \text{ s}^{-1}$ for 1 ROME–BP and 2 ROME–BP systems, respectively, which correspond to those obtained above within 10% experimental error.

The solid curves for the 1 ROME–BP system with $[\text{H}_2\text{SO}_4] = 0.5$ and 1.0 M in figure 10 and for the 2 ROME–BP system with $[\text{H}_2\text{SO}_4] = 0.1$ and 1.0 M in figure 11 are calculated by (16) with $[\text{BP}] = 6.7 \times 10^{-3} \text{ M}$ and the determined values of k_0 ,

Figure 13. Plots of the decay rate constant (k_{obsd}) of $^3\text{2 ROME}^*$ as a function of $[\text{H}_2\text{SO}_4]$ observed at 430 nm after laser pulsing at 355 nm in the $^3\text{2 ROME}$ ($3.0 \times 10^{-3} \text{ M}$)–BP ($6.7 \times 10^{-3} \text{ M}$)– H_2SO_4 (1.0 M) system in acetonitrile–water (4:1 v/v) at 290 K (Yamaji *et al* 1992).

k_{ex} , K_1 and $K'_2 \cdot k_p$. The calculated values are consistent with those obtained experimentally within 10% error. This fact suggests that (12') is available for the kinetic analysis of the present system.

According to scheme 4, ϕ_{ion} is formulated as

$$\phi_{\text{ion}} = (K_1 \cdot K'_2 \cdot [\text{BP}] \cdot [\text{H}_2\text{SO}_4] \cdot k_{\text{el}}) \cdot (k_0 + K_1 \cdot [\text{BP}] \cdot k_{\text{ex}} + K_1 \cdot K'_2 \cdot [\text{BP}] \cdot [\text{H}_2\text{SO}_4] \cdot k_p)^{-1}. \quad (19)$$

When we define the ratio, $\gamma = k_{\text{el}}/k_p$ and put into (19) the determined values of k_0 , k_{ex} , K_1 , $K'_2 \cdot k_p$, $[\text{BP}] = 6.7 \times 10^{-3} \text{ M}$ and $[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$, we have $\gamma = 1.0$ and 0.60 for 1 ROME and 2 ROME systems, respectively. These values indicate that the intraexciplex electron transfer reaction effectively occurs to yield $\text{ROME}^{\cdot+}$ and $>\dot{\text{C}}\text{OH}$. This reason is considered as follows. By the intraexciplex electron transfer in $^3(\text{ROME} \cdots >\dot{\text{C}}\text{OH})^*$, the triplet radical pair may be initially produced in a solvent cage according to the spin conservation rule.

where $^3(\text{ROME}^{\cdot+} + >\dot{\text{C}}\text{OH})$ represents the triplet radical pair in a solvent cage. Hence, the geminate recombination between the triplet radicals is impossible without spin inversion, and the radicals can escape from the solvent cage without the back-electron transfer. In other words, once intraexciplex electron transfer occurs, the triplet radical pair, $^3(\text{ROME}^{\cdot+} + >\dot{\text{C}}\text{OH})$ readily dissociates into $\text{ROME}^{\cdot+}$ and $>\dot{\text{C}}\text{OH}$ with high efficiency.

It should be noted that the pK_a value in the ground state of BP has a large negative value (-5.7) (Bonner and Phillips 1966), and no protonation to BP occurs in the ground state under the experimental conditions. On the other hand, protonation to the triplet exciplex, $^3(\text{ROME} \cdots >\text{CO})^*$ takes place. In $^3(\text{ROME} \cdots >\text{CO})^*$, slight electron migration may occur from $^3\text{ROME}^*$ to BP since $^3(\text{ROME} \cdots >\text{CO})^*$ has

weak charge-transfer character. At higher acid concentrations, the protonated exciplex, $^3(\text{ROMe}\cdots > \dot{\text{C}}\text{OH})^*$ is, therefore, produced by protonation to $^3(\text{ROMe}\cdots > \text{CO})^*$. The electron affinity of the protonated BP ($> \dot{\text{C}}\text{OH}$) in the exciplex may become large compared to that of BP resulting in the intraexciplex electron transfer.

When 1-naphthol (ROH) is used instead of 1 ROME, the proton-enhanced hydrogen atom transfer reaction occurs via the intracomplex electron transfer reaction as follows.

where $^3(\text{ROH}^{\cdot+} + > \dot{\text{C}}\text{OH})$ represents the triplet radical pair in a solvent cage. The 1-naphthol cation radical ($\text{ROH}^{\cdot+}$) could not be detected experimentally (Kaneko *et al* 1993). The result shows that $\text{ROH}^{\cdot+}$ dissociates very rapidly into the 1-naphthoxy radical, $\dot{\text{R}}\text{O}$ and H^+ , since the pK_a value of $\text{ROH}^{\cdot+}$ is considered to be very negative. Comparing (20) with (21), the present study strongly supports the mechanism on the proton-enhanced hydrogen atom transfer reaction.

2.4 The intramolecular hydrogen atom transfer reaction of $\text{BP}-(\text{CH}_2)_3\text{-ROH}$ and proton-induced electron transfer of $\text{BP}-(\text{CH}_2)_3\text{-ROME}$ in the triplet state (Sekiguchi *et al* 1993)

As to the structures of $^3(\text{ROH}\cdots > \text{CO})^*$ and $^3(\text{ROMe}\cdots > \text{CO})^*$, it is considered to have a sandwich-like structure which is locally excited because the triplet-triplet absorption spectra of $^3\text{ROH}^*$ and $^3\text{ROME}^*$ are similar to those of $^3(\text{ROH}\cdots > \text{CO})^*$ and $^3(\text{ROMe}\cdots > \text{CO})^*$, respectively. However, little information on structures of triplet exciplexes has been offered yet though it is of great interest to reveal the conformations of triplet exciplexes for the HT and ionization reactions.

One of the most useful methods for the study of chromophore interactions is to link the chromophores with a methylene chain $-(\text{CH}_2)_n-$ to restrict their conformation. According to Hirayama's " $n = 3$ rule" (Hirayama 1965), it is known that the two chromophores linked by $-(\text{CH}_2)_3-$ must be situated face-to-face upon their interaction. Thus, the problem on the structures of $^3(\text{ROH}\cdots > \text{CO})^*$ and $^3(\text{ROMe}\cdots > \text{CO})^*$ for HT and ionization will be answered by using the linked molecular systems of hydroxynaphthylpropylbenzophenone ($\text{BP}-(\text{CH}_2)_3\text{-ROH}$) and methoxynaphthylpropylbenzophenone ($\text{BP}-(\text{CH}_2)_3\text{-ROME}$), respectively.

2.4a The intramolecular hydrogen atom transfer reaction in the triplet state of $\text{BP}-(\text{CH}_2)_3\text{-ROH}$: The intramolecular HT reaction in the triplet state of $\text{BP}-(\text{CH}_2)_3\text{-ROH}$ has been revealed. After 355-nm laser excitation of $\text{BP}-(\text{CH}_2)_3\text{-ROH}$, intramolecular triplet energy transfer (intra-ET) from the triplet benzophenone moiety ($^3\text{BP}^*$) to the naphthol moiety ($-\text{ROH}$) occurs to produce the triplet naphthol moiety ($^3\text{ROH}^*$) within 100 ps as well as the case of the naphthalene-BP system (Lamola *et al* 1965). The transient absorption spectra have been observed after a 355-nm laser pulse to $\text{BP}-(\text{CH}_2)_3\text{-ROH}$ (3.0×10^{-3} M) in acetonitrile-water (4:1 *v/v*) at 295 K. At 25 ns after a pulse, the transient absorption spectrum has the 430-nm band which resembles the triplet-triplet ($T-T$) absorption of 1-naphthol (Shizuka

et al 1985a; Kaneko *et al* 1993; Yamaji *et al* 1993). Therefore, in the present system of BP-(CH₂)₃-ROH, we can conclude that the intra-ET from ³BP* to -ROH occurs within laser pulse duration, resulting in BP-(CH₂)₃-³ROH*,

After the intra-ET reaction of BP-(CH₂)₃-ROH, with a lapse of time, the 430-nm band of BP-(CH₂)₃-³ROH* decreases in intensity with an isosbestic point, accompanying an increase in intensities of the 550-nm and the 400-nm bands for the benzo-phenone ketyl radical moiety (>C $\dot{\text{O}}\text{H}$ -) and the naphthoxy radical moiety (-R $\dot{\text{O}}$), respectively (Shizuka *et al* 1985a; Kaneko *et al* 1993). The time traces of the transient absorbance changes have been observed at 430 nm for ³ROH* and 550 nm for >C $\dot{\text{O}}\text{H}$ - after laser pulsing to BP-(CH₂)₃-ROH (3.0 × 10⁻³ M) in acetonitrile-water (4:1 v/v) at 295 K. The first-order rate constant (*k*_{obsd}) for the decay at 430 nm is almost identical with that for the rise at 550 nm (9.8 × 10⁶ s⁻¹) within experimental error (10%), indicating that the HT reaction occurs from ³ROH* to BP-. Since the *k*_{obsd} value (9.8 × 10⁶ s⁻¹) is independent of [BP-(CH₂)₃-ROH] (≤ 6.0 × 10⁻³ M), it is concluded that the HT reaction is an intramolecular one (intra-HT) of BP-(CH₂)₃-³ROH* to produce >C $\dot{\text{O}}\text{H}$ -(CH₂)₃-R $\dot{\text{O}}$ with rate constant (9.8 × 10⁶ s⁻¹) in the range of [BP-(CH₂)₃-ROH] studied. The efficiency (φ_{HT}) for the intra-HT reaction is 1.0 for BP-(CH₂)₃-ROH in acetonitrile-water (4:1 v/v). This φ_{HT} value implies that the intra-HT reaction of BP-(CH₂)₃-ROH occurs very efficiently.

The plots of the rate constant (*k*_{obsd}) for intra-HT vs [H₂SO₄] (≤ 0.5 M) have been obtained after a laser pulse to BP-(CH₂)₃-ROH (3.0 × 10⁻³ M) in acetonitrile-water (4:1 v/v). The *k*_{obsd} value increases linearly with increase of [H₂SO₄]. Therefore, *k*_{obsd} is also represented as

$$k_{\text{obsd}} = k_d + k_s \cdot [\text{H}_2\text{SO}_4]. \quad (26)$$

From the slope and the intercept of the line, we have *k*_s = 3.3 × 10⁶ M⁻¹ s⁻¹ and *k*_d = 9.8 × 10⁵ s⁻¹. On the other hand, the efficiency of intra-HT (φ_{HT}) was 1.0 in the range of [H₂SO₄] (≤ 0.5 M) studied as mentioned above. As a result, for the proton effect on intra-HT of BP-(CH₂)₃-ROH, only the rate constant for intra-HT is enhanced by protons.

In order to account for the results obtained on intra-HT of BP-(CH₂)₃-ROH, we propose the intra-HT mechanism as shown in scheme 5 analogous to that for inter-HT of the ROH-BP system (Kaneko *et al* 1993), where ³(BP-(CH₂)₃-ROH)*, ³(>C $\dot{\text{O}}\text{H}$ -(CH₂)₃-ROH)* and ³(>C $\dot{\text{O}}\text{H}$ -(CH₂)₃-ROH⁺) denote the intramolecular triplet exciplex with a sandwich-like structure, the protonated intramolecular triplet exciplex and the triplet radical pair produced by the intraexciplex electron transfer (intra-el), respectively, *k*₀, *k*'₀ and *k*''₀ are the corresponding decay rate constants of BP-(CH₂)₃-³ROH*, ³(BP-(CH₂)₃-ROH)* and ³(>C $\dot{\text{O}}\text{H}$ -(CH₂)₃-ROH)* to the ground BP-(CH₂)₃-ROH, respectively, *k*_{HT} and *k*_{ei} the rate constants for intra-HT of ³(BP-(CH₂)₃-ROH)* to >C $\dot{\text{O}}\text{H}$ -(CH₂)₃-R $\dot{\text{O}}$ and intra-el of ³(>C $\dot{\text{O}}\text{H}$ -(CH₂)₃-ROH)* to ³(>C $\dot{\text{O}}\text{H}$ -(CH₂)₃-ROH⁺), respectively, and *K*₁ and *K*₂ the corresponding equilibrium constants of formation of the triplet exciplex and the protonation of the triplet exciplex, respectively.

Scheme 5.

2.4b The intramolecular proton-induced electron transfer in the triplet state of BP-(CH₂)₃-ROME: The intramolecular *p-eT* reaction of BP-(CH₂)₃-ROME in the triplet state is as follows: After 355-nm laser excitation of BP-(CH₂)₃-ROME, the intra-ET from ³BP* – to the methoxynaphthalene moiety (–ROME) occurs to produce the triplet methoxynaphthalene moiety (³ROME*) as well as in the case of BP-(CH₂)₃-ROH. The transient absorption spectra have been observed after 355-nm laser pulsing to BP-(CH₂)₃-ROME (3.0 × 10^{−3} M) in acetonitrile–water (4:1 *v/v*) at 295 K with [H₂SO₄] = 0, 0.005 and 0.5 M. The transient spectrum observed at 400 ns after laser pulsing in BP-(CH₂)₃-ROME without H₂SO₄ shows the 435-nm band which resembles *T*–*T* absorption of 1-ROME (Shizuka *et al* 1985b; Yamaji *et al* 1992). The 435-nm band decays with the first order rate constant (1.8 × 10⁵ s^{−1}) in the absence of protons. However, in the presence of protons, with lapse of time, the 550-nm band for >C•OH– and the 380- and 650-nm bands for the methoxynaphthalene cation radical moiety (–ROME^{•+}) (Shizuka *et al* 1985b; Yamaji *et al* 1992) increase in intensity with isosbestic points, while the 435-nm band decreases.

The time traces of the transient absorbance changes have been observed at 435 nm for ³ROME*, 550 nm for >C•OH– and 650 nm for –ROME^{•+} after laser pulsing to BP-(CH₂)₃-ROME (3.0 × 10^{−3} M) in acetonitrile–water (4:1 *v/v*) with [H₂SO₄] = 0.5 M at 295 K. The first-order rate constant (*k*_{obsd} = 6.8 × 10⁶ s^{−1}) for the decay at 435 nm was the same as those for the rises of >C•OH– at 550 nm and –ROME^{•+} at 650 nm within experimental error (10%), and independent of [BP-(CH₂)₃-ROME] (≤ 6.0 × 10^{−3} M) in acetonitrile–water (4:1 *v/v*) with [H₂SO₄] = 0.5 M at 295 K. From the above results, the ionization of BP-(CH₂)₃-³ROME* is concluded to occur only in the presence of protons to produce >C•OH–(CH₂)₃-ROME^{•+} by intra-el.

The efficiencies (*φ*_{ion}) of the ionization for >C•OH–(CH₂)₃-ROME^{•+} are 0.3 and 1.0 for BP-(CH₂)₃-ROME in acetonitrile–water (4:1 *v/v*) with [H₂SO₄] = 0.005 and 0.5 M, respectively. These values of *φ*_{ion} show that protons promote the ionization efficiency for BP-(CH₂)₃-ROME as well as for intermolecular ROME–BP systems (Yamaji *et al* 1992).

Scheme 6.

We also investigated the proton effect on the rate constant (k_{obsd}) for intra-*p*-ion of BP-(CH₂)₃-ROME. The plots of k_{obsd} vs $[\text{H}_2\text{SO}_4]$ (≤ 1.0 M) have been obtained after laser pulsing of BP-(CH₂)₃-ROME (3.0×10^{-3} M) in acetonitrile–water (4:1 *v/v*). The k_{obsd} value increases linearly, proportional to $[\text{H}_2\text{SO}_4]$. Therefore, k_{obsd} is reexpressed with the use of (26). From the slope and the intercept of the line, we have $k_s = 1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $k_d = 1.8 \times 10^5 \text{ s}^{-1}$ for the intra-*p*-ion of BP-(CH₂)₃-ROME.

The intra-*p*-ion mechanism for BP-(CH₂)₃-ROME is proposed as shown in scheme 6, referring to those of the ROME–BP systems (Yamaji *et al* 1992) and intra-HT, where $^3(\text{BP}-(\text{CH}_2)_3-\text{ROME})^*$, $^3(>\dot{\text{C}}\text{OH}-(\text{CH}_2)_3-\text{ROME})^*$ and $^3(>\dot{\text{C}}\text{OH}-(\text{CH}_2)_3-\text{ROME}^+)$ denote the corresponding intramolecular triplet exciplex with a sandwich-like structure, the protonated intramolecular triplet exciplex and the intramolecular triplet radical pair produced by intra-el, respectively, k_0 , k_{ex} and k_0'' are the decay rate constants of BP-(CH₂)₃- $^3\text{ROME}^*$, $^3(\text{BP}-(\text{CH}_2)_3-\text{ROME})^*$ and $^3(>\dot{\text{C}}\text{OH}-(\text{CH}_2)_3-\text{ROME})^*$ to the ground BP-(CH₂)₃-ROME, respectively, k_{el} the rate constant for intra-el of $^3(>\dot{\text{C}}\text{OH}-(\text{CH}_2)_3-\text{ROME})^*$ to $^3(>\dot{\text{C}}\text{OH}-(\text{CH}_2)_3-\text{ROME}^+)$, and K_1 and K_2 the corresponding equilibrium constants for formation of the triplet exciplex and protonation of the triplet exciplex, respectively.

2.4c Conformation of triplet exciplexes: As mentioned above, it has been observed that intra-HT and intra-*p*-ion of BP-(CH₂)₃-ROH and BP-(CH₂)₃-ROME take place as well as the intermolecular ones of the ROH–BP and ROME–BP systems, respectively. For both intermolecular and intramolecular reactions, the mechanisms can be explained considering the triplet exciplex and the protonated triplet exciplex. When the chromophores are linked with $-(\text{CH}_2)_3-$, it is enabled to take a stacked configuration of chromophores, which has a weak charge-transfer interaction. Therefore, it can be concluded that the structures of the triplet exciplex and the protonated triplet exciplex for intra-HT and intra-*p*-ion are sandwich-like as illustrated in schemes 5 and 6, respectively.

2.5 The hydrogen-atom transfer reaction of triplet hydroxynaphthylammonium ion to benzophenone

The HT reaction of triplet naphthalene derivative with both the groups, $-\text{NH}_3^+$ and $-\text{OH}$, of the hydroxynaphthylammonium ion (HORNH_3^+) has been investigated in order to elucidate the reactivity of the substituent group for HT and its mechanism.

The transient absorption spectra have been observed after a laser pulse at 355 nm in the HORNH_3^+ ($8.0 \times 10^{-3} \text{ M}$)–BP ($1.2 \times 10^{-3} \text{ M}$) systems with $[\text{H}_2\text{SO}_4] = 0.015 \text{ M}$ and 0.5 M , respectively, in MeOH–water (9:1 v/v) at 290 K. While the 430-nm band for triplet HORNH_3^+ ($^3\text{HORNH}_3^{+\ast}$) decreases with isosbestic points at 490 and 610 nm, new transient absorption bands appear at 455, 545 and 800 nm with lapse of time. The 545-nm band is known to be $>\dot{\text{C}}\text{OH}$ with its molar absorption coefficient $\epsilon = 3220 \text{ M}^{-1} \text{ cm}^{-1}$ at 545 nm (Land 1968). The transient absorption bands at 455 and 800 nm are ascribed to the 5-hydroxy-1-naphthylamine cation radical ($\text{HORNH}_2^{\cdot+}$) since they are similar to the absorption spectrum of HORNH_2^+ obtained after γ -radiolysis of HORNH_2 in PVC film (unpublished data). The change from the absorption spectrum of triplet HORNH_3^+ , $^3(\text{HORNH}_3^+)^{\ast}$ to that of the hydroxynaphthylamine cation radical ($\text{HORNH}_2^{\cdot+}$) demonstrates that the $-\text{NH}_3^+$ group is more reactive for HT of the HORNH_3^+ –BP system than the $-\text{OH}$ group. The rate constant for HT increases with an increase of $[\text{BP}]$ showing a leveling-off at higher $[\text{BP}]$ while it decreases with increase of acid concentration. However, at higher acid concentrations, the rate constant shows a leveling off. Therefore, it is impossible to explain the above experimental results by the simple mechanism for the RNH_3^+ –BP system (Kohno *et al* 1991). The hybrid mechanism from those for the RNH_3^+ –BP (Kohno *et al* 1991) and ROH –BP (Kaneko *et al* 1993) systems has been proposed for the HT reaction of the HORNH_3^+ –BP system as shown in scheme 7. It has been concluded that the more protic hydrogen atom is the more reactive in HT.

3. Conclusion

After 355-nm laser pulsing in the naphthalene derivative (RNH_3^+ , ROH, ROME and HORNH_3^+)-BP systems, the ET from $^3\text{BP}^*$ occurs to naphthalene derivatives in the nanosecond time scale.

It has been shown that the HT and $p\text{-}eT$ reactions from triplet naphthalene derivatives ($^3\text{RNH}_3^{+*}$, $^3\text{ROH}^*$, $^3\text{ROME}^*$ and $^3\text{HORNH}_3^{+*}$) take place to BP via triplet exciplexes, intermolecularly and intramolecularly, on a microsecond time scale. It has been shown that the triplet exciplexes have a sandwich-like structure with weak CT character. There are proton effects on the above HT and $p\text{-}eT$ reactions originating from the protonated triplet exciplexes.

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