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Accounts

Triplet Energy Transfer and Triplet Exciplex Formation of Benzophenone[#]

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Photochemical and photophysical aspects of (1) triplet energy transfer (TET) from triplet benzophenone (BP) to naphthalene derivatives (NpD) and (2) formation and decay processes of triplet exciplexes between ^{3}NpD* and BP have been studied by 355-nm laser photolysis techniques in the liquid phase. As an initial event, TET occurs from ^{3}BP* to NpD competing with H-atom transfer (HT), electron transfer (ET), and induced quenching (IQ) on the nanosecond time scale. The TET rate constant increases with an increase of solvent polarity while that of HT decreases, indicating that the ^{3}(n, π^*) state of BP is slightly mixed with ^{1}(π, π^*) in polar media. After formation of ^{3}NpD* by TET from ^{3}BP*, chemical reactions via triplet exciplexes between ^{3}NpD* and BP having loose sandwich-like structures with weak charge transfer character take place in the microsecond time scale, depending on the substituent groups of NpD. (1) HT from triplet 2-naphthylammoniun ion and triplet naphthol to BP occurs efficiently to yield the 2-naphthylamine cation radical and naphthoxy radical plus the benzophenone ketyl radical, respectively. The more protic H-atom in NpD is the more reactive in HT. (2) The proton-induced ET from triplet methoxynaphthalene to BP takes place effectively via the protonated triplet exciplex to give the methoxynaphthalene cation and benzophenone ketyl radical. (3) Hydrogen bonding-induced ET from triplet *N*, *N*-dialkyl-1-naphthylamine to BP occurs to yield the *N*-dialkyl-1-naphthylamine cation radical and benzophenone anion radical in the presence of protic solvents.

A large number of studies on the photoreduction of triplet aromatic ketones by alkanes, alcohols, amines, etc. have been carried out experimentally and theoretically since such a photoreaction is preceded by elemental chemical reactions, H-atom and electron transfers.[1—44] The mechanism of the primary photoreduction of benzophenone (BP) has been extensively studied by means of product analysis and laser flash photolysis techniques.[10,45—72] The H-atom abstraction of triplet BP (^{3}BP*) from H-atom donors occurs to yield the BP ketyl radical (BPK). On the other hand, it has been shown that the photoreduction of ^{3}BP* with amines undergoes electron transfer, followed by proton transfer to give BPK.[2,11,17,33b,36—42]

In the past two decades, we have had considerable interest in photophysical and photochemical behavior of aromatic compounds in the presence of protons:[45] proton transfer reactions and proton-induced quenching,[46—49] a one-way proton-transfer reaction in the excited state of hydrogen-bonded complexes,[50] and examples of the absence of excited-state prototropic equilibrium.[51] These are photophysical and photochemical phenomena in the excited singlet state of aromatic compounds upon direct excitation.

In the course of research on the excited-state proton-transfer reactions with proton-induced quenching, in 1983, we found the H-atom transfer (HT) from triplet 2-naphthylammonium ion to the ground state of BP.[52] The HT reaction from triplet 1-naphthol to BP is shown to proceed via a triplet exciplex.[53] At the initial event, triplet naphthalene derivatives (NpD) are formed by the triplet energy transfer (TET) of ^{3}BP* on a nanosecond time scale, followed by the formation and decay processes of the triplet exciplexes on a microsecond time scale.[54,55]

Since the first report on the triplet sensitization of naphthalene by ^{3}BP* in a rigid matrix by Trenin and Ermolaev,[56] a large number of investigations on triplet energy transfer have been carried out experimentally and theoretically.[10,57—74] However, until recently, little attention has been paid to the interactions of triplet-sensitized compounds with the ground state of energy-donor molecules. We have been interested in photophysical and photochemical profiles between triplet aromatic compounds (especially for ^{3}NpD*) and BP.

It has been shown that new types of photochemical reactions such as HT,[52,53,75—77] proton-enhanced[76,77] and proton-reduced HT,[75] proton-induced electron transfer (ET),[76—80] and hydrogen-bonding-induced ET reaction[81] take place ef-

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ficiently via triplet exciplexes having loose sandwich-like structures with weak charge-transfer (CT) character.[53,75—81] Upon direct excitation, it is well-known that NpOH and naphthylammonium ion undergo proton transfer in the excited singlet state (S_1) while in the triplet state (T_1), HT occurs efficiently. This may be due to the difference in the electronic structures between S_1 and T_1 states. The former has an ionic structure and the latter has a biradical-like electronic structure. The proton effects on the triplet exciplexes have been revealed to be as remarkable as those on the S_1 state, where proton-induced quenching (chemical quenching) takes place.[45—49]

This account consists of two subjects. (1) TET from $^3BP^*$ to aromatic compounds (mainly NpD) and (2) photophysics and photochemistry of the triplet exciplexes between $^3NpD^*$ and BP. In the first part, TET of $^3BP^*$ is explained from the following viewpoints: solvent effects on TET from $^3BP^*$ to NpD competing with other processes of HT, ET, and induced quenching (IQ). The dynamic behavior of $^3BP^*$ for the cases of the small (or negative) triplet energy differences is also discussed. In the second part, the formation and decay (HT, ET, and IQ) processes of the triplet exciplexes having loose sandwich-like structures with CT character are explained. Especially, it is emphasized that protons significantly affect HT and ET reactions via triplet exciplexes.

[1] Triplet Energy Transfer of Benzophenone

The formation of $^3BP^*$ [$^3(n, \pi^*)$] produced by intersystem crossing of the excited singlet state of BP [$^1(\pi, \pi^*)$] produced upon 355-nm laser excitation is very fast with a time constant of ca. 10 ps[82,83] according to the El-Sayed rule.[84] The TET reaction from $^3BP^*$ (triplet energy, E_T = 289.1 kJ mol^{-1})[85] to NpD competes with other processes such as HT, ET, and IQ. After TET, $^3NpD^*$ reacts with the ground state of BP to form a triplet exciplex. In this part, the dynamic profiles of triplet exciplexes of $^3NpD^*$ with BP are discussed on the basis of kinetic data obtained by nanosecond laser flash photolysis at 355 nm.

1-1. Solvent Dependence of Triplet Energy Transfer Competing with H-Atom Transfer between Triplet Benzophenone and Naphthol.[53,77,86,87] Figure 1a shows the time-resolved absorption spectra obtained after 355 nm laser pulsing to the BP (6.7×10^{-3} mol dm^{-3})-1-naphthol (NpOH; 2.0×10^{-3} mol dm^{-3}) system in acetonitrile (ACN) at room temperature.[86,87] At a low concentration of 1-NpOH (1×10^{-2} mol dm^{-3}), very few complexes between NpOH and BP are produced in the ground state. The E_T value of 1-NpOH is known to be 244.8 kJ mol^{-1}. The $T_n \leftarrow T_1$ absorption peak of BP at 520 nm decreases with an isosbestic point at 463 nm while that of NpOH at 430 nm increases in intensity. From the transient spectra, it is concluded that TET from $^3BP^*$ to NpOH occurs efficiently in ACN. On the other hand, the reaction of $^3BP^*$ with NpOH in CCl_4 (dielectric constant, d = 2.23) is different from that in ACN (d = 37.5). Figure 1b shows the transient absorption spectra obtained after 355 nm laser pulsing to the BP (6.7×10^{-3} mol dm^{-3})-1-NpOH (2.0×10^{-3} mol dm^{-3}) system in CCl_4.[86] With a decrease of the $T_n \leftarrow T_1$ absorption of BP at 530 nm, both absorption peaks derived from the 1-naphthoxy radical (1-NpO•) at 395 nm and BPK at 545 nm appear. From these spectral changes, it is revealed that in CCl_4, HT from NpOH to $^3BP^*$ predominates over TET from $^3BP^*$ to NpOH. By using the molar absorption coefficients (ε) of ^{31}-NpOH*, BPK, and NpO•, the quantum yields (Φ_{TET} and Φ_{HT}) of TET and HT are determined. The intensity of the incident laser pulse can be determined by the absorption of $^3BP^*$. The quantum yield (Φ_{IQ}) of IQ is defined by Eq. 1,[53,76]

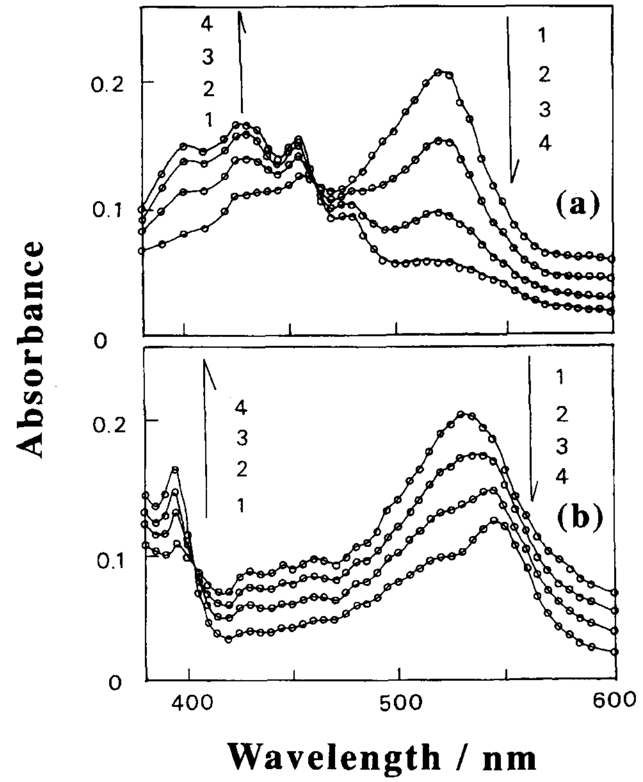
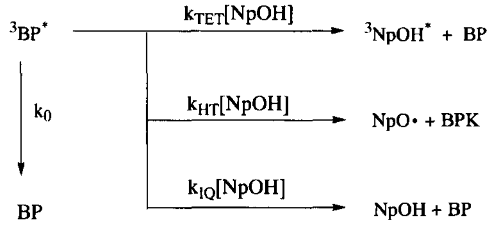


Fig. 1. (a) Transient absorption spectra at (1) 35, (2) 80, (3) 150, and (4) 250 ns after 355-nm laser pulsing in the NpOH (2.0×10^{-3} mol dm^{-3})-BP (6.7×10^{-3} mol dm^{-3}) system in ACN. (b) Transient absorption spectra at (1) 30, (2) 60, (3) 100, and (4) 200 ns after 355- nm laser pulsing in the NpOH (2.0×10^{-3} mol dm^{-3})-BP (6.7×10^{-3} mol dm^{-3}) system in CCl_4.

$$\Phi_{IQ} = 1 - \Phi_{TET} - \Phi_{HT} \qquad (1)$$

The decay processes of $^3BP^*$ in the presence of NpOH are expressed by Scheme 1.

Figure 2a shows the plots of the quantum yields for TET,



Scheme 1.

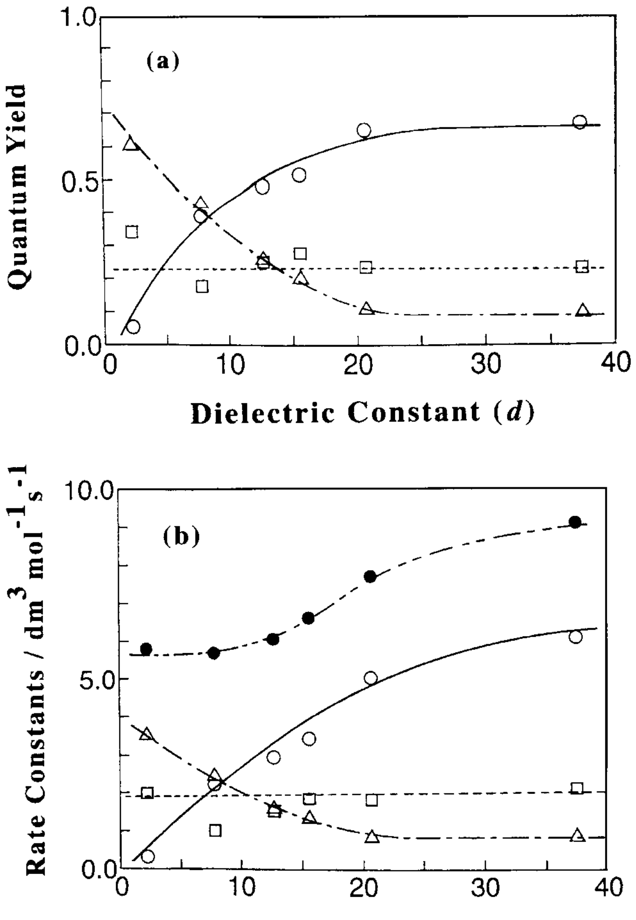


Fig. 2. (a) Plots of the quantum yields of TET (○), HT (△), and IQ (□) as a function of *d*. (b) Plots of the rate constants of the quenching of ^{3}BP* (●), TET (○), HT (△), and IQ (□) as a function of *d*.

HT, and IQ as a function of the *d* value of the solvent used.[86] The value of $\Phi_{\rm TET}$ increases with an increase of *d*, and becomes almost constant (ca. 0.65) in the region $d \geq 20$. On the contrary, the $\Phi_{\rm HT}$ value decreases with an increase of *d*, giving a constant value of ca. 0.1 in the region $d \geq 20$. The $\Phi_{\rm IQ}$ value seems to be ca. 0.25 independent of *d*.

The quenching rate constants ($k_{\rm q}$) of ^{3}BP* by NpOH are determined in various solvents by laser photolysis techniques. Plots of the observed first-order rate ($k_{\rm obsd}$) for the decay of ^{3}BP* as a function of [NpOH] give a straight line in all solvents used. Therefore, $k_{\rm obsd}$ is expressed by Eq. 2.

$$k_{\rm obsd} = k_0 + k_{\rm q}[\rm NpOH] \qquad (2)$$

From the slope and intercept of the line, the $k_{\rm q}$ and k_0 values are determined.

As shown in Scheme 1, the $k_{\rm q}$ value consists of the rate constants of the respective processes.

$$k_{\rm q} = k_{\rm TET} + k_{\rm HT} + k_{\rm IQ} \qquad (3)$$

where $k_{\rm TET}$, $k_{\rm HT}$, and $k_{\rm IQ}$ are the rate constants of TET, HT, and IQ, respectively. These values are calculated by the products of $k_{\rm q}$ and the quantum yield of each process when $k_{\rm q}[\rm NpOH] \gg k_0$ is established in the range $[\rm NpOH] \geq 10^{-3}$ mol dm^{-3}. The obtained values of $k_{\rm q}$, $k_{\rm TET}$, $k_{\rm HT}$, and $k_{\rm IQ}$ are plotted as a function of *d* in Fig. 2b.[86] With an increase of *d*, the $k_{\rm TET}$ value increases up to 6.0×10^9 dm^3 mol^{-1} s^{-1}. In contrast, the $k_{\rm HT}$ decreases from ca. 6.0×10^9 to 1.0×10^9 dm^3 mol^{-1} s^{-1} with an increase of *d*.

As described above, the quenching of ^{3}BP* by NpOH accompanying TET, HT, and IQ processes takes place in an encounter complex. The TET rate constant increases with an increase of the solvent polarity. According to the Dexter theory,[73] the electron exchange mechanism which requires overlap of the electronic orbitals between donor and acceptor molecules is plausible to rationalize the TET reaction for such a collisional situation. The theory predicts that the possibility of TET by the exchange mechanism is proportional to d^{-2}. However, our result is against the prediction. On the other hand, it has been considered that the rate of HT depends on the bond energy of the H-atom of the substrates. The present system employed only NpOH as a substrate. Thus, the quantum yield and rate constant for HT must be affected by the solvent polarity.

In order to interpret the solvent effects on TET and HT, the following possible explanations have been proposed: (1) The solvent dependence of TET in the present system should be interpreted in terms of not only the electron exchange mechanism (Dexter theory)[73] but also the dipole–dipole interaction mechanism (Förster theory).[89] In a polar solvent, the ^{3}(n, π*) state is destabilized in energy compared with that in a nonpolar solvent where the ^{1}(π, π*) state is stabilized in polar media. Therefore, the energy gap between the ^{3}(n, π*) and ^{1}(π, π*) states of BP in polar media becomes smaller than that in nonpolar media. The degree of perturbation between ^{3}(n, π*) and ^{1}(π, π*) states increases with an increase of the solvent polarity. In other words, the ^{1}(π, π*) character in the ^{3}(n, π*) state of BP in polar media increases through spin-orbit coupling in the more polar solvent, resulting in an increase of the more possibility for the TET process from ^{3}BP* to NpOH to occur by the dipole–dipole interaction mechanism.[89] Concurrently, the ^{3}(n, π*) state of BP mixed with the ^{1}(π, π*) state in polar media reduces the HT reactivity of ^{3}BP*. (2) The solvent polarity may affect the selectivity of the configurations of an encounter complex suitable for TET and HT. It is necessary that the carbonyl group of ^{3}BP* approaches the hydroxy group of NpOH for the HT reaction to occur in an encounter complex. In a polar solvent, solvent molecules would solvate around the hydroxy group of NpOH or the carbonyl group of ^{3}BP* to hinder the approach to each other, resulting in enhancement of the TET reaction.

After the TET from ^{3}BP* to NpOH, the triplet exciplex formation of ^{3}NpOH* with the ground BP results in the HT reaction via the triplet exciplex, as described later.

In general, the TET efficiency is shown to be less than unity.

1-2. Triplet Energy Transfer from Triplet Benzophenone to *N*,*N*-Dimethylnaphthyl-1-amine Competing with Induced-Quenching and Electron Transfer; Solvent

Effects.[81,90] Judging from the oxidation potential ($E_{ox} = 0.75$ V vs. SCE in ACN)[40,91,92] of *N*,*N*-dimethyl-1-naphthylamine (DMNA), we anticipate that ET from DMNA to $^3BP^*$ is possible, since *N*,*N*-diethyl-1-naphthylamine (DENA) with ($E_{ox} = 0.76$ V vs. SCE in ACN)[91] is known to be an electron donor to $^3BP^*$ in ACN.[40,91,92] On the other hand, TET from $^3BP^*$ to DMNA is also possible since the E_T value of BP ($E_T = 289.1$ kJ mol^{-1} in polar media)[85] is greater than that of DMNA (225.9 kJ mol^{-1}).

Figure 3a shows the transient absorption spectra obtained by 355-nm laser photolysis in the BP (6.7×10^{-3} mol dm^{-3})–DMNA (5.0×10^{-4} mol dm^{-3}) system in ACN at 295 K.[81,90] The transient absorption peak at 520 nm observed at 100 ns after laser pulsing is ascribed to the $T_n \leftarrow T_1$ absorption of BP in ACN.[75,76,79] With a lapse of time, the $T_n \leftarrow T_1$ absorption at 520 nm decreases in intensity with increases of absorbances at 550 and 370 nm with an accompanying isosbestic point at 535 nm. The transient absorption spectrum at 540 nm can be assigned to be the $T_n \leftarrow T_1$ absorption spectrum of DMNA (ε of $^3DMNA^*$ at 540 nm is determined to be 5600 mol dm^{-3} cm^{-1}). Therefore, the spectral changes in Fig. 3a show TET from $^3BP^*$ to DMNA to produce $^3DMNA^*$. Subsequently, $^3DMNA^*$ reacts with the ground state of BP to form a triplet exciplex, as discussed later.

The first-order rates (k_{obsd}) for the decay of $^3BP^*$ in ACN give a straight line against [DMNA]. Thus,

$$k_{obsd} = k_0 + k_q[\mathrm{DMNA}] \qquad (4)$$

From the slope and intercept of the line, the values of k_q and k_0 are 1.1×10^{10} dm^3 mol^{-1} s^{-1} and 3.7×10^5 s^{-1}, respectively. The efficiency (ϕ_{TET}) for TET from $^3BP^*$ to DMNA can be expressed by use of ε values of the $T_n \leftarrow T_1$ absorptions of BP and DMNA, and the net maximum absorbances (OD_{520} and OD_{550}) for $^3BP^*$ at 520 nm and $^3DMNA^*$ at 550 nm in Fig. 3a.

$$\phi_{TET} = OD_{550}\varepsilon_{520}OD_{520}^{-1}\varepsilon_{550}^{-1} \qquad (5)$$

The ϕ_{TET} value is determined to be 0.58 in ACN. The residual efficiency of 0.42 is due to the DMNA-induced quenching of $^3BP^*$ ($\phi_{IQ} = 0.42$). The value of k_{TET} is determined to be 6.4×10^9 dm^3 mol^{-1} s^{-1} by use of Eq. 6, which is close to that in a diffusion-controlled process.

$$k_{TET} = \phi_{TET}k_q \qquad (6)$$

When the solvent is changed from ACN to ACN–H_2O (4 : 1 v/v) for the BP–DMNA system, a different reaction from TET is observed. Figure 3b shows the transient absorption spectra obtained by 355-nm laser photolysis in the BP (6.7×10^{-3} mol dm^{-3})–DMNA (5.0×10^{-4} mol dm^{-3}) system in ACN–H_2O (4 : 1 v/v) at 295 K.[81,90] The $T_n \leftarrow T_1$ absorption band of BP at 520 nm decays with isosbestic points at 550 and 445 nm, while absorption peaks at 370, 420, and 630 nm appear with a lapse of time. The final absorption spectrum can be reproduced with the use of those of DMNA cation ($DMNA^{+\bullet}$) and BP anion ($BP^{-\bullet}$) radicals. The absorption spectra of $DMNA^{+\bullet}$ ($\varepsilon = 2300$ dm^3 mol^{-1} cm^{-1} at 650 nm) and $BP^{-\bullet}$ ($\varepsilon = 5500$ dm^3 mol^{-1} cm^{-1} at 630 nm) are shown in Fig. 3c.

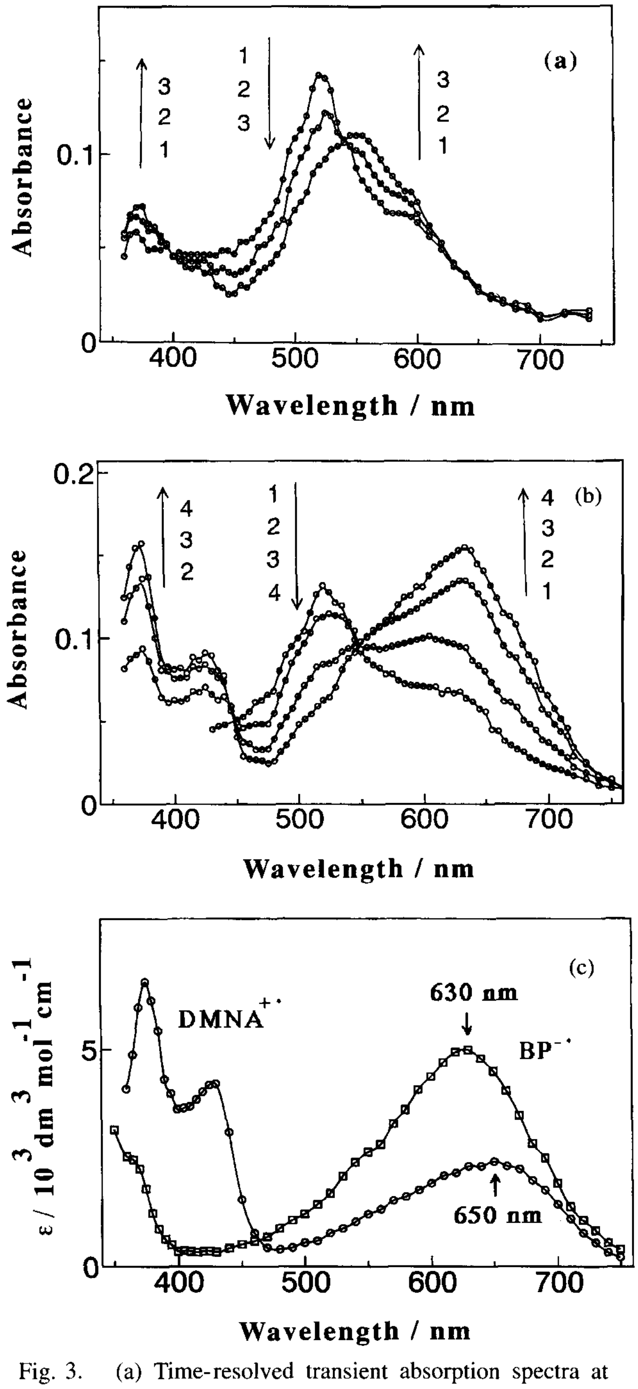


Fig. 3. (a) Time-resolved transient absorption spectra at (1) 100, (2) 220, and (3) 540 ns observed after 355-nm laser photolysis in the BP (6.7×10^{-3} mol dm^{-3})–DMNA (5.0×10^{-4} mol dm^{-3}) system in ACN. (b) Time-resolved transient absorption spectra at (1) 80, (2) 150, (3) 300, and (4) 600 ns observed after 355-nm laser photolysis in the BP (6.7×10^{-3} mol dm^{-3})–DMNA (5.0×10^{-4} mol dm^{-3}) system in ACN–H_2O (4 : 1 v/v). (c) The absorption spectra of $DMAN^{+\bullet}$ (○) and $BP^{-\bullet}$ (□) in ACN–H_2O (4 : 1 v/v).

The spectral changes in Fig. 3b, therefore, show that the ET reaction from DMNA to $^3BP^*$ takes place in ACN–H_2O (4 : 1 v/v) without TET. The values of k_0 and k_q are obtained to be 4.8×10^5 s^{-1} and 9.1×10^9 dm^3 mol^{-1} s^{-1}, respectively. By kinetic analyses, the efficiency for ET (ϕ_{ET}) is determined to be unity.

$$k_{\mathrm{ET}} = \phi_{\mathrm{ET}} k_{\mathrm{q}} \qquad (7)$$

From Eq. 7, the k_{ET} value is obtained to be 9.1×10^9 dm^3 mol^{-1} s^{-1} in ACN–H_2O (4 : 1 v/v), which is close to the diffusion-controlled rate.

The ET reaction from DMNA to ^{3}BP* occurs very efficiently in the presence of water in ACN, while TET without ET takes place in ACN. These reactions may proceed via a collision complex, probably a triplet exciplex having weak CT character. Hydrogen bonding may take place at the carbonyl group in the exciplex, resulting in an increase of the electron affinity of BP. Consequently, ET would occur to yield BP$^{-\bullet}$ and DMNA$^{+\bullet}$. In addition, the solvation energies for BP$^{-\bullet}$ and DMNA$^{+\bullet}$ increase in the presence of water, which would enhance the ET reaction.

1-3. Electron Transfer vs. Triplet Energy Transfer between Triplet Benzophenone and Naphthyloxide Anion.[93] In the BP–naphthyloxide (NpO$^-$) system, competitive reactions are anticipated upon photoexcitation of BP at 355 nm: (1) ET to produce NpO· and BP$^{-\bullet}$ as an electron donor–acceptor system and (2) TET from ^{3}BP* to NpO$^-$ to form ^{3}NpO^{-*}. The transient absorption spectrum observed after depletion of ^{3}BP* is due to those of NpO$^\bullet$ and BP$^{-\bullet}$ upon 355-nm laser excitation in the BP–NpO$^-$ system in ACN–H_2O (4 : 1 v/v) with KOH. The efficiency of radical formation of BP$^{-\bullet}$ is unity. Thus, the quenching of ^{3}BP* by NpO$^-$ is governed by the ET process.

The triplet energy difference between NpO$^-$ and BP is ca. 52 kJ mol^{-1}. On the other hand, the free energy change (ΔG_{ET}) for ET is calculated by using the reduction potential (E_{red}) of BP and the oxidation potential (E_{ox}) of NpO$^-$.

$$\Delta G_{\mathrm{ET}} = 96.5(E_{\mathrm{ox}} - E_{\mathrm{red}}) - E_{\mathrm{T}}(\mathrm{BP}) \quad \text{in kJ mol}^{-1} \qquad (8)$$

The ΔG_{ET} value is ca. -65.3 kJ mol^{-1} which allows an exothermic ET process to proceed.

TET is interpreted in terms of the electron exchange mechanism by Dexter,[73] as stated above. That is, ET and back ET occur simultaneously or stepwise in a collision complex in the liquid phase. Considering the Dexter mechanism, the reaction for the priority of ET over TET in the ^{3}BP*–NpO$^-$ system can be expressed as follows. The first step of the electronic interpretation in the collision complex of ^{3}BP* and NpO$^-$ would be ET according to the electron exchange mechanism to form the triplet radical pair between BP$^{-\bullet}$ and NpO·. However, the triplet radical pair would be separated very quickly and stabilized by solvation in aqueous ACN before back ET, since the attractive force originating from the Coulombic interaction in the neutral-anion radical pair (NpO· and BP$^{-\bullet}$) is very weak compared with that in an anion–cation radical pair. As a result, NpO· and BP$^{-\bullet}$ are produced efficiently from the triplet radical pair without back ET.

1-4. Photochemical Reactions of Triplet Benzophenone with Aromatic Compounds without Triplet Energy Transfer.[95–98] The interaction of ^{3}BP* with aromatic compounds whose triplet energies are larger than that of BP is our another interest. The deactivation processes of ^{3}BP* by toluene derivatives (TD) in benzene are found to be HT and IQ.[96] The quantum yields for the BPK formation (Φ_{BPK}) are shown as a function of [TD] in Fig. 4. The Φ_{BPK} value is related with the HT efficiency (α_{HT}) and rate constants.

$$\Phi_{\mathrm{BPK}} = k_{\mathrm{q}}[\mathrm{TD}]\alpha_{\mathrm{HT}}\Phi_{\mathrm{ISC}}^{\mathrm{BP}}(k_0 + k_{\mathrm{q}}[\mathrm{TD}])^{-1} \qquad (9)$$

where $\Phi_{\mathrm{ISC}}^{\mathrm{BP}}$ is the triplet yield of BP (1.0),[85] k_{q} (3.1×10^5 mol dm^{-3} s^{-1}) and k_0 (3.3×10^5 s^{-1}). The α_{HT} values are determined to be 0.77 ± 0.04 by best-fitting Eq. 9 to the experimental Φ_{BPK} values. The rate constants (k_{HT} and k_{IQ}) for HT and IQ are given by

$$k_{\mathrm{HT}} = \alpha_{\mathrm{HT}} k_{\mathrm{q}} = 2.4\times10^5 \text{ mol dm}^{-3}\text{ s}^{-1} \qquad (10)$$

$$k_{\mathrm{IQ}} = k_{\mathrm{q}} - k_{\mathrm{HT}} = 7.1\times10^4 \text{ mol dm}^{-3}\text{ s}^{-1} \qquad (11)$$

For the BP-anisole derivative (AD) system in ACN–H_2O (4 : 1 v/v), the decay processes of ^{3}BP* are ET and IQ. These processes would proceed via a triplet exciplex with CT character, $^3(\mathrm{BP}^{\delta-}\cdots\mathrm{RH}^{\delta+})^*_{\mathrm{cage}}$ as shown in Scheme 2.[96]

Hydroxyanilinium ion (HAI) has two H-atom donor sites where the HT reactions of ^{3}BP* may take place. Laser photolysis studies on the BP–HAI system at 355 nm revealed that the HT reaction occurred not from the hydroxy group but from the ammonium group.[98] The selective HT reaction of ^{3}BP* from HAI is rationalized by considering the CT character of the collision complex leading to the triplet exciplex. It is found that the more protic the H-atom is, the more reactive for HT by ^{3}BP*.

Halogenated toluene derivatives (HTD) have been employed in laser photolysis studies on the IQ process competitive with HT of ^{3}BP* through the heavy atom effects on the rate constants (k_{HT} and k_{IQ}).[95] It is found that the k_{IQ} value increases proportionally with increasing the squared summation of the spin-orbit coupling constant (ξ) of atoms involved in HTD. The k_{HT} values are independent of ξ. The heavy atom effects on k_{IQ} indicate that the IQ process is intersystem

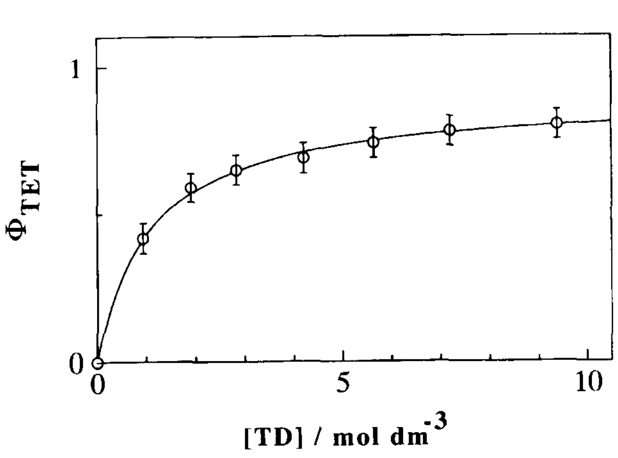
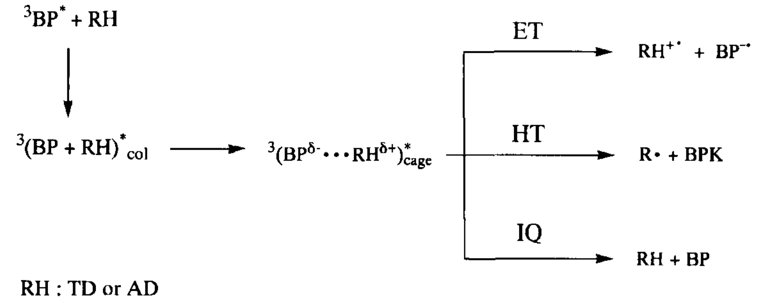


Fig. 4. Plots of the quantum yield of the BPK formation against [TD] for the BP–TD system in benzene. The solid curve was calculated by Eq. 9.



Scheme 2.

crossing induced by the spin-orbit interaction between $^{3}BP^{*}$ and HTD.

When the exothermic difference ($\Delta E_T = E_T^D - E_T^A$) in triplet energies between the energy-donor and acceptor is more than ca. 16.7 kJ mol^{-1}, formation of sensitized species in solution is produced by collisions.

Formation of a triplet-equilibrium for the BP–dibenzothiophene (DBT) system with $\Delta E_T = -1.3$ kJ mol^{-1} has been studied in ACN by 355-nm laser flash photolysis.[97] The absolute rate constants for the forward TET from $^{3}DBT^{*}$ ($k_1 = 3.1 \times 10^9$ dm^3 mol s^{-1}) and the back TET from $^{3}DBT^{*}$ to BP ($k_{-1} = 2.0 \times 10^9$ dm^3 mol s^{-1}) are determined. The triplet-equilibrium constant ($K_1 = 1.7$) between the $^{3}BP^{*}$–DBT and BP–$^{3}DBT^{*}$ systems is obtained at 295 K. The ratio of the rate constants (k_1/k_{-1}) is in agreement with the K_1 value. It is revealed that the triplet-equilibrium formation in the BP–DBT system is promoted by the entropy change ($\Delta S = 8.4$ J K^{-1} mol^{-1}) rather than by the enthalpy change ($\Delta H = 1.3$ kJ mol^{-1}).

[2] Formation and Decay Processes of the Triplet Exciplexes between Triplet Naphthalene Derivatives and Benzophenone

As an initial event, TET from $^{3}BP^{*}$ to NpD competing with other processes takes place in a nanosecond time scale. Subsequently, $^{3}NpD^{*}$ reacts with the ground-state of BP to produce the triplet exciplexes having loose sandwich-like structures with weak CT character. The electronic structures of the triplet exciplexes have weak CT character from NpD to BP site on the following experimental bases: (1) The transient absorption spectra of $^{3}NpD^{*}$ produced by triplet sensitization of BP are very similar to those of free $^{3}NpD^{*}$; and (2) the reaction profiles of triplet exciplexes for HT and ET are affected by protons and protic solvents through the carbonyl group of BP site. The decay processes including HT, ET, and IQ via the triplet exciplexes occur on a microsecond time scale.

2-1. H-Atom Transfer from Triplet 2-Naphthylammonium Ion to Benzophenone via a Triplet Exciplex; Proton-Reduced H-Atom Transfer.[75] The laser flash photolysis study at 355 nm in the 2-naphthylammoniun ion (NAI) and BP system has been carried out in methanol (MeOH)–H_2O (9 : 1 v/v) at 290 K. At first, $^{3}BP^{*}$ is quenched by NAI in a diffusion process to produce $^{3}NAI^{*}$ competing with HT from MeOH and NAI. Subsequently, on a microsecond time scale, transient absorption spectrum of the 2-naphthylamine cation radical ($NpA^{+\bullet}$) and BPK is obtained after depletion of $^{3}NAI^{*}$, as shown in Fig. 5. The radical formation demonstrates HT from $^{3}NAI^{*}$ to BP. The decay rate (k_{obsd}) of $^{3}NAI^{*}$ increases with an increase of [BP]. At higher BP concentrations, a leveling off is seen in Fig. 6, showing that the decay processes of $^{3}NAI^{*}$ with BP proceed via an intermediate (triplet exciplex). The k_{obsd} value decreases drastically with an increase of acid concentration. The mechanism of the HT reaction can be accounted for by the intra-triplet-exciplex HT reaction. At higher acid concentrations, the triplet exciplex, $^{3}(NAI \cdots BP)^{*}$ is decomposed into NAI, BP and H^{+} by protonation to the carbonyl site of the triplet exciplex, resulting in suppression of the rate for HT. The schematic processes of the present HT reaction are depicted in Scheme 3, where k_1 ($= k_1/k_{-1}$) $= 110$

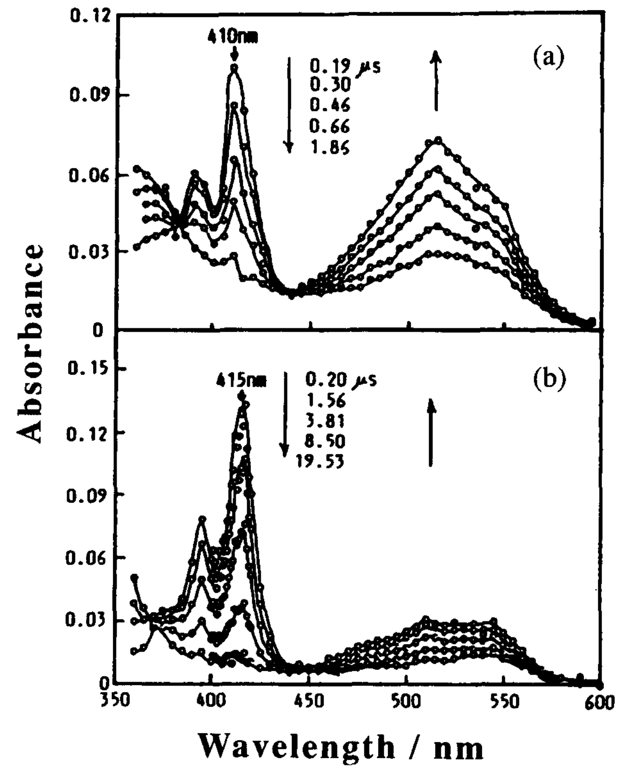


Fig. 5. Time-resolved transient absorption spectra for the BP (1.12×10^{-2} mol dm^{-3})–NAI (3.0×10^{-3} mol dm^{-3}) system with [H_2SO_4] = (a) 0.015 and (b) 0.5 mol dm^{-3} in MeOH–H_2O (9 : 1 v/v) obtained by laser flash photolysis at 355 nm on the microsecond time region.

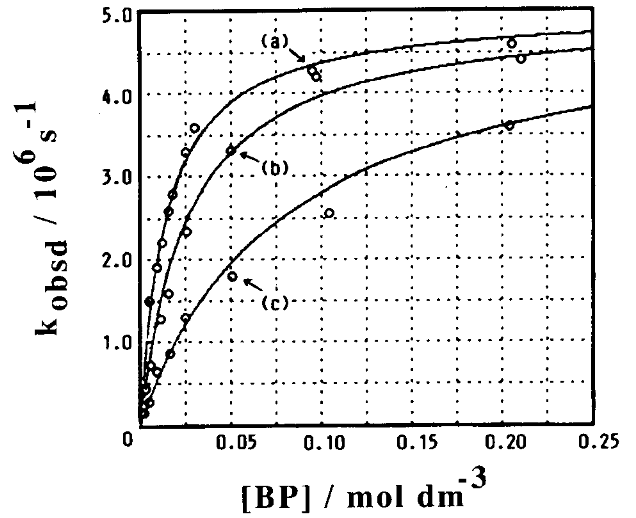
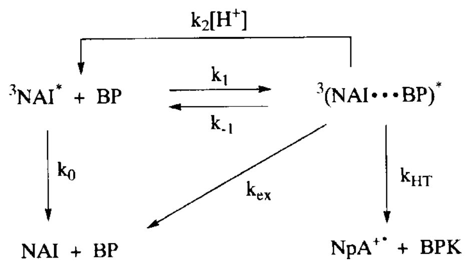


Fig. 6. Plots of the decay rate (k_{obsd}) of $^3NAI^*$ as a function of [BP] in the presence of [H_2SO_4] = (a) 0.015, (b) 0.05, and (c) 0.2 mol dm^{-3}.



Scheme 3.

mol dm^{-3}, $k_0 = 1\times10^4$ s^{-1}, k' ($= k_{HT}+k_{ex}$) $= 5\times10^6$ s^{-1}, $k_2'/k_1 = 40$ mol dm^{-3} ($k_2' = k_2[H^+]$), and $k_{HT}{\sim}k'$ are determined by kinetic analyses. The decay rate (k_{obsd}) of $^3NAI^*$ in the $HClO_4$ system is the same as that of the H_2SO_4 system, indicating that H_2SO_4 acted as a monobasic acid in a $MeOH$–H_2O (9 : 1 v/v) mixture. No effect of the counter anion $SO_4{}^{2-}$ is confirmed.[99] At a low acid concentration (0.015 mol dm^{-3}), the efficiency for HT is evaluated to be 0.95.

2-2. H-Atom Transfer of Triplet Naphthol to Benzophenone via a Triplet Exciplex; Proton-Enhanced H-Atom Transfer.[53,76] The laser flash photolysis at 355 nm in the 1-NpOH and BP system with and without H_2SO_4 has been carried out in ACN–H_2O (4 : 1 v/v) and methanol at 290 K.[76] For the BP (6.7×10^{-3} dm^3 mol^{-1})–1-NpOH (3.0×10^{-3} dm^3 mol^{-1}) system containing [H_2SO_4] = 0 and 0.5 mol dm^{-3} in ACN–H_2O (4 : 1 v/v), $^3BP^*$ produced upon 355-nm laser excitation is quenched by NpOH in diffusion processes with the rate constants (8.4×10^9 and 9.3×10^9 dm^3 mol^{-1} s^{-1}, respectively) for TET, HT, and IQ processes. $^3NpOH^*$ (E_T = 244.8 kJ mol^{-1}) is produced in the nanosecond region by TET from $^3BP^*$ to NpOH with efficiencies of 0.73 and 0.39 for [H_2SO_4] = 0 and 0.5 mol dm^{-3}, respectively. Subsequently, on the microsecond region, the HT reaction from $^3NpOH^*$ to BP occurs to yield 1-NpO• and BPK with efficiencies of 0.73 and 0.85 for [H_2SO_4] = 0 and 0.5 mol dm^{-3}, respectively. Figures 7a and 7b show the transient absorption spectra obtained at 0.2—7.0 μs after laser pulsing at 355 nm in the BP (6.7×10^{-3} dm^3 mol^{-1})–1-NpOH (3.0×10^{-3} dm^3 mol^{-1}) system containing [H_2SO_4] = 0 and 0.5 mol dm^{-3}, respectively, in ACN–H_2O (4 : 1 v/v) at 290 K. In both Figs. 7a and 7b, the 430 nm band for $^3NpOH^*$ decreases with an increase in intensities of the 545 nm and the 400 nm bands for BPK and 1-NpO•, respectively, with an accompanying isosbestic point at 490 nm. In contrast to the case of the NAI–BP system,[75] the decay rate (k_{obsd}) of $^3NpOH^*$ linearly increases with an increase of [H_2SO_4]. As for an increase of [BP], the k_{obsd} value increases nonlinearly, which shows a negative curve in both systems with and without H_2SO_4. Especially for the methanol solution without H_2SO_4, a leveling off is clearly observed at high [BP] ($\geqq$ 0.5 mol dm^{-3}). In the absence of H_2SO_4, the HT mechanism from $^3NpOH^*$ to BP can be expressed by the intracomplex HT reaction of the triplet exciplex, $^3(NpOH\cdots BP)^*$ with an equilibrium constant (K_1 = 6.7 dm^3 mol^{-1} in ACN–H_2O (4 : 1 v/v) and 4.2 dm^3 mol^{-1} in MeOH). The mechanism of the proton-enhanced HT reaction is explained as follows. The protonated triplet exciplex, $^3(NpOH\cdots PBP)^*$ formed in a prototropic equilibrium with the triplet exciplex having CT character undergoes the intraexciplex ET reaction to give the triplet radical pair of the NpOH cation radical ($NpOH^{+\bullet}$) and BPK which rapidly decomposes into NpO•, BPK, and H^+. The mechanism of the HT reactions for HT from $^3NpOH^*$ to BP and for proton-enhanced HT is shown in Scheme 4. The electron affinity of BP in the exciplex increases by pro-

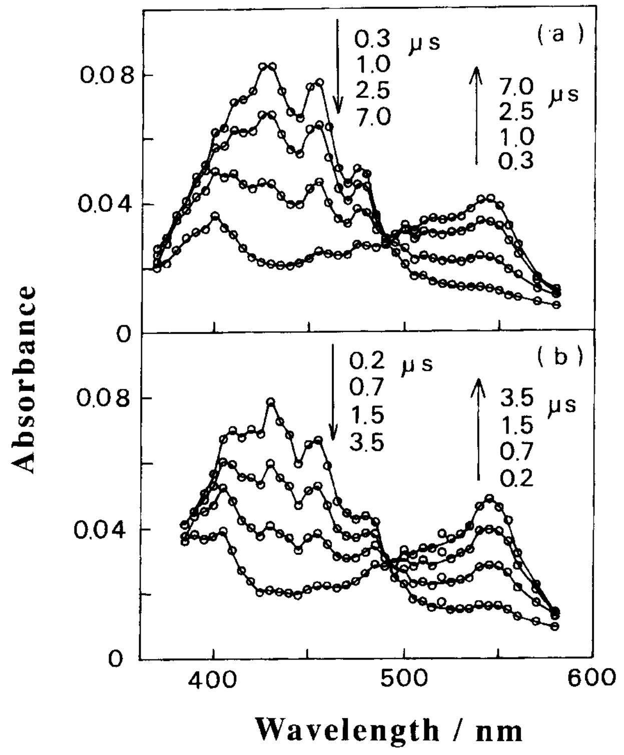
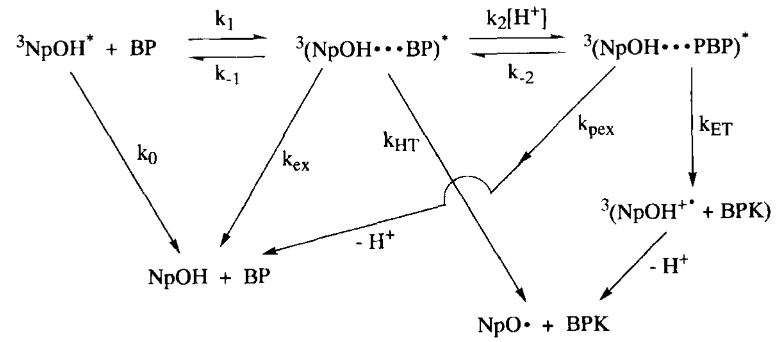


Fig. 7. The temporal absorption spectra on the microsecond time scale observed after 355-nm laser pulsing in the BP (6.7×10^{-3} mol dm^{-3})–NpOH (3.0×10^{-3} mol dm^{-3}) system with [H_2SO_4] = (a) 0 and (b) 0.5 mol dm^{-3} in ACN–H_2O (4 : 1 v/v).



Scheme 4.

tonation to the carbonyl site, resulting in the intraexciplex ET reaction.

2-3. H-Atom Transfer from Triplet 5-Hydroxy-1-naphthylammonium Ion to Benzophenone via a Triplet Exciplex.[100] Laser flash photolysis studies on HT from triplet (5-hydroxy-1-naphthyl)ammonium ion (HNAI) to BP in MeOH–H_2O (9 : 1 v/v) at 295 K have been carried out in order to elucidate which H-atom of the substituent groups of OH and NH_3^+ is more reactive for HT.[100] It is found that HT to BP from $^3HNAI^*$ sensitized by $^3BP^*$ takes place to yield 5-hydroxy-1-naphthylamine cation radical ($HNpA^{+\bullet}$) and BPK with efficiencies of 0.92 and 0.48 in the presence of $[H_2SO_4] = 0.015$ and 0.5 mol dm^{-3}, respectively. The decay rate (k_{obsd}) of $^3HNAI^*$ decreases with increasing acid concentration, approaching a constant value at higher acid. This behavior is interpreted by the hybrid HT mechanism; we conclude that the more protic H-atom in NpD is the more reactive for HT via the triplet exciplex.

2-4. Proton-Induced Electron Transfer from Triplet Methoxynaphthalene to Benzophenone via a Triplet Exciplex.[77—80] A laser flash photolysis study on the methoxynaphthalene (MeONp)–BP–H_2SO_4 system has been made in ACN–H_2O (4 : 1 v/v).[79] It has been found that the proton-assisted photoionization of $^3MeONp^*$ produced by triplet sensitization of BP at 355 nm occurs efficiently to produce the corresponding cation radical ($MeONp^{+\bullet}$) and BPK. The TET reaction from $^3BP^*$ to MeONp takes place as the primary event to produce $^3MeONp^*$. The 1 : 1 triplet exciplex having a weak CT structure is readily formed between $^3MeONp^*$ and BP with an equilibrium constant ($K_1 = 10.1$ mol dm^{-3} for 1-MeONp and 4.0 mol dm^{-3} for 2-MeONp at 290 K). In the presence of protons, the triplet protonated complex is formed by protonation to the triplet exciplex.

It is noteworthy that the pK_a value in the ground state of BP is very negative (-5.7)[101] showing that the protonation to BP is extremely difficult. However, the triplet exciplex with CT character is easily protonated at the carbonyl site in the triplet exciplex. The protonation to the exciplex seems easier than that to $^3BP^*$ ($pK_a^* = 0.18$).[102] The intracomplex ET reaction of the protonated triplet exciplex takes place efficiently to produce the triplet radical pair of $MeONp^{+\bullet}$ and BPK, which dissociates instantaneously into free $MeONp^{+\bullet}$ and BPK. Figure 8 shows the time-resolved transient absorption spectra on a microsecond time scale in the 1-MeONp (3.0×10^{-3} mol dm^{-3})–BP (6.7×10^{-3} mol dm^{-3})–H_2SO_4 (1 mol dm^{-3}) system in ACN–H_2O (4 : 1 v/v) obtained after 355-nm laser pulsing. The $T_n \leftarrow T_1$ band of MeONp at 435 nm ($\varepsilon = 10500$ dm^3 mol^{-1} cm^{-1}) decreases with an increase of the bands at 600 nm for $MeONp^{+\bullet}$ ($\varepsilon = 3400$ dm^3 mol^{-1} cm^{-1}) and 545 nm for BPK ($\varepsilon = 3220$ dm^3 mol^{-1} cm^{-1}) with a lapse of time.

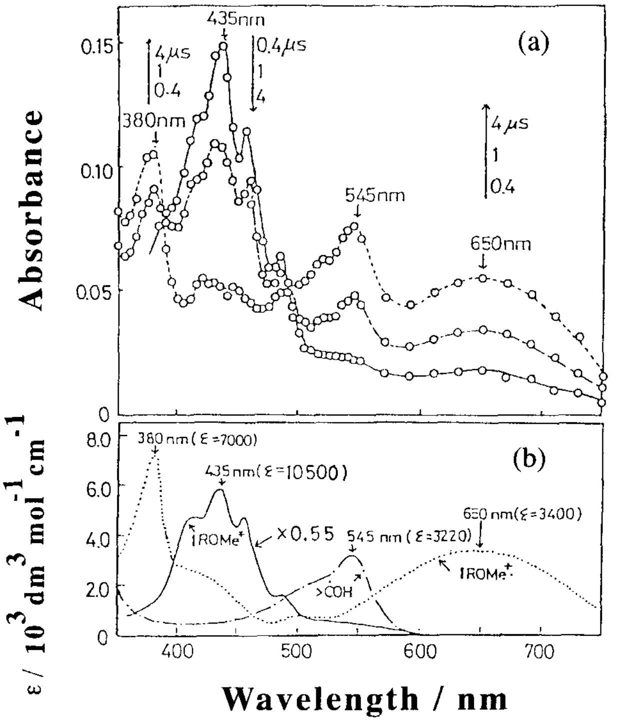
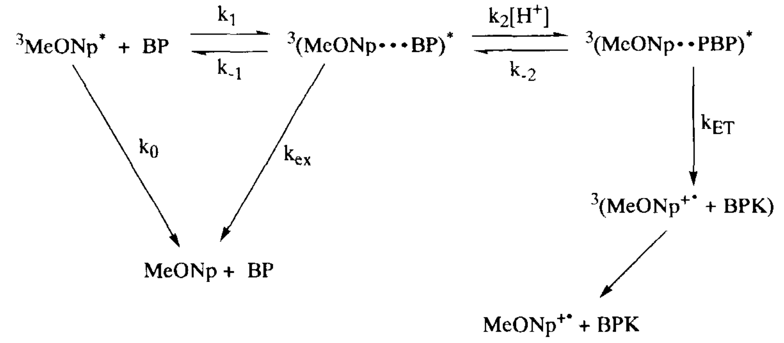


Fig. 8. (a) Time-resolved transient absorption spectra on the microsecond time scale observed after 355-nm laser pulsing in the BP (6.7×10^{-3} mol dm^{-3})-1-MeONp (3.0×10^{-3} mol dm^{-3})–H_2SO_4 (1.0 mol dm^{-3}) system in ACN–H_2O (4 : 1 v/v). (b) Reference absorption spectra of ^{3}1-MeONP*, BPK, and 1-MeONp$^{+\bullet}$.

The mechanism for the proton-induced ET reaction in the $^3MeONp^*$ and BP system with protons can be accounted for by Scheme 5. The electron affinity of the protonated BP (PBP) in the exciplex, $^3(MeONp\cdots PBP)^*$ becomes large compared to that of BP resulting in the intraexciplex ET. In the absence of protons, $^3MeONp^*$ decays via the triplet exciplex, $^3(MeONp\cdots BP)^*$ to the ground states of MeONp and BP.

When BP is substituted for acetophenone (AP), $MeONp^{+\bullet}$



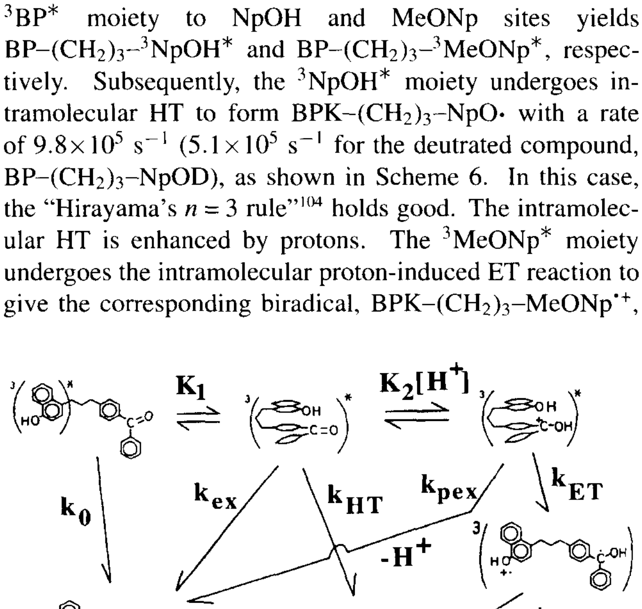
Scheme 5.

is produced only in the presence of protons after the depletion of ^{3}MeONp* formed by TET from ^{3}AP*.[78] This ET reaction can be interpreted by the triplet-exciplex mechanism.

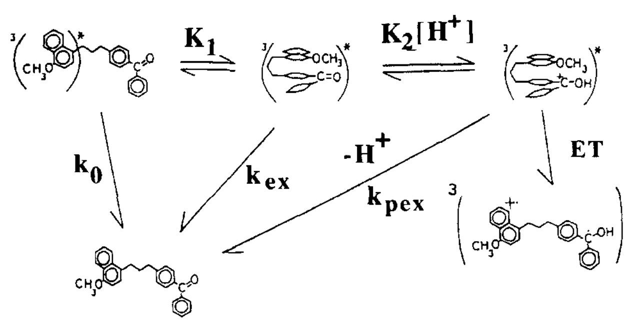
The decay process of the triplet exciplexes formed between ^{3}NpD* and BP is found to be promoted by their CT character since the rate constant of the nonradiative deactivation process increases with decreasing of the oxidation potentials of NpD.[103] The intersystem crossing from the triplet exciplex to the ground states of NpD and BP is enhanced by the CT character of the triplet exciplex.

2-5. Intramolecular H-Atom Transfer of 4-[3-(4-Hydroxy-1-naphthyl)propyl]benzophenone and Intramolecular Electron Transfer of 4- [3-(4-Methoxy-1-naphthyl)-propyl]benzophenone via Triplet Exciplexes.[77] Laser flash photolysis studies at 355 nm have been carried out on the intramolecular HT reaction of 4-[3-(4-hydroxy-1-naphthyl)propyl]benzophenone (BP–$(CH_2)_3$–NpOH) and the intramolecular proton-induced ET reaction of 4-[3-(4-methoxy-1-naphthyl)propyl]benzophenone (BP–$(CH_2)_3$–MeONp) in ACN–H_2O (4 : 1 v/v) at 295 K.[77]

As the primary events, intramolecular TET from ^{3}BP* moiety to NpOH and MeONp sites yields BP–$(CH_2)_3$–^{3}NpOH* and BP–$(CH_2)_3$–^{3}MeONp*, respectively. Subsequently, the ^{3}NpOH* moiety undergoes intramolecular HT to form BPK–$(CH_2)_3$–NpO• with a rate of 9.8×10^5 s^{-1} (5.1×10^5 s^{-1} for the deutrated compound, BP–$(CH_2)_3$–NpOD), as shown in Scheme 6. In this case, the "Hirayama's $n = 3$ rule"[104] holds good. The intramolecular HT is enhanced by protons. The ^{3}MeONp* moiety undergoes the intramolecular proton-induced ET reaction to give the corresponding biradical, BPK–$(CH_2)_3$–MeONp$^{\bullet+}$, as shown in Scheme 7. On the basis of the mechanisms for intramolecular HT and proton-induced ET reactions between the two chromophores linked with an oligopropyl chain, the structures of the triplet exciplexes are suggested to be sandwich-like with weak CT character.



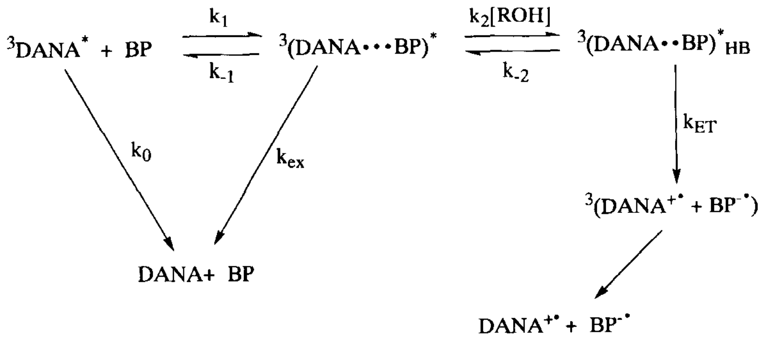
Scheme 6.



Scheme 7.

2-6. Hydrogen-Bonding Induced Electron Transfer from Triplet *N*,*N*-Dialkyl-1-naphthylamines to Benzophenone via Triplet Exciplexes.[81,90] Laser flash photolysis studies at 355 nm on the photoreactions in the BP and *N*,*N*-dialkyl-1-naphthylamine (DANA, representative of *N*,*N*-dimethyl-1-naphthylamine (DMNA) and *N*,*N*-diethyl-1-naphthylamine (DENA)) system have been carried out with and without H_2O and MeOH in ACN at 295 K.[81,90]

On the nanosecond time scale, TET from ^{3}BP* to DANA occurs with these efficiencies ($\phi_{TET} = 0.74$ for DMNA and 0.61 for DENA), regardless of the presence of H_2O and MeOH. After the formation of ^{3}DANA*, the triplet exciplex, ^{3}(DANA···BP)* with weak CT character is produced with an equilibrium constant, K_1 (10 dm^3 mol^{-1} for DMNA and 9 dm^3 mol^{-1} for DENA) between ^{3}DANA* and BP. In the presence of H_2O and MeOH, it is found that the intraexciplex ET takes place to give DANA$^{+\bullet}$ and BP$^{-\bullet}$ via the hydrogen-bonded (HB) triplet exciplex, ^{3}(DANA···BP)$^*_{HB}$. Scheme 8 shows the mechanism for the formation of DANA$^{+\bullet}$ and BP$^{-\bullet}$. The kinetic parameters for the triplet exciplex formation and HB triplet exciplexes are listed in Table 1. In the absence of H_2O or MeOH, the triplet exciplex decays to the ground states of DANA and BP with the rate constants, k_0 and k_{ex}. The K_2 values (0.55 dm^3 mol^{-1} for DMNA and 0.50 dm^3 mol^{-1} for DENA) by H_2O are slightly larger than those (0.45 dm^3 mol^{-1} for DMNA and 0.40 dm^3 mol^{-1} for DENA) by MeOH. The difference in the K_2 value may orig-



Scheme 8.

Table 1. Kinetic Parameters for the BP–DANA System in ACN and ACN–H_2O Systems[a)]

	$k_0/10^4\ s^{-1}$	$k_{ex}/10^6\ s^{-1}$	$K_1/dm^3\ mol^{-1}$	$K_2/dm^3\ mol^{-1}$ b)	$k_{ET}/10^7\ s^{-1}$ b)
DMNA	3.0	2.5	10	0.55 (0.45)	2.5 (2.4)
DENA	7.5	3.4	9	0.50 (0.40)	1.4 (1.3)

a) Data from Ref. 81. b) The values in parentheses are for the ACN–MeOH solution. See text for details.

inate from the HB ability related to the pK_a values of MeOH (16)[105] and H_2O (14).[105] The efficiency, ϕ_{ET} for ET induced by HB in the triplet exciplex is evaluated to be unity. The rate constants, k_{ET} for the intraexciplex ET induced by HB are determined to be 2.5×10^7 s^{-1} for DMNA and 1.4×10^7 s^{-1} for DENA, which are independent of HB species. It is revealed that the driving force for intraexciplex ET is a negatively enlarged reduction potential of BP in the triplet exciplex due to HB to the carbonyl group of BP in the triplet exciplex.

2-7. Thermochemical Aspects on H-Atom Transfer from Triplet Naphthol to Benzophenone and Proton-Induced Electron Transfer from Triplet Methoxynaphthalene to Benzophenone.[80] Temperature effects (275—320 K) on HT and proton-induced ET via triplet exciplexes in the 1-NpOH–BP and 1-MeONp–BP systems in ACN–H_2O (4 : 1 v/v) were studied by 355 nm laser flash photolysis.[80] At first, TET from ^{3}BP* ($E_T = 289.1$ kJ mol^{-1})[85] to NpOH ($E_T = 244.8$ kJ mol^{-1})[37] takes place on the nanosecond time scale. Subsequently, the HT reaction from ^{3}NpOH* to BP occurs via the triplet exciplex. The HT rate in the NpOH–BP system increases with an increase of temperature. The thermodynamic parameters for HT via the triplet exciplex are obtained; the enthalpy change, $\Delta H_1 = -8.4$ kJ mol^{-1}, the entropy change, $\Delta S_1 = -20.0$ J K^{-1} mol^{-1} for the formation of the triplet exciplex, the frequency factor, $A_{ex} = 7.7\times10^6$ s^{-1} and activation energy, $\Delta E_{ex} = 14.7$ kJ mol^{-1}, for the intraexciplex HT. The negatively small values of ΔH_1 and ΔS_1 suggest that the triplet exciplex has a loose sandwich-like structure. The corresponding parameters for the MeONp–BP system are $\Delta H_1 = -9.2$ kJ mol^{-1} and $\Delta S_1 = -23.3$ J K^{-1} mol^{-1} for the formation of the triplet exciplex. Kinetic parameters obtained in the NpOH–BP and MeONp–BP are summarized in Table 2. In addition, the enthalpy change ΔH_{ET} for the intraexciplex ET to give MeONp$^{+\bullet}$ and BPK is estimated to be -87.4 kJ mol^{-1}, which is highly exothermic. Therefore, once ^{3}MeONp* ($E_T = 249.8$ kJ mol^{-1}) is produced in the presence of BP and protons, ET proceeds according to the proton-induced ET mechanism.[77—80] The frequency factor A_{ET} for ET in the protonated triplet exciplex of NpOH is greater than that of MeONp by three orders of magnitude. The difference in the A_{ET} values may be caused mainly by the following reasons. (1) Formation of HB between H_2O and NpOH in the protonated triplet exciplex enhances the ET process in the former case,[106,107] and (2) the distance between NpOH and protonated BPK in the protonated triplet exciplex of NpOH with a sandwich-like structure is shorter than that between MeONp and the protonated BPK in the protonated triplet exciplex of MeONp, since the methyl group is more bulky compared with the H-atom. The energy diagram for HT via the triplet exciplex of NpOH, ^{3}(NpOH···BP)* system without protons is shown in Fig. 9, where the ΔE_{ex} value denotes the activation barrier for the HT reaction.

Similar energy diagrams for proton-induced HT via the protonated triplet exciplex of NpOH with proton and for

Table 2. Thermochemical and Kinetic Parameters Obtained for the NpOH–BP and MeONp–BP Systems[a)]

	ΔH_1	ΔS_1	ΔE_{ex}	A_{ex}	$\Delta H_2+\Delta E_{ET}$	A_{ET}
	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	10^9 s^{-1}	kJ mol^{-1} b)	s^{-1} b)
NpOH	−8.4	−20.0	14.6	7.7	20.1	8.6×10^{10}
MeONp	−9.2	−23.3	15.1	2.9	20.5	1.1×10^7

a) Data from Ref. 80. See text for details. b) In the presence of H_2SO_4.

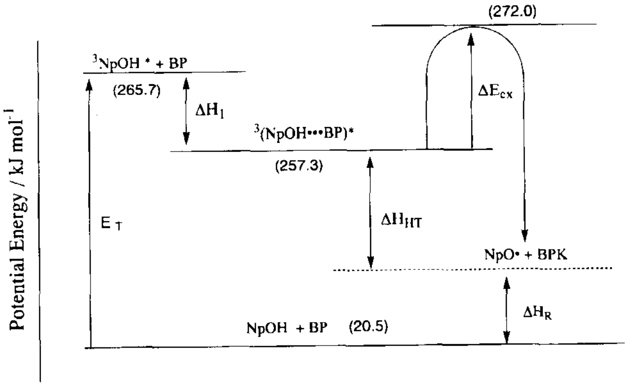


Fig. 9. Energy diagram for HT via the triplet exciplex in the BP–NpOH system without protons.

proton-induced ET via the protonated triplet exciplex of MeONp with proton are obtained.

It is concluded that the negatively small values of ΔH_l and ΔS_l are due to loose sandwich-like structures of triplet exciplexes.

[3] Concluding Remarks

From laser flash photolysis studies at 355 nm on TET and the triplet exciplex formation of BP, the following concluding remarks can be drawn;

1. The TET reaction from ^{3}BP* to NpOH is competitive with HT and IQ. The rate constant of TET increases with an increase of *d*, while that of HT decreases with an increase of *d*, indicating that the ^{3}(n, π*) state of BP is slightly mixed with the ^{1}(π, π*) state in polar media. Therefore, the TET reaction of BP proceeds not only due to the electron exchange mechanism (Dexter theory)[73] but also due to the dipole–dipole interaction mechanism (Förster theory).[89]
2. The TET efficiency from ^{3}BP* to NpD is less than unity competing with HT, ET, and IQ. These processes originate from a triplet exciplex between ^{3}BP* and NpD on a nanosecond time scale. Solvent effects on the processes are appreciable.
3. It is found that the more protic H-atom in aromatic compounds is, the more reactive for HT of ^{3}BP*. Thus, we say that the HT reaction occurs via the triplet exciplex rather than via the H-atom abstraction in these systems.
4. After the TET from ^{3}BP* to NpD, intracomplex reactions in the triplet exciplexes between ^{3}NpD* and BP having loose sandwich-like structures with weak CT character take place on a microsecond time scale.
5. The HT reactions from ^{3}NAI* and ^{3}NpOH* to BP occur efficiently to give NpA$^{+•}$ and NpO• plus BPK, respectively. Proton effects on HT are remarkable. The former is reduced since the protonated triplet exciplex is unstable due to Coulombic repulsion, resulting in the dissociation into ^{3}NAI*, BP, and H$^+$. The latter is enhanced by protons. The intraexciplex ET reaction in the protonated triplet exciplex ^{3}(NpOH···PBP)* occurs to yield NpOH$^{+•}$ and BPK, where the former dissociates very quickly into NpO• and H$^+$ (proton-enhanced HT). The electron affinity of BP in the triplet exciplex increases remarkably by protonation.
6. The HT reaction is easy to occur for ^{3}NpD* containing protic H-atom(s).
7. Proton-induced ET reaction from ^{3}MeONp* to BP takes place effectively via the protonated triplet exciplex to give MeONp$^{+•}$ and BPK.
8. HB-induced ET reaction from ^{3}DANA* to BP occurs to give DANA$^{+•}$ and BP$^{-•}$. The electron affinity of BP in the triplet exciplex slightly increases by HB of protic solvents (H_2O and MeOH).

The reaction mechanisms for triplet exciplexes with CT character would be applicable to the photochemical reactions in the triplet state.

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Abbreviation

ACN	acetonitrile
AD	anisole derivative(s)
AP	acetophenone
BP	benzophenone
BPK	benzophenone ketyl radical
BP$^{-•}$	benzophenone anion radical
CT	charge transfer
d	dielectric constant
DANA	*N*,*N*-dialkyl-1-naphthylamine
DANA$^{+•}$	*N*,*N*-dialkyl-1-naphthylamine cation radical
DBT	dibenzothiophene
DENA	*N*,*N*-diethyl-1-naphthylamine
DMNA	*N*,*N*-dimethyl-1-naphthylamine
DMNA$^{+•}$	*N*,*N*-dimethyl-1-naphthylamine cation radical
ET	electron transfer
HAI	hydroxyammonium ion
HB	hydrogen bonding
HNAI	5-hydroxy-1-naphthylammonium ion
HNpA$^{+•}$	5-hydroxy-1-naphthylamine cation radical
HT	hydrogen atom transfer
HTD	halogenated toluene derivative(s)
IQ	induced quenching
MeOH	methanol
MeONp	methoxynaphthalene
MeONp$^{+•}$	methoxynaphthalene cation radical
NAI	2-naphthylammonium ion
NpA$^{+•}$	2-naphthylamine cation radical
NpD	naphthalene derivative(s)
NpOH	naphthol
NpOH$^{+•}$	naphthol cation radical
NpO•	naphthoxy radical

NpO^-	naphthyloxide anion
PBP	protonated benzophenone
TD	toluene derivative(s)
TET	triplet energy transfer
ε	molar absorption coefficient

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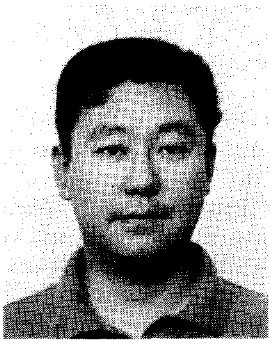

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