Laser Flash Photolysis Studies on Intramolecular Hydrogen Atom Transfer of [(Hydroxynaphthyl)propyl]benzophenone and Intramolecular Proton-Induced Electron Transfer of [(Methoxynaphthyl)propyl]benzophenone via Triplet Exciplexes

Tetsuhiro Sekiguchi, Minoru Yamaji, Hitoshi Tatemitsu,¹ Yoshiteru Sakata,¹ and Haruo Shizuka[•]

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

Received: December 29, 1992; In Final Form: March 31, 1993

Laser photolysis studies at 355 nm have been carried out on the intramolecular hydrogen atom transfer (intra-HT) reaction of [(hydroxynaphthyl)propyl]benzophenone, BP-(CH₂)₃-ROH, and the proton-induced intramolecular ionization (intra-p-ion) reaction of [(methoxynaphthyl)propyl]benzophenone, BP-(CH₂)₃-ROMe, in acetonitrile-water (4:1 v/v) at 295 K. After 355-nm laser pulsing to BP-(CH₂)₃-ROH and BP-(CH₂)₃-ROMe, the intramolecular triplet energy transfer (intra-ET) reactions from the triplet moiety (³BP^{*}) to the naphthol (ROH) and methoxynaphthalene (ROMe) moieties occur to yield $BP-(CH_2)_3-3ROH^*$ and BP- $(CH_2)_3$ -3ROMe* on a nanosecond time scale. The former triplet molecule (BP-(CH_2)_3-3ROH*) undergoes intramolecular hydrogen atom transfer (intra-HT) with an efficiency (ϕ_{HT}) of unity to yield a biradical molecule with benzophenone ketyl radical (>COH-) and naphthoxy radical (RO[•]) moieties (>COH-(CH₂)₃-RO[•]). The rate constant $(k_{\rm HT})$ for intra-HT was determined to be 9.8 \times 10⁵ s⁻¹ and independent of [BP-(CH₂)₃-ROH]. The deuterium isotope effect on intra-HT was examined by using BP-(CH₂)₃-ROD. The rate constant $(k_{\rm DT})$ for intra-DT was determined to be 5.1 × 10⁵ s⁻¹. In the presence of protons, the rate constant of intra-HT is enhanced proportional to the acid concentration though the value of ϕ_{HT} (=1.0) is independent of the acid concentration. The triplet molecule $(BP-(CH_2)_3-^3ROMe^*)$ undergoes ionization only in the presence of protons (intra-p-ion) to yield a biradical molecule with >COH- and methoxynaphthalene cation radical (-ROMe*+) moieties (>COH-(CH₂)₃-ROMe⁺⁺) with efficiencies (ϕ_{el}) of 0.3 for [H₂SO₄] = 0.005 M and 1.0 for [H₂SO₄] = 0.5 M in acetonitrile-water (4:1 v/v) at 295 K. The rate constant for intra-p-ion increases with an increase of the acid concentration. The mechanisms for intra-HT and intra-p-ion were interpreted by considering the intramolecular triplet exciplexes, $^{3}(>CO-(CH_{2})_{3}-ROH)^{*}$ and $^{3}(>CO-(CH_{2})_{3}-ROMe)^{*}$, and the intramolecular protonated triplet exciplexes, 3(>+COH-(CH₂)₃-ROH)* and 3(>+COH-(CH₂)₃-ROMe)*, respectively. On the basis of the mechanism for intra-HT and intra-p-ion of the two chromophores linked with a propyrene chain, the structures of the triplet exciplex and protonated triplet exciplex are suggested to be sandwichlike with weak charge-transfer character.

Introduction

Triplet carbonyl compounds produced upon direct photoexcitation are well-known to occur by hydrogen atom transfer or electron transfer followed by proton transfer from a variety of substrates, such as hydrocarbons, alcohols, and amines. A large number of studies on hydrogen atom transfer reactions have been reported.²⁻¹⁴ However, little attention has been paid to hydrogen atom transfer from triplet aromatic compounds produced by triplet carbonyl compounds to carbonyl ones until we reported on triplet naphthalene derivatives.¹⁵⁻¹⁸

In previous papers, we reported by laser flash photolysis that the hydrogen atom transfer (HT) reactions occur from triplet naphthylammonium ion $({}^{3}RNH_{3}^{+*})$ or triplet naphthol $({}^{3}ROH^{*})$ to benzophenone (BP or >CO) to produce naphthylamine cation radical $(RNH_2^{\bullet+})$ or naphthoxy radical (RO^{\bullet}) plus benzophenone ketyl radical (>COH) via the triplet exciplex, 3(RNH3+...>CO)* 17 or ³(ROH····>CO)*.¹⁸ In the presence of protons, the rate constant for HT of ³RNH₃^{+*} is significantly reduced due to the Coulombic repulsion in the protonated triplet exciplex, 3(RNH3+...>+-COH)^{*,17} On the other hand, the rate constant and the efficiency for HT of ³ROH^{*} are both enhanced due to formation of the protonated triplet exciplex, ³(ROH···>+COH)*. That is, the intraexciplex electron transfer (intra-el) in ³(ROH···>+COH)* promotes the production of the triplet radical pair, ³(ROH^{•+} + >COH), which rapidly dissociates into $RO^{\bullet} + H^{+} + >COH$ without back electron transfer, though ${}^{3}(ROH^{+} + >\dot{C}OH)$ was not observed experimentally.18

³(ROMe···>+COH)*
$$\xrightarrow{\text{intra-el}}$$
 ³(ROMe*+ +>+COH) (1)

$${}^{3}(\text{ROH}^{*+} + > \dot{\text{COH}}) \rightarrow \text{RO}^{*} + \text{H}^{+} + > \dot{\text{COH}}$$
(2)

The formation of the triplet radical pair is supported by showing the proton-induced ionization (p-ion) of methoxynaphthalenes¹⁹ whose triplets have an isoelectric structure to those of ³ROH^{*}. In the absence of protons, the triplet methoxynaphthalene (³ROMe^{*}) produced by triplet energy transfer from triplet benzophenone (³BP^{*}) forms the triplet exciplex ³(ROMe···>CO)^{*}, which causes no reaction. However, in the presence of protons, the methoxynaphthalene cation radical (ROMe···) and >COH were produced. The p-ion was explained considering intra-el in the protonated triplet exciplex, ³(ROMe····)^{*}.

$$^{3}(\text{ROMe} \rightarrow ^{+}\text{COH})^{*} \xrightarrow{\text{intra-el}} ^{3}(\text{ROMe}^{*+} + > \dot{\text{COH}})$$
 (3)

$${}^{3}(\text{ROMe}^{*+} + > \dot{\text{COH}}) \rightarrow \text{ROMe}^{*+} + > \dot{\text{COH}}$$
(4)

Comparing eqs 1 and 2 with eqs 3 and 4, respectively, the formation of the triplet radical pair is demonstrated, and the triplet exciplex and the protonated triplet exciplex play important roles in the promotion of the HT and ionization reactions of triplet naphthalene derivatives. The structures of $3(ROH - >CO)^*$ and $3-(ROM - >CO)^*$ are considered to have a sandwichlike structure that is locally excited because the triplet-triplet absorption spectra of ${}^{3}ROH^{*}$ and ${}^{3}ROMe^{*}$ are similar to those of ${}^{3}(ROH \cdot ... > CO)^{*}$ and ${}^{3}(ROMe \cdot ... > CO)^{*}$, respectively. However, the information on structures of triplet exciplexes is limited though the conformations of triplet exciplexes for the HT and ionization reactions are of great interest.

One of the most useful methods for the studies on chromophore interactions is to link the chromophores with a methylene chain $((CH_2)_n)$ to restrict the possible conformation. According to "the Hirayama's n = 3 rule",²⁰ it is known that two chromophores linked by $(CH_2)_3$ must be positioned face to face for them to interact.²¹ Thus, the problem of the structures of $3(ROH - CO)^*$ and $3(ROM - CO)^*$ for HT and ionization will be answered by using the linked molecules.

In the present paper, we have investigated by laser flash photolyses the intramolecular HT of [(hydroxynaphthyl)propyl]benzophenone, BP-(CH₂)₃-ROH, and the intramolecular protoninduced electron transfer of [(methoxynaphthyl)propyl]benzophenone, BP-(CH₂)₃-ROMe, and the proton effects on both reactions. The structures of the triplet exciplexes for HT and ionization are discussed.

Experimental Section

Apparatus. Laser flash photolysis was carried out at 295 K by using third harmonics (355 nm) of a Nd³⁺-YAG laser from J.K.Lasers (HY 500); the pulse duration and energy were 8 ns and 70 mJ/pulse, respectively. The detection system of transient absorption has been reported elsewhere.¹⁷

The UV-vis, NMR, IR, and mass spectra were recorded on a Jasco Ubest-50, a Bruker-AM360 (360 MHz), a Hitachi 270-30, and a Denshi Kagaku EMD-005, respectively. Liquid chromatography was performed on a Nihon Bunsekikogyo LC-20.

Materials. Synthesis of Chalcone (2). To a stirred solution of 1^{22} (362 mg, 1.35 mmol) and 1-formyl-4-methoxy-naphthalene (262 mg, 1.41 mmol) in 12 mL of ethanol was added an aqueous solution (4 mL) of sodium hydroxide (0.57 g, 14.3 mmol). Stirring was continued at room temperature for 18 h. Precipitates were collected, washed with water, and dried. Recrystallization from benzene-hexane gave 453 mg (77%) of 2 as yellow needles, mp 153.0–153.5 °C; IR (neat) 1650 cm⁻¹ (C=O); ¹H NMR (360 MHz, CDCl₃) δ 4.03 (s, 3, OCH₃), 4.08 (A₂B₂, 4, ethylene acetal), 6.84 (d, J = 8.3 Hz, 1, ArH ortho to OMe), 7.32 (m, 3, phenyl), 7.5–7.6 (m, 5, Ar H and methin), 7.68 (d, J = 8.3 Hz, 2, phenyl), 8.21 (d, J = 8.3 Hz, 1, Ar H), 8.31 (d, J = 8.3 Hz, 1, Ar H), 8.436 (M⁺).

4-(3-(4-Methoxynaphthyl)-1-oxopropyl)benzophenone Ethylene Acetal (3). Hydrogenation of the unsaturated ketone 2 (3.69 g, 8.46 mmol) was carried out in dioxane (70 mL) over 5% Pd–C (0.9 g) for 18 h at room temperature. The filtrate was concentrated to give 3.62 g (98%) of crude 3 as a colorless oil: IR (neat) 1686 cm⁻¹ (C==O); ¹H NMR (360 MHz, CDCl₃) δ 3.38 (A₂B₂, 4, ethylene), 3.96 (s, 3, OCH₃), 4.04 (A₂B₂, 4, ethylene acetal), 6.71 (d, J = 7.5 Hz, 1, Ar H ortho to OMe), 7.29 (m, 4, Ar H), 7.47 (m, 4, Ar H), 7.59 (d, J = 8.3 Hz, 2, Ar H), 7.89 (d, J = 8.3 Hz, 2, Ar H), 7.94 (d, J = 7.9 Hz, 1, Ar H), 8.30 (d, J = 7.9 Hz, 1, Ar H); MS 438 (M⁺).

4-(3-(4-Methoxynaphthyl)propyl)benzophenone Ethylene Acetal (4). A mixture of 3 (2.42 g, 5.5 mmol), potassium hydroxide (1.2 g, 21 mmol), and hydrazine hydrate (20 mL) in diethylene glycol (45 mL) was refluxed for 1 h. After hydrazine and water were distilled off, the temperature of the reaction mixture was raised to 220 °C and it was refluxed at that temperature for 4 h. After cooling, water was added to the mixture and the reactant was extracted with ether. The extracts were washed with water and dried over MgSO₄. Removal of the solvent gave 1.91 g (82%) of crude 4 as a colorless oil: ¹H NMR (360 MHz, CDCl₃) δ 2.00 (q, 2, CH₂CH₂CH₂), 2.69 (t, J = 7.5 Hz, 2, Ar CH₂), 2.98 (t, J = 7.5 Hz, 2, Ar CH₂), 4.04 (s, 3, OMe), 4.05 (A₂B₂, 4, ethylene acetal), 6.65 (d, J = 7.5 Hz, 1, Ar H ortho to OMe), 7.1–7.5 (m, 12, Ar H), 7.86 (m, 1, Ar H), 8.19 (m, 1, Ar H); MS 424 (M⁺).

4-(3-(4-Hydroxynaphthyl)propyl)benzophenone (BP-(CH2)3-ROH, 5). To a solution of 4 (0.763 g, 1.80 mmol) in THF (15 mL) was added an aqueous solution (3 mL) of 1 N HCl and the mixture was stirred at 40 °C for 14 h. After reaction was over, water was added to the mixture and it was extracted with ether. The extracts were washed with water and dried (MgSO₄). Removal of the solvent gave 0.62 g (94%) of crude 5. Purification by liquid chromatography, followed by column chromatography on silica gel with hexane-AcOEt (9:1), yielded pure 5 as colorless solid, mp 35-36 °C: IR (neat) 1642, 3392 cm⁻¹; ¹H NMR (360 MHz, CDCl₃) δ 2.04 (q, J = 7.5 Hz, 2, CH₂CH₂CH₂), 2.75 (t, J = 7.5 Hz, 2, Ar CH₂), 2.99 (t, J = 7.5 Hz, 2, Ar CH₂), 6.72 (br s, 1, OH), 6.75 (d, J = 7.5 Hz, 1, Ar H ortho to OH), 7.06(d, J = 7.5 Hz, 1, Ar H meta to OH), 7.2–7.8 (m, 11, Ar H), 7.87 (d, J = 7.9 Hz, 1, peri Ar H adjacent to CH₂), 8.27 (d, J= 7.9 Hz, 1, peri Ar H adjacent to OH); MS 366 (M^+). Anal. Calcd for C₂₆H₂₂O₂: C, 85.22; H, 6.05. Found: C, 85.02; H, 5.94

4-(3-(4-Methoxynaphthyl)propyl)benzophenone (BP-(CH₂)₃-ROMe, 6). A stirred mixture of 5 (0.62 g, 1.69 mmol), potassium carbonate (0.5 g), and dimethyl sulfate (0.3 mL, 3.2 mmol) in acetone (20 mL) was refluxed for 24 h. Water was added to the reaction mixture and it was extracted with ether. After the usual workup, the crude product was purified by column chromatography on silica gel with benzene to give 0.50 g (78%) of 6 as colorless oil. Further purification was carried out by liquid chromatography. 6: IR (neat) 1656 cm⁻¹; ¹H NMR (360 MHz, CDCl₃) δ 2.07 (q, J = 7.5 Hz, 2, CH₂CH₂CH₂), 2.76 (t, J = 7.5 Hz, 2, Ar CH₂), 3.01 (t, J = 7.5 Hz, 2, Ar CH₂), 3.93 (s, 3, OMe), 6.69 (d, J = 7.9 Hz, 1, Ar H ortho to OMe), 7.1–7.8 (m, 12, Ar H), 7.87 (d, J = 8.3 Hz, 1, peri Ar H adjacent to CH₂), 8.30 (d, J = 8.3 Hz, 1, peri Ar H adjacent to OMe); MS 366 (M⁺).

Deuterated BP-(CH₂)₃-ROH (BP-(CH₂)₃-ROD). After BP-(CH₂)₃-ROH was solved in NaOD solution, D_2SO_4 was added into the solution. Perticipate was washed with D_2O and dried in vacuo (Chart I).

Acetonitrile (Spectrosol, Wako), H_2SO_4 (97%, Wako) and D_2O (Uvasol, Merck) were used as supplied. Deionized water was distilled. H_2SO_4 was used as the proton source, since the counterion (SO_4^{2-}) of H_2SO_4 does not quench triplet molecules.²³ A mixture of acetonitrile–water (4:1 v/v) was used as solvent in the present study.

Sample Preparations. The concentrations of BP-(CH₂)₃-ROH, BP-(CH₂)₃-ROD, and BP-(CH₂)₃-ROMe were typically 3.0×10^{-3} M throughout the present study. All samples were degassed by freeze-pump-thaw cycles on a high-vacuum line in a quartz cell with 10-mm path length. The transient spectral data were obtained by using fresh samples to avoid excessive exposure to laser pulses.

Results and Discussion

Absorption Spectra in the Ground State. The absorption spectra of BP-(CH₂)₃-ROH and BP-(CH₂)₃-ROMe in acetonitrilewater (4:1 v/v) are almost identical with a superposition of those of 1-naphthol-BP and 1-methoxynaphthalene-BP systems under equimolar conditions at 295 K as shown in parts a and b of Figure 1, respectively. In the presence of protons ([H₂SO₄] \leq 1.0 M), absorption spectra of both BP-(CH₂)₃-ROH and BP-(CH₂)₃-ROH and BP-(CH₂)₃-ROMe exhibited no differences from those in the absence of protons. Therefore, we concluded that neither interaction between the moieties of BP- and -ROH (or BP- and -ROMe) nor protonation to BP-(CH₂)₃-ROH (or BP-(CH₂)₃-ROMe) occurs in the ground state.

Laser Photolysis of $BP-(CH_2)_3$ -ROH. It has been reported that, in the case of $BP-(CH_2)_3$ -naphthalene, the intramolecular

CHART I







4

Figure 1. (a) Absorption spectra of BP- $(CH_2)_3$ -ROH (—) and the mixture of 1-ROH and BP (1:1 mol/mol) (- -) in acetonitrile-water (4:1 v/v) at 295 K. (b) Absorption spectra of BP- $(CH_2)_3$ -ROMe (—) and the mixture of 1-ROMe and BP (1:1 mol/mol) (- -) in acetonitrile-water (4:1 v/v) at 295 K.

triplet energy transfer (intra-ET) from the triplet BP moiety $(-^{3}BP^{*})$ to the naphthalene moiety completed within 100 ps after photoexcitation.²⁴ For the case of BP-(CH₂)₃-ROH, upon laser excitation at 355 nm, the intra-ET reaction from $^{3}BP^{*}$ -to naphthol moiety (ROH) is expected to occur to form the triplet naphthol moiety ($^{3}ROH^{*}$). Figure 2 shows the transient absorption spectra observed after a 355-nm laser pulse to BP-(CH₂)₃-ROH ($_{3.0} \times 10^{-3}$ M) in acetonitrile-water (4:1 v/v) at 295 K. The transient absorption spectrum taken at 25 ns after a pulse has a 430-nm band, which resembles the triplet-triplet (T-T) absorption of 1-naphthol.^{16,18} Therefore, in the present system of BP-(CH₂)₃-ROH, we can conclude that the intra-ET from $^{3}BP^{*}$ to ROH occurs within laser pulse duration, resulting in BP-(CH₂)₃-

$$^{3}BP^{*}-(CH_{2})_{3}-ROH \xrightarrow{intra-ET} BP-(CH_{2})_{3}-^{3}ROH^{*}$$
 (5)

After the intra-ET reaction of $BP-(CH_2)_3-ROH$, with a lapse of time, the 430-nm band of $BP-(CH_2)_3-ROH^*$ decreases in intensity with an isosbestic points at 410 and 505 nm, accompanying an increase in intensity at 550 and 400 nm corresponding to the benzophenone ketyl radical moiety (>COH-) and the naphthoxy radical moiety (RO*), respectively, as shown in Figure 2.



Figure 2. Time-resolved transient absorption spectra observed at (1) 25, (2) 75, (3) 150, and (4) 300 ns after a 355-nm laser pulse to $BP-(CH_2)_3-ROH$ (3.0 × 10⁻³ M) in acetonitrile-water (4:1 v/v) at 295 K.



Figure 3. Time traces of the observed absorbance change (\bullet) for transient species at (a) 430 nm (³ROH^{*}) and (b) 550 nm (>COH-) after a 355-nm laser pulse to BP-(CH₂)₃-ROH (3.0 × 10⁻³ M) in acetonitrile-water (4:1 v/v) at 295 K. The plots (\blacktriangle) in (a) were calculated for the net absorbance change of ³ROH^{*} according to eq 7. The solid curves were drawn by the best fitting method.

Figure 3 shows the time traces of the transient absorbance changes observed at 430 nm (a) for ${}^{3}ROH^{*}$ and 550 nm (b) for ${}^{\circ}COH$ - 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 was 9.8 × 10⁶ s⁻¹, which is almost identical with that for the rise at 550 nm within



Figure 4. Plots of the observed rate constants (k_{obsd}) for the decay at 430 nm (O) and the rise at 550 nm (Δ) as a function of [BP-(CH₂)₃-ROH] obtained after a 355-nm laser pulse in BP-(CH₂)₃-ROH in acetonitrile-water (4:1 v/v) at 295 K.

experimental error (10%), indicating that the hydrogen atom transfer (HT) reaction occurs from ${}^{3}ROH^{*}$ to BP. In order to make clear whether the HT reaction is inter- or intramolecular one, we measured the k_{obsd} values for the HT reaction at various concentrations of BP-(CH₂)₃-ROH.

Figure 4 shows the plots of k_{obsd} vs [BP-(CH₂)₃-ROH] obtained after 355-nm laser pulsing to BP-(CH₂)₃-ROH in acetonitrilewater (4:1 v/v) at 295 K. The plots show the constant value (9.8 × 10⁶ s⁻¹) independent of [BP-(CH₂)₃-ROH] ($\leq 6.0 \times 10^{-3}$ M). Therefore, we concluded that the HT reaction of BP-(CH₂)₃-³ROH* is intramolecular (intra-HT) and produces >COH-(CH₂)₃-RO• with the rate constant (9.8 × 10⁶ s⁻¹) in the studied range of [BP-(CH₂)₃-ROH].

The efficiency (ϕ_{HT}) for the intra-HT reaction can be obtained according to eq 6.

$$\phi_{\rm HT} = \Delta [>\dot{\rm COH} - ({\rm CH}_2)_3 - {\rm RO}^{\bullet}] / \Delta [{\rm BP} - ({\rm CH}_2)_3 - {}^3{\rm ROH}^{\ast}]$$
 (6)

Here, Δ [>ĊOH-(CH₂)₃-RO[•]] and Δ [BP-(CH₂)₃-³ROH^{*}] are the concentration changes of [>ĊOH-(CH₂)₃-RO[•]] and [BP-(CH₂)₃-³ROH^{*}] produced and reduced by intra-HT, respectively. On the other hand, the absorbance change, Δ OD at the observing wavelength, λ , can be written as

$$\Delta OD = \epsilon(>\dot{C}OH-(CH_2)_3-RO^{\bullet})\Delta[>\dot{C}OH-(CH_2)_3-RO^{\bullet}] - \epsilon(BP-(CH_2)_3-^3ROH^{*})\Delta[BP-(CH_2)_3-^3ROH^{*}]$$
(7)

Here, $\epsilon(BP-(CH_2)_3-^3ROH^*)$ and $\epsilon(>\dot{C}OH-(CH_2)_3-RO^*)$ are the molar absorption coefficients of $BP-(CH_2)_3-^3ROH^*$ and $>\dot{C}OH-(CH_2)_3-RO^*$ at wavelength λ , respectively. Since the correct values of $\epsilon(BP-(CH_2)_3-^3ROH^*)$ and $\epsilon(>\dot{C}OH-(CH_2)_3-^3ROH^*)$ are unknown, we approximated the molar absorption coefficients by using those of the triplet 1-naphthol²⁵ for the former (7300 M⁻¹ cm⁻¹ at 430 nm and 460 M⁻¹ cm⁻¹ at 550 nm) and the sum of the molar absorption coefficients of the benzophenone ketyl radical (3220 M⁻¹ cm⁻¹ at 545 nm²⁶) and the 1-naphthoxy radical (830 M⁻¹ cm⁻¹ at 550 nm^{16,27}) for the latter (810 M⁻¹ cm⁻¹ at 430 nm and 4050 M⁻¹ cm⁻¹ at 550 nm, respectively).

$$\Delta OD = (-\epsilon (BP-(CH_2)_3 - {}^{3}ROH^*) + \phi_{HT}\epsilon (>\dot{C}OH-(CH_2)_3 - RO^*))\Delta [BP-(CH_2)_3 - {}^{3}ROH^*]$$
(8)

From eqs 6 and 7, we obtain

With the use of the assumed ϵ values and the observed ΔOD shown in Figure 3 and eq 8, we obtained a ϕ_{HT} value to be 1.0 for BP-(CH₂)₃-ROH in acetonitrile-water (4:1 v/v). Consid-



Figure 5. Time-resolved transient absorption spectra observed at (1) 50, (2) 140, and (3) 330 ns after a 355-nm laser pulse to BP-(CH₂)₃-ROD $(3.0 \times 10^{-3} \text{ M})$ in acetonitrile-D₂O (4:1 v/v) at 295 K.



Figure 6. Plots of the decay rate constants (k_{obsd}) of ³ROH^{*} at 430 nm as a function of [H₂SO₄] obtained after a 355-nm laser pulse in BP-(CH₂)₃-ROH in acetonitrile-water (4:1 v/v) at 295 K.

ering the experimental error, the ϕ_{HT} value implies that the intra-HT reaction of BP-(CH₂)₃-ROH occurs very efficiently.

Deuterium Isotope Effect on Intra-HT. We performed 355nm laser irradiation to BP-(CH₂)₃-ROD in order to elucidate the deuterium isotope effect on the intra-HT reaction. Considering the case of BP-(CH₂)₃-ROH, an intramolecular deuterium transfer (intra-DT) should occur after laser photolysis of BP- $(CH_2)_3$ -ROD. Figure 5 shows the transient absorption spectra observed after a 355-nm laser pulse to BP-(CH₂)₃-ROD (3.0 \times 10^{-3} M) in acetonitrile-D₂O (4:1 v/v) at 295 K. The transient spectrum taken at 50 ns after a laser pulse shows a band at 430 nm, which can be assigned to the triplet deutrated naphthol moiety (³ROD^{*}) produced by intra-ET. With the lapse of time, the 430-nm band diminishes with an isosbestic point at 492 nm, while both the 545-nm band assigned to the deuterated ketyl radical moiety (>COD) and the ca. 400-nm band for -RO appear. These spectral changes demonstrate the intra-DT reaction of BP- $(CH_2)_3$ -ROD. The rate constant (k_{DT}) for intra-DT was determined to be 5.1 \times 10⁵ s⁻¹. Since the rate constant ($k_{\rm HT}$) for intra-HT was found to be 9.8×10^5 s⁻¹, the isotope effect of $k_{\rm HT}/k_{\rm DT}$ is determined to be 1.9, which is consistent with a value (1.7 ± 0.3) obtained for the H-D effect in other proton-transfer reactions.28

Proton Effect on Intra-HT: the Reaction Mechanism. In a previous paper on the intermolecular HT (inter-HT) reaction from ³ROH* to BP, we reported that the rate constant and the efficiency for inter-HT are significantly enhanced by addition of protons to the ROH-BP system.¹⁸ In order to elucidate the effect of protons on the intra-HT reaction, we carried out 355-nm laser photolysis of BP-(CH₂)₃-ROH in acetonitrile-water (4:1 v/v) with various concentrations of H₂SO₄.

Figure 6 shows the plots of the rate constant (k_{obsd}) for intra-HT vs $[H_2SO_4]$ (≤ 0.5 M) obtained after a laser photolysis of

SCHEME I



BP-(CH₂)₃-ROH (3.0 × 10⁻³ M) in acetonitrile-water (4:1 v/v). The k_{obsd} value increases linearly with an increase of [H₂SO₄]. Therefore, k_{obsd} is represented as eq 9.

$$k_{\text{obsd}} = k_{\text{d}} + k_{\text{s}}[\text{H}_2\text{SO}_4]$$
(9)

From the slope and the intercept of the line, we have $k_s = 3.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_d = 9.8 \times 10^5 \text{ s}^{-1}$. On the other hand, the efficiency of intra-HT (ϕ_{HT}) was determined to be 1.0 in the studied range of [H₂SO₄] ($\leq 0.5 \text{ M}$) as mentioned above. In the case of the intra-HT reaction of BP-(CH₂)₃-ROH, only the rate constant for intra-HT is enhanced by the addition of protons.

In order to account for the obtained results on intra-HT of $BP-(CH_2)_3-ROH$, we propose the intra-HT mechanism analogous to that for inter-HT¹⁸ (Scheme I), where ${}^{3}(BP-(CH_{2})_{3}-$ ROH)*, $^{3}(>+COH-(CH_{2})_{3}-ROH)*$, and $^{3}(>COH-(CH_{2})_{3}-$ ROH⁺⁺) denote the intramolecular triplet exciplex with a sandwichlike 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- $^{3}ROH^{*}$, $^{3}(BP-CH_{2})_{3}$ - $^{$ (CH₂)₃-ROH)*, and ³(>+COH-(CH₂)₃-ROH)* to the ground **BP**-(CH₂)₃-ROH, respectively, $k_{\rm HT}$ and $k_{\rm el}$ are the rate constants for intra-HT of ${}^{3}(BP-(CH_{2})_{3}-ROH)*$ to >COH-(CH₂)₃-RO* and intra-el of $^{3}(>+COH-(CH_{2})_{3}-ROH)$ to $^{3}(>COH-(CH_{2})_{3}-$ ROH⁺⁺), respectively, and K_1 and K_2 are the corresponding equilibrium constants for formation to the triplet exciplex and the protonation of the triplet exciplex, respectively.

According to Scheme I, the rate constant (k_{obsd}) for intra-HT is formulated as

$$k_{\text{obsd}} = \frac{k_0 + k_{\text{ex}}K_1 + k_p K_1 K_2 [\text{H}^+]}{1 + K_1 + K_1 K_2 [\text{H}^+]}$$
(10)

Here, $k_{ex} = k'_0 + k_{HT}$ and $k_p = k''_0 + k_{el}$. Since the activity of H₂SO₄ in acetonitrile-water (4:1 v/v) is unknown, we denote K'_2 and [H₂SO₄] for K_2 and [H⁺], respectively. Thus, we obtain eq 10'.

$$k_{\text{obsd}} = \frac{k_0 + k_{\text{ex}}K_1 + k_p K_1 K'_2 [\text{H}_2 \text{SO}_4]}{1 + K_1 + K_1 K'_2 [\text{H}_2 \text{SO}_4]}$$
(10')

On the assumption that $1 + K_1 \gg K_1 K'_2[H_2SO_4]$, eq 10' is rearranged to

$$k_{\text{obsd}} = (k_0 + k_{\text{ex}}K_1)(1 + K_1)^{-1} + k_p K_1 K_2'(1 + K_1)^{-1} [\text{H}_2 \text{SO}_4]$$
(11)

Comparing eq 9 with eq 11, we have

$$k_{\rm d} = (k_0 + k_{\rm ex}K_1)(1 + K_1)^{-1} = 9.8 \times 10^6 \,{\rm s}^{-1}$$
 (12)

$$k_{\rm s} = k_{\rm p} K_1 K'_2 (1 + K_1)^{-1} = 3.3 \times 10^6 \,{\rm M}^{-1} \,{\rm s}^{-1}$$
 (13)

Though it is impossible to determine the exact values of k_0 , k_{ex} , K_1 , K'_2 , and k_p for intra-HT of BP-(CH₂)₃-ROH, we estimate these values in the following way. We have obtained the decay rate constant of ³ROH^{*} for inter-HT ($k_0 = 1.4 \times 10^4 \text{ s}^{-1}$).¹⁸ When we use this k_0 value for intra-HT and assume $k_0 \ll k_{ex}K_1$, eq 12 is approximately expressed as

$$k_{\rm d} = k_{\rm ex} K_1 (1 + K_1)^{-1} = 9.8 \times 10^6 \,\rm s^{-1}$$
 (14)

Since the term $K_1(1 + K_1)^{-1} < 1$, we can estimate k_{ex} and $k_p K'_2$ by eqs 14 and 13, respectively,

$$k_{\rm ex} > 9.8 \times 10^6 \,{\rm s}^{-1}$$
 (a)

$$k_{\rm n}K'_2 > 3.3 \times 10^6 \,{\rm s}^{-1}$$
 (b)

On the other hand, we have introduced the assumption $1 + K_1 \gg K_1K'_2[H_2SO_4]$, i.e., $k_p \gg k_pK'_2K_1(1 + K_1)^{-1}[H_2SO_4] = k_s[H_2-SO_4]$. In the studied range of $[H_2SO_4]$ (≤ 0.5 M), we can estimate k_p with eq 13,

$$k_{\rm p} \gg 1.7 \times 10^6 \,{\rm s}^{-1}$$
 (c)

In our previous report on inter-HT, we obtained $k_{\rm ex} = 9.1 \times 10^6$ s⁻¹ and $k_{\rm p}K'_2 = 1.2 \times 10^7 \, {\rm M}^{-1} \, {\rm s}^{-1.18}$ Considering these values with eqs a and b, we estimate $k_{\rm ex} \simeq 10^7 \, {\rm s}^{-1}$ and $k_{\rm p}K'_2 \simeq 10^7 \, {\rm M}^{-1}$ s⁻¹ for intra-HT. With the use of eq 14, eq c and the estimated values of $k_{\rm ex}$ and $k_{\rm p}K'_2$, we have $K_1 \simeq 10^{-1}$ and $K'_2 \simeq 10^{-1} \, {\rm M}^{-1}$, respectively.

The efficiency of intra-HT ($\phi_{\rm HT}$) was found to be unity in acetonitrile-water (4:1 v/v) at 295 K independent of [H₂SO₄]. According to Scheme I, $\phi_{\rm HT}$ can be expressed as

$$\phi_{\rm HT} = \frac{k_{\rm HT}K_1 + k_{\rm el}K_1K'_2[{\rm H}_2{\rm SO}_4]}{k_0 + k_{\rm ex}K_1 + k_{\rm p}K_1K'_2[{\rm H}_2{\rm SO}_4]}$$
(15)

where $k_{\rm ex} = k'_0 + k_{\rm HT}$ and $k_{\rm p} = k''_0 + k_{\rm el}$. The experimental results ($\phi_{\rm HT} = 1.0$ independent of [H₂SO₄]) indicate that $k_{\rm ex} \simeq k_{\rm HT}$ and $k_{\rm p} \simeq k_{\rm el}$. Therefore, once ³(BP-(CH₂)₃-ROH)* is produced, it is fated to the HT reaction with $\phi_{\rm HT} = 1.0$.

Laser Photolysis of BP-(CH₂)₃-ROMe. In the ROMe-BP system, we reported that the methoxynaphthalene cation radical (ROMe^{•+}) is produced by proton-induced intraexciplex electron transfer only in the presence of protons.^{19,29} In the linked



WAVELENGTH / nm

Figure 7. Time-resolved transient absorption spectra observed after a 355-nm laser pulse to BP-(CH₂)₃-ROMe $(3.0 \times 10^{-3} \text{ M})$ with (a) [H₂-SO₄] = 0 M at 0.4 (O), 2.0 (Δ), and 15.2 μ s (\Box), (b) [H₂SO₄] = 0.005 M at 0.2 (O), 1.0 (Δ), and 3.0 μ s (\Box), and (c) [H₂SO₄] = 0.5 M at 40 (O), 150 (Δ), and 300 ns (\Box) in acetonitrile-water (4:1 v/v) at 295 K.



Figure 8. Time traces of the observed absorbance change (\bullet) for transient species at (a) 435 nm (³ROMe^{*}), (b) 550 nm (>COH-), and (c) 650 nm (ROMe^{*+}) after a 355-nm laser pulse to BP-(CH₂)₃-ROMe (3.0 × 10⁻³ M) with [H₂SO₄] = 0.5 M in acetonitrile-water (4:1 v/v) at 295 K. The plots (\blacktriangle) in (a) were calculated for the net absorbance change of ³ROMe^{*} according to eq 17. The solid curves were drawn by the best fitting method.

molecular system of $BP-(CH_2)_3-ROMe$, it is also expected that the proton-induced electron transfer occurs via a triplet exciplex having a sandwichlike structure.

After 355-nm laser excitation of BP–(CH₂)₃–ROMe, the intra-ET reaction from ³BP* to the methoxynaphthalene moiety (ROMe) occurs to produce the triplet methoxynaphthalene moiety (³ROMe*) as was the case with BP–(CH₂)₃–ROH. Figure 7 shows the transient absorption spectra 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 $[H_2SO_4] = 0$ M (a), 0.005 M (b), and 0.5 M (c). The transient spectrum of BP-(CH₂)₃-ROMe observed at 400 ns after laser pulsing without added H₂SO₄ shows a 435-nm band that resembles the T-T absorption of 1-ROMe.¹⁹ The 435-nm band decays with a first-order rate constant (1.8 × 10⁵ s⁻¹) in the absence of protons. However, in the presence of acid, with a lapse of time, the 550-nm band for >COH- and the 380- and 650-nm bands for the methoxynaphthalene cation radical moiety (-ROMe⁺⁺) increase in intensity with isosbestic points at 500 nm while the 435-nm band decreases as shown in Figure 7b.c.

Figure 8 shows the time traces of the transient absorbance changes observed at 435 nm (a) for ³ROMe^{*}, 550 nm (b) for >COH-, and 650 nm (c) 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 ($k_{obsd} = 6.8 \times 10^6 \text{ s}^{-1}$) for the decay at 435 nm was the same as those for the rises of >COH- at 550 nm and ROMe^{*+} at 650 nm within experimental error (10%) and independent of [BP-(CH₂)₃-ROMe] ($\leq 6.0 \times 10^{-3}$ 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 >COH-(CH₂)₃-ROMe^{*+} by intra-el.

The efficiency (ϕ_{ion}) of the ionization for >COH-(CH₂)₃-ROMe⁺⁺ is defined according to eq 16

$$\phi_{ion} = \Delta [>\dot{C}OH - (CH_2)_3 - ROMe^{**}] / \Delta [BP - (CH_2)_3 - {}^3ROMe^{*}]$$
(16)

Here, Δ [>COH-(CH₂)₃-ROMe^{*+}] and Δ [BP-(CH₂)₃-3ROMe^{*}] are the concentration changes of [>COH-(CH₂)₃-ROMe^{*+}] and [BP-(CH₂)₃-3ROMe^{*}] produced and reduced by intra-el, respectively. Both concentration changes are expressed in terms of the absorbance change Δ OD at the observing wavelength λ and the molar absorption coefficients of BP-(CH₂)₃-3ROMe^{*} and >COH-(CH₂)₃-ROMe^{*+}, ϵ (BP-(CH₂)₃-3ROMe^{*}) and ϵ -(>COH-(CH₂)₃-ROMe^{*+}), at wavelength λ , respectively.

$$\Delta OD = \epsilon(>\dot{C}OH-(CH_2)_3-ROMe^{*+}) \times$$

$$\Delta[>\dot{C}OH-(CH_2)_3-ROMe^{*+}] -$$

$$\epsilon(BP-(CH_2)_3-^3ROMe^*)\Delta[BP-(CH_2)_3-^3ROMe^*] (17)$$

For the values of ϵ (BP-(CH₂)₃-³ROMe^{*}) and ϵ (>COH-(CH₂)₃-ROMe^{*+}), we substituted those of 1-ROMe (10 500 M⁻¹ cm⁻¹ at 435 nm) and 1-ROMe^{*+} (3400 M⁻¹ cm⁻¹ at 650 nm).¹⁹ From eqs 16 and 17, we have

$$\Delta OD = (-\epsilon (BP-(CH_2)_3 - {}^3ROMe^*) + \phi_{HT}\epsilon (>\dot{C}OH-(CH_2)_3 - ROMe^{**}))\Delta [BP-(CH_2)_3 - {}^3ROMe^*]$$
(18)

With the use of the substituted ϵ , the observed ΔOD values, and eq 18, we obtained the ϕ_{ion} value to be 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 of BP-(CH₂)₃-ROMe as observed in the case of the intermolecular ROMe-BP systems.¹⁹

We also investigated the proton effect on the rate constant (k_{obsd}) for intra-p-ion of BP-(CH₂)₃-ROMe.

Figure 9 shows the plots of k_{obsd} vs $[H_2SO_4] (\le 1.0 \text{ M})$ obtained after a laser pulse to BP- $(CH_2)_3$ -ROMe $(3.0 \times 10^{-3} \text{ M})$ in acetonitrile-water (4:1 v/v). The k_{obsd} value increases linearly proportional to $[H_2SO_4]$. Therefore, k_{obsd} is reexpressed with the use of eq 9. From the slope and the intercept of the line, we determined that $k_s = 1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $k_d = 1.8 \times 10^5 \text{ s}^{-1}$ in the intra-p-ion reaction of BP- $(CH_2)_3$ -ROMe.

A intra-p-ion mechanism for $BP-(CH_2)_3$ -ROMe was proposed to be similar to that of the ROMe-BP systems¹⁹ and intra-HT



Figure 9. Plots of the decay rate constants (k_{obed}) of ³ROMe^{*} at 435 nm as a function of [H₂SO₄] obtained after a 355-nm laser pulse in BP-(CH₂)₃-ROMe in acetonitrile-water (4:1 v/v) at 295 K.

mentioned above (Scheme II), where ${}^{3}(BP-(CH_{2})_{3}-ROMe)^{*}$, ${}^{3}(>^{+}COH-(CH_{2})_{3}-ROMe)^{*}$, and ${}^{3}(>^{C}OH-(CH_{2})_{3}-ROMe^{*+})$ denote the corresponding intramolecular triplet exciplex with a sandwichlike 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-ROMe^{*}, ${}^{3}(BP-(CH_{2})_{3}-ROMe)^{*}$, and ${}^{3}(>^{+}-COH-(CH_{2})_{3}-ROMe)^{*}$ to the ground BP-(CH₂)₃-ROMe, respectively, k_{el} is the rate constant for intra-el of ${}^{3}(>^{+}COH-(CH_{2})_{3}-ROMe)^{*}$ to ${}^{3}(>^{+}COH-(CH_{2})_{3}-ROMe)^{*}$), and K_{1} and K_{2} are the corresponding equilibrium constants for formation of the triplet exciplex and protonation of the triplet exciplex, respectively.

According to Scheme II, the rate constant (k_{obsd}) for intrap-ion is formulated as well as that for intra-HT by eq 10 or 10'. When we apply the assumption that $1 + K_1 \gg K_1 K'_2 [H_2 SO_4]$ to the intra-p-ion mechanism, we can derive eqs 19 and 20.

$$k_{\rm d} = (k_0 + k_{\rm ex}K_1)(1 + K_1)^{-1} = 1.8 \times 10^5 \,{\rm s}^{-1}$$
 (19)

$$k_{\rm s} = k_{\rm p} K_1 K'_2 (1 + K_1)^{-1} = 1.55 \times 10^7 \,{\rm M}^{-1} \,{\rm s}^{-1}$$
 (20)

It is again impossible to determine the exact values of k_0 , k_{ex} , K_1 , K'_2 , and k_p for intra-p-ion of BP-(CH₂)₃-ROMe. For the k_0 and k_{ex} values of BP-(CH₂)₃-ROMe, we substituted the obtained values in the 1-ROMe-BP system ($k_0 = 6.8 \times 10^4 \text{ s}^{-1}$ and $k_{ex} = 1.6 \times 10^6 \text{ s}^{-1}$).¹⁹ With the use of the substituted values of k_0 and k_{ex} and eq 19, we determined $K_1 = 7.9 \times 10^{-2}$. With the use of this K_1 value, we estimated $K'k_p = 1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. On the other hand, we previously introduced the assumption $k_p \gg$

SCHEME II

 k_{s} [H₂SO₄]. In the studied range of [H₂SO₄] (\leq 1.0 M), we can estimate k_{p} as follows:

$$k_{\rm p} \gg 1.55 \times 10^7 \,{\rm s}^{-1}$$
 (d)

From inequality (d) and the estimated value of K'_2k_p (1.4 × 10⁸ M⁻¹s⁻¹), we approximate K'_2 to be $K'_2 \simeq 10^{-1}$ M⁻¹. This estimated value of K'_2 is consistent in the order of magnitude with that obtained for intra-HT ($K'_2 \simeq 10^{-1}$ M⁻¹), which can be interpreted as a small difference in the proton affinity between the intramolecular triplet exciplexes ³(BP-(CH₂)₃-ROH)* and ³(BP-(CH₂)₃-ROMe)*.

The efficiency of intra-p-ion (ϕ_{ion}) was found to be 0.3 and 1.0 for BP-(CH₂)₃-ROMe in acetonitrile-water (4:1 v/v) with [H₂-SO₄] = 0.005 and 0.5 M, respectively. According to Scheme II, ϕ_{ion} can be written

$$\phi_{\rm ion} = \frac{k_{\rm el}K_1K'_2[{\rm H}_2{\rm SO}_4]}{k_0 + k_{\rm ex}K_1 + k_{\rm p}K_1K'_2[{\rm H}_2{\rm SO}_4]}$$
(21)

where $k_p = k''_0 + k_{el}$. Equation 21 can be expressed with the use of eqs 19 and 20 as

$$\phi_{\rm ion} = \frac{\lambda k_{\rm s}[\rm H_2SO_4]}{k_{\rm d} + k_{\rm s}[\rm H_2SO_4]}$$
(22)

where λ is the ratio $k_{\rm el}/k_{\rm p}$. With the use of eq 22 and the experimentally obtained values of $k_{\rm d}$, $k_{\rm s}$, and $\phi_{\rm ion}$, the values of λ are determined to be 1.0 and 0.98 for the cases with [H₂SO₄] = 0.005 and 0.5 M, respectively. These values indicate that the intra-p-ion reaction for BP-(CH₂)₃-ROMe effectively occurs, as well as that for the 1-ROMe-BP system.¹⁹ Due to the relatively large electron affinity of the protonated BP moiety (>+COH-) in the protonated triplet exciplex compared to that of BP in the triplet exciplex, the intra-el may occur efficiently.

The Structure of Triplet Exciplexes. As mentioned above, it is 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 by considering the triplet exciplex and the protonated triplet exciplex. In contrast to the intramolecular cases of (CH₂)₃, we have performed preliminary laser photolysis experiments on the linked chromophores with CH₂, BP-CH₂-ROH, and no HT was observed. This result indicates that the hydrogen atom transfers not through the CH₂ chain, but between chromophores. In the case of CH₂, it may be impossible to form the suitable configuration of chromophores for intra-HT. However, when the chromophores are linked with (CH₂)₃, a stacked



configuration of chromophores, which has a weak charge-transfer interaction, can be formed. Therefore, we conclude that the structures of the triplet exciplex and the protonated triplet exciplex for intra-HT and intra-p-ion are sandwichlike as illustrated in Schemes I and II.

Concluding Remarks

The 355-nm laser photolyses studies in the linked molecules, BP-(CH₂)₃-ROH and BP-(CH₂)₃-ROMe, revealed the following:

(1) The intramolecular hydrogen atom transfer (intra-HT) of BP-(CH₂)₃-ROH occurs effectively to yield > $\dot{C}OH-(CH_2)_3$ -RO, and with an increase of acid concentration, the rate constant of intra-HT increases linearly. The mechanism for intra-HT is interpreted by Scheme I.

(2) The intramolecular electron transfer of $BP-(CH_2)_3$ -ROMe occurs to yield $>COH-(CH_2)_3-ROMe^{+}$ only in the presence of protons. The rate constant of intramolecular proton-induced electron transfer is enhanced proportional to the concentration of acid. The mechanism of proton-induced electron transfer is illustrated by Scheme II.

(3) Both the intramolecular hydrogen atom transfer and protoninduced electron transfer reactions occur via the triplet exciplex and the protonated triplet exciplex that have sandwichlike structures with weak charge-transfer character.

Acknowledgment. We thank Dr. Jerome P. Lillis at the Institute of Physical and Chemical Research (RIKEN) for useful discussion.

References and Notes

(1) The Institute of Science and Industrial Research, Osaka University, Suita, Osaka 565, Japan. (2) Scaiano, J. C. J. Photochem. 1973/1974, 2, 81.

(3) Wagner, P. J.; Hammond, G. S. Adv. Photochem. 1968, 5, 21. Wagner, P. J. Acc. Chem. Res. 1971, 4, 168. Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. J. Am. Chem. Soc. 1986, 108, 7727. Wagner, P. J. Top. Curr. Chem. 1976, 66, 1.

(4) Turro, N. J.; Dalton, J. C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D.; Niemczyk, M.; Schore, N. Acc. Chem. Res. 1972, 5, 92. Dalton, J. C.; Turro, N. J. Annu. Rev. Phys. Chem. 1970, 21, 499.

(5) Turro, N. J. Modern Molecular Photochemistry; Benjamin/Cummings: Menlo Park, 1978.

(6) Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. Chem. Rev. 1973, 73, 141

(7) Formosinho, S. J. J. Chem. Soc., Faraday Trans. 2 1976, 72, 1913. Formoshinho, S. J. J. Chem. Soc., Faraday Trans. 2 1987, 74, 1978.

(8) Okada, T.; Tashita, N.; Mataga, N. Chem. Phys. Lett. 1980, 75, 220. Okada, T.; Karaki, T.; Mataga, N. J. Am. Chem. Soc. 1982, 104, 7191. Arimitsu, S.; Masuhara, H.; Tsubomura, H. J. Phys. Chem. 1975, 79, 1255.

(9) Peters, K. S.; Freilich, S. C.; Shaefer, C. G. J. Am. Chem. Soc. 1980, 102, 5701. Simon, J. D.; Peters, K. S. J. Am. Chem. Soc. 1981, 103, 6403. Simon, J. D.; Peters, K. S. Acc. Chem. Res. 1984, 17, 277. Simon, J. D.; Peters, K. S. J. Am. Chem. Soc. 1982, 104, 6542. Peters, K. S.; Pang, E.; Rudzki, J. J. Am. Chem. Soc. 1982, 104, 5535. Manring, L. E.; Peters, K. S. J. Am. Chem. Soc. 1983, 105, 5708.

(10) Hoshino, M.; Shizuka, H. J. Phys. Chem. 1987, 91, 714. Hoshino, M.; Seki, H.; Kaneko, M.; Kinoshita, K.; Shizuka, H. Chem. Phys. Lett. 1986, 132, 209.

(11) Devadoss, C.; Fessenden, R. W. J. Phys. Chem. 1990, 94, 4540. Devadoss, C.; Fessenden, R. W. J. Phys. Chem. 1991, 95, 7253

(12) Miyasaka, H.; Morita, K.; Kamada, K.; Nagata, T.; Kiri, M.; Mataga, N. Bull. Chem. Soc. Jpn. 1991, 64, 3229. (13) Hoshino, M.; Shizuka, H. In Photo-induced Electron Transfer; Fox,

M. A., Chanon, N., Eds.; Elsevier: Amsterdam, 1988; Part C, p 313.

(14) Hoshino, M.; Shizuka, H. In New Aspects of Radiation Curing in Polymer Science and Technology; Fouassier, J. P., Rabek, J. F., Eds.; Elsevier: London, in press; Vol. 2.

(15) Shizuka, H.; Fukushima, M. Chem. Phys. Lett. 1983, 101, 598.

(16) Shizuka, H.; Hagiwara, H.; Fukushima, M. J. Am. Chem. Soc. 1985, 107, 7816.

(17) Kohno, S.; Hoshino, M.; Shizuka, H. J. Phys. Chem. 1991, 95, 5489. (18) Kaneko, S.; Yamaji, M.; Hoshino, M.; Shizuka, H. J. Phys. Chem. 1992, 96, 8028.

(19) Yamaji, M.; Sekiguchi, T.; Hoshino, M.; Shizuka, H. J. Phys. Chem. 1992, 96, 9353.

(20) Hirayama, F. J. Chem. Phys. 1965, 42, 3163.

(21) Scaiano, J. C.; McGimpsey, W. G.; Leigh, W. J.; Jakobs, S. J. Org. Chem. 1987, 52, 4540

(22) Mashuhara, H.; Maeda, Y.; Nakajo, H.; Mataga, N.; Tomita, K.; Tatemitsu, H.; Sakata, Y.; Misumi, S. J. Am. Chem. Soc. 1981, 103, 634.

(23) Shizuka, H.; Obuchi, H. J. Phys. Chem. 1982, 86, 1297. (24) Lamola, A. A.; Leermarkers, P. A.; Byers, G. W.; Hammond, G. S.

J. Am. Chem. Soc. 1965, 87, 2322. (25) Yamaji, M.; Tanaka, T.; Shizuka, H. Chem. Phys. Lett. 1993, 202,

191 (26) Land, E. J. Proc. R. Soc. 1968, A305, 457.

(27) Das, P. K.; Encinas, M. V.; Scaiano, J. C. J. Am. Chem. Soc. 1981, 103. 4162.

(28) Shizuka, H.; Tobita, S. J. Am. Chem. Soc. 1982, 104, 6919.

(29) Shizuka, H.; Hagiwara, H.; Satoh, H.; Fukushima, M. J. Chem. Soc., Chem. Commun. 1985, 1454.