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Intramolecular Binaphthyl Formation from Radical Cations of Tri-1-naphthyl Phosphate and Related Compounds in Photoinduced Electron-Transfer Reactions Sensitized by 9,10-Dicyanoanthracene

Mitsunobu Nakamura,*,† Reizo Dohno,†,§ and Tetsuro Majima*,‡

Department of Engineering Science, Himeji Institute of Technology, Shosha 2167, Himeji, Hyogo 671-2201, Japan, and The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

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The photoinduced electron transfer of tri-1-naphthyl phosphate and related compounds sensitized by 9,10-dicyanoanthracene (DCA) in acetonitrile produces 1,1′-binaphthyl and the corresponding biaryl. The quenching rate constant of the DCA fluorescence is calculated to be equal to the diffusion-controlled rate constant from the Stern−Volmer analysis and the fluorescence lifetime measurement. The free energy change calculated from the redox potentials and excitation energy of the singlet excited DCA indicates that the quenching process occurs exergonically to give the tri-1-naphthyl phosphate radical cation and DCA radical anion through electron transfer from tri-1-naphthyl phosphate to the singlet excited DCA at the diffusion-controlled rate. On the basis of spectroscopic and kinetic studies with laser flash photolysis, pulse radiolysis, and γ-radiolysis, the radical cation of tri-1-naphthyl phosphate forms an intramolecular π-dimer radical cation with face-to-face interaction between the two naphthyl groups within 8 ns of the electron pulse. The 1,1′-binaphthyl radical cation is eliminated at the rate constant of $k_r = 5.3 \times 10^5$ s^{-1} from the intramolecular π-dimer radical cation. Branching ratios of the reaction pathways are estimated for the reactive intermediates such as the tri-1-naphthyl phosphate radical cation and its intramolecular π-dimer radical cation from the rate constants and quantum yields. The electron-withdrawing character of the P(O) group in the O−P(O)−O spacer is responsible for the elimination of the binaphthyl radical cation. The DCA-sensitized photoinduced electron-transfer reaction of the tri-1-naphthyl phosphate is compared with the direct photoreaction.

Introduction

Photochemical reactions of organophosphorus compounds have been widely studied from both mechanistic and synthetic points of view.[1−3] The photochemistry of monoaryl phosphates has been studied as caged compounds to clarify biochemical processes.[2,3] The heterolytic cleavage of a C−O bond predominantly occurs as the initial process in the photochemical reactions of aryl phosphates.[3] For instance, photoirradiation of *m*-nitrophenyl phosphate in an aqueous solution at 313 nm gives nitrophenol and phosphoric acid.[4] On the the other hand, *p*-nitrophenyl phosphate has little reactivity during the photolysis, while an addition reaction occurs with pyridine to give 1-phenylpyridinium 4′-phosphate during the photoirradiation in the presence of pyridine.[1e,f] The substituent and its position on the phenyl group are important factors for the reactivity.

The photochemical reactions of di- or triaryl phosphates are different from those of aryl phosphates. The photoirradiations of the triphenyl phosphates having para substituents give biphenyl derivatives in methanol in which biphenyl elimination is enhanced by the *p*-methoxyl substituent.[5] It has also been reported that the excited diaryl methylphophonates and triaryl phosphates form an intramolecular excimer between two aryl groups in which two homolytic C−O bond cleavages occur to produce the biaryl by ipso−ipso coupling.[6] The excited diaryl methylphosphonates having electron-donating and -withdrawing aryl groups form an intramolecular exciplex in which a heterolytic C−O bond cleavage for the electron-donating aryl group occurs that produces the

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[†] Himeji Institute of Technology.

[‡] Osaka University.

[§] Deceased.

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aryl cation succeeding the intramolecular rearrangement to the electron-withdrawing aryl group. Triplet-sensitized reactions of the di- and trinaphthyl esters by benzophenone also occur to produce the binaphthyl. These intramolecular biaryl formations are attributed to both the formation of an intramolecular excimer or exciplex and the electron-withdrawing character of the P(O) group of the O−P(O)−O spacer between two aryl groups. It has been reported that an intramolecular excimer forms in 1,3-diarylpropanes and bis(4-methoxy-1-phenoxy)dimethylsilane and decays without the formation of the biaryl.[6e,7] No intramolecular excimer forms in the di- or triaryl esters such as carbonate, borate, and sulfite.[6e]

The photoinduced electron-transfer reactions of organophosphorus compounds have been studied for trivalent phosphorus compounds such as trialkylphosphines and trialkyl phosphites in which radical cations of these compounds are generated and oxidized by methanol to give trialkylphosphine oxides and trialkyl phosphates.[1d] We have recently reported that 9,10-dicyanoanthracene (DCA)-sensitized photoinduced electron-transfer reaction of tri-1-naphthyl phosphate occurs and initially forms the tri-1-naphthyl phosphate radical cation and 1,1′-binaphthyl as the final product.[8]

Although photoinduced electron-transfer reactions of organic compounds have been extensively investigated,[9] little is known about organophosphorus compounds. Studies of the electron-transfer reactions of aryl phosphates and phosphonates are of particular importance for caged compounds and organic syntheses. In this paper, we report the mechanistic study of the DCA-sensitized photoinduced electron-transfer reaction of trinaphthyl phosphates (**1**) and dinaphthyl methylphosphonates (**2**) in which the initially formed radical cations of **1** and **2** change to the intramolecular π-dimer radical cations between two naphthyl groups and a binaphthyl radical cation is subsequently eliminated. As a comparison, the DCA-sensitized photoinduced electron-transfer reaction of mononaphthyl phosphates (**3**) is reported.

It has been reported that intramolecular π-dimer radical cations form between two aromatic groups in various diarylalkanes on the basis of the absorption spectra, although there is no data available for the dimerization rate constant or equilibrium constant between the monomer and dimer radical cations.[10] We have estimated the rate constant and equilibrium constant between the radical cations of **1** and **2** and the intramolecular π-dimer radical cations because the rate of formation of binaphthyl radical cation from the intramolecular π-dimer radical cations can be directly measured using the transient absorption measurements. The reactivity of the intramolecular π-dimer radical cations of **1** and **2** can be compared with that of the other intramolecular π-dimer radical cations and is discussed with respect to the character of the spacer between the two aromatic groups.

Results

Product Analyses in Photoirradiation. Photoirradiation (cutoff < 355 nm) of an argon-saturated acetonitrile solution containing 5.0×10^{-5} M DCA and 1.0×10^{-2} M tri-1-naphthyl phosphate (**1a**) for 1 h gave 1,1′-binaphthyl (**4a**) and 1-naphthyl phosphate (**5a**) in a 1:1 ratio with a quantum yield of 0.0013 (Scheme 1). Upon photoirradiation of a mixture of DCA and di-1-naphthyl methylphosphonate (**2a**) in a manner similar to that already described, **4a** and methylphosphonic acid (**5′**) were produced. Photoirradiation of tris(4-methoxy-1-naphthyl) phosphate (**1b**) or bis(4-methoxy-1-naphthyl) methylphosphonate (**2b**) with DCA in acetonitrile also gave 4,4′-dimethoxy-1,1′-binaphthyl (**4b**) and 4-methoxy-1-naphthyl phosphate (**5b**) or **5′**, respectively. Table 1 summarizes the product yields and quantum yields of **4**. Trace amounts of other products were also obtained, although they were not identified. Therefore, the main product of the photosensitized reactions of **1** and **2** was **4**. The material balances showed that the naphthyl groups of the consumed **1a** and **2b** transformed almost quantitatively into **4a** and **4b**, respectively. No reaction occurred upon the photoirradiation of the diethyl naphthyl phosphates (**3**) with DCA. The photoirradiation of a mixture of DCA and di-1-naphthoxymethane (**6**) was also carried out for comparison with **1a** and **2a**; however, no reaction occurred. These results suggest that the formation of **4** intramolecularly occurs.

Laser Flash Photolyses. A time-resolved spectroscopic study using the laser flash photolysis technique was carried out to obtain kinetic information about the photoreactions. The transient absorption spectra were measured by the laser flash photolyses (355 nm) of a mixture of **1a** (1.0×10^{-2} M) and DCA (5.0×10^{-5} M) in argon-saturated acetonitrile. Figure 1 shows the transient absorption spectrum with peaks at approximately 430 and 710 nm in the range of 430−750 nm observed 20 ns after a 4 ns flash (open circle).

The peak of the transient absorption at 430 nm disappeared in the presence of 5.0×10^{-4} M *trans*-4,4′-dimethoxystilbene (DMS) as a radical-cation scavenger used to form the DMS radical cation ($DMS^{\bullet+}$) of which a transient absorption appeared at 530 nm, while the peak at 700 nm was not quenched.[11] The peak at 700 nm was quenched in the presence of oxygen, while that at 430 nm was not influenced (closed circle in Figure 1). The peaks at 430 and 700 nm are assigned to the radical cation of **1a** ($\mathbf{1a}^{\bullet+}$) and the DCA radical anion ($DCA^{\bullet-}$),

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Scheme 1

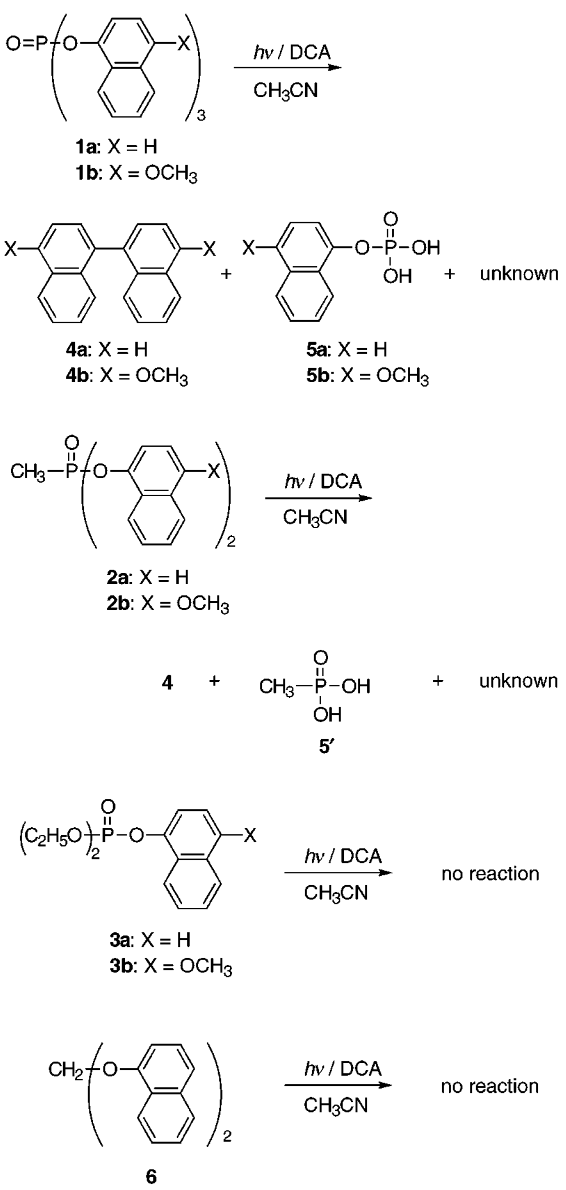

Table 1. DCA-Sensitized Photoinduced Electron-Transfer Reactions of 1 and 2 in Acetonitrile[a]

substrate	convn[a]/%	yield/% 4	yield/% 5	$\phi_4/10^{-3}$
1a	15	10	13	1.3
1b	38	26	28	3.1
2a	14	7	10	1.0
2b	16	7	12	1.0

[a] Irradiated to the mixture of substrate (1.0 × 10^{-2} M) and DCA (5.0 × 10^{-5} M) in argon-saturated acetonitrile for 1 h.

respectively. The transient absorption spectrum observed 20 ns after a 4 ns flash (open circle in Figure 1a) was subtracted from that of **1a**$^{\bullet+}$ (closed circle in Figure 1a) to give the difference spectrum, which was similar to that of DCA$^{\bullet-}$.[11] These results indicate that an electron transfer occurs during the photoirradiation of the mixture of **1a** and DCA in acetonitrile to form **1a**$^{\bullet+}$ and DCA$^{\bullet-}$. Since **1a**$^{\bullet+}$ is scavenged by DMS to quantitatively give DMS$^{\bullet+}$, the quantum yield for the formation of **1a**$^{\bullet+}$ is determined to be 0.77 from a comparison of the concentration of DMS$^{\bullet+}$ with that for a biphenyl/DCA/DMS mixture using the absorption coefficient of DMS$^{\bullet+}$ at 530 nm (ϵ_{530} = 65 600 M^{-1} cm^{-1}) and the quantum yield for the formation of biphenyl$^{\bullet+}$ ($\phi_{Bp^{\bullet+}}$ = 0.83).[11]

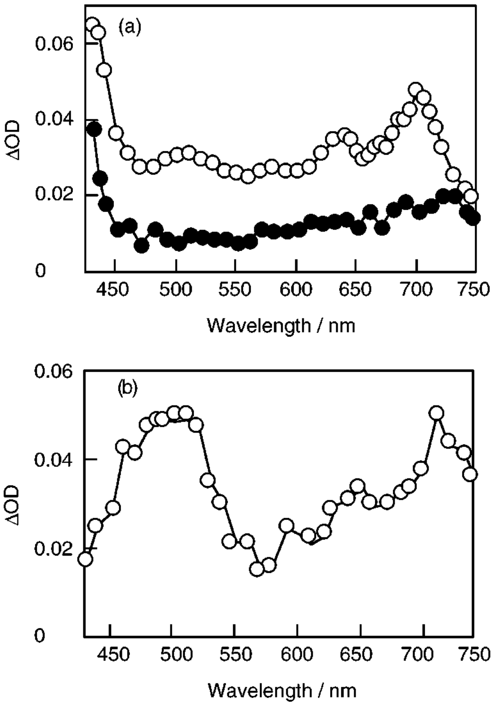

Figure 1. Transient absorption spectra observed immediately after a flash during laser flash photolysis, **1a**-DCA in argon- (open circle) and oxygen-saturated (solid circle) acetonitrile (a) and a mixture of **1a** and 9-methylacridinium perchlorate in argon-saturated acetonitrile (b).

Laser flash photolysis of a mixture of **1a** and 9-methylacridinium perchlorate was also performed in argon-saturated acetonitrile. A transient absorption spectrum with peaks at around 500 and 725 nm was observed 20 ns after a 4 ns flash (Figure 1b). Since the peak at 500 nm is assigned to the acridinyl radical,[12] the peak at 725 nm is assigned to **1a**$^{\bullet+}$. The peak at 430 nm assigned to **1a**$^{\bullet+}$ is probably obscured by the intense peak of the acridinyl radical at 500 nm. It is noted that **1a**$^{\bullet+}$ has absorption peaks at 430 and 725 nm.

Fluorescence Measurements. Fluorescence quenching experiments were performed to determine the rate constant of the electron transfer. The Stern–Volmer analysis gives the constant ($k_q\tau$) where k_q and τ are the rate constants of the fluorescence quenching and fluorescence lifetime, respectively. The k_q value of the quenching of the singlet excited DCA (^{1}DCA*) by **1**–**3** is equal to the rate constant (k_{et}) of the electron transfer from **1**–**3** to ^{1}DCA* in the present reactions ($k_q = k_{et}$). The k_{et} value can be calculated from the $k_q\tau_{DCA}$ value from the Stern–Volmer analysis and lifetime of ^{1}DCA* (τ_{DCA}) directly measured by the single-photon counting method.

The fluorescence of DCA in acetonitrile (5.0 × 10^{-5} M) was quenched by **1**–**3** without the formation of a new emission band in the range of 400–700 nm. For example, Figure 2 shows the quenching of DCA fluorescence by **1a** at several concentrations. The values of $k_q\tau$ = 240–320 M^{-1} were obtained from the Stern–Volmer analyses and are summarized in Table 2. Using 14.9 ns of τ_{DCA} in acetonitrile,[11] k_q values of 1.6 – 2.1 × 10^{10} M s^{-1} were

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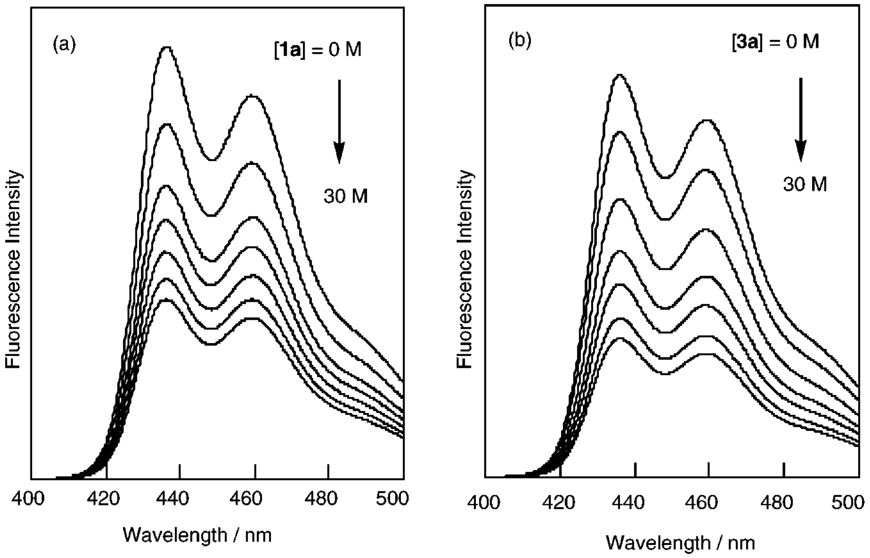

Figure 2. Spectral changes of the DCA fluorescence with the addition of **1a** (a) and **3a** (b). Excitation wavelength $\lambda_{ex} = 375$ nm, 5.0×10^{-5} M DCA in acetonitrile. Arrows show decrease in the intensity with increasing concentration of **1a** or **3a**.

Table 2. The $k_q\tau$, k_q, E^{ox}, and ΔG values of 1−3

substrate	$k_q\tau^a$/M^{-1}	$k_q{}^b$/10^{10} M^{-1} s^{-1}	$E^{ox\,c}$/V	ΔG^d/kcal mol^{-1}
1a	240	1.6	1.45	−15.7
1b	310	2.1	1.38	−23.5
2a	273	1.6	1.41	−16.8
2b	319	2.1	1.18	−25.1
3a	267	1.8	1.06	−14.1
3b	288	1.9	1.13	−24.0

[a] From the fluorescence quenching of DCA (5.0×10^{-5} M) in acetonitrile. [b] Calculated from $k_q\tau$ and $\tau_{DCA} = 14.9$ ns in acetonitrile.[10] [c] Oxidation potentials (vs SCE) of substrates (1.0×10^{-2} M) were measured in dry acetonitrile containing 0.1 M of Bu_4NClO_4. [d] Free energy changes of the electron transfer from substrate to ^{1}DCA* calculated using the Rehm−Weller equation.

calculated. These k_q values are approximately equal to the diffusion-controlled rate constant of acetonitrile at room temperature ($k_{diff} = 2.0 \times 10^{10}$ M^{-1} s^{-1}). Therefore, the electron transfer from naphthyl esters to ^{1}DCA* occurs at the diffusion-controlled rate.

Oxidation Potential. Oxidation potentials, E^{ox}, of **1**−**3** were measured to be 1.0×10^{-2} M by cyclic voltammetry using a platinum electrode in dry acetonitrile containing 0.10 M Bu_4NClO_4 as the supporting electrolyte. Compounds **1**−**3** were oxidized in the region of 1.06−1.45 V (Table 2).[13] Compounds **1a**−**3a** with no substituent on the naphthyl groups were oxidized at similar potentials (1.38 ± 0.06 V). The E^{ox} values of **1b**−**3b** with a methoxyl substituent on the naphthyl groups were 1.00 ± 0.04 V. The E^{ox} value was dependent on the substituent of the naphthyl groups but independent of the number of aryl groups. Taking into account these results together with an E^{ox} of 1.05 and 0.80 V for 1-methoxynaphthalene and 1,4-dimethoxynaphthalene, respectively, it is clear that one naphthyl group is involved in the oxidation of **1**−**3** and that 1-methoxynaphthalene and 1,4-dimethoxynaphthalene are more easily oxidized than **1a**−**3a** and **1b**−**3b** because of the electron-withdrawing P(O) group of the O−P(O)−O spacer. The oxidation of **1a**−**3a** with no methoxy substituent on the naphthyl group irreversibly occurred similar to naphthalene. The oxidation of **1b** and **2b** occurred irreversibly, while **3b** was oxidized reversibly. This fact suggests that the intramolecular reaction occurs in the radical cations of **1b** and **2b**, but not in **3b**.

It is known that the free energy change is exergonic when an electron transfer occurs at the diffusion-controlled rate. The free energy change during the electron transfer is calculated from the oxidation and reduction potentials of the donor and acceptor molecules, respectively, and the excitation energy according to the Rehm−Weller equation.[14] The half-wave reduction potential of DCA and the excitation energy of ^{1}DCA* have been reported to be −0.91 V (vs SCE) and 66.4 kcal mol^{-1}, respectively.[11] Since the half-peak oxidation potentials of the naphthyl esters were measured in the present study, the free energy changes in the electron transfer from the naphthyl esters to ^{1}DCA* (ΔG_{et}) were calculated to be negative (Table 2). These results indicate that the electron transfer from the naphthyl ester (**1**−**3**) to ^{1}DCA* is exergonic.

***γ*-Radiolyses at 77 K.** The assignments of radical cations can be confirmed by their absorption spectra observed during γ-radiolyses in butyl chloride rigid matrices at 77 K. It was established that a substrate radical cation is effectively and selectively formed from the initial hole trapping process.[15]

The absorption spectrum of $\mathbf{3a}^{\bullet+}$ was observed with peaks at 400, 680, and 720 nm during the γ-radiolysis of 3.0×10^{-2} M **3a** in a butyl chloride rigid matrix at 77 K (Figure 3a). These peaks disappeared with increasing temperature (<90 K), while a new peak appeared at 600 nm. These spectral changes were dependent on the concentration of **3a** and were not observed below 3.0×10^{-2} M. The absorption spectrum and spectral changes of the naphthalene radical cation have been reported by Arai et al. during the γ-radiolysis of naphthalene in a

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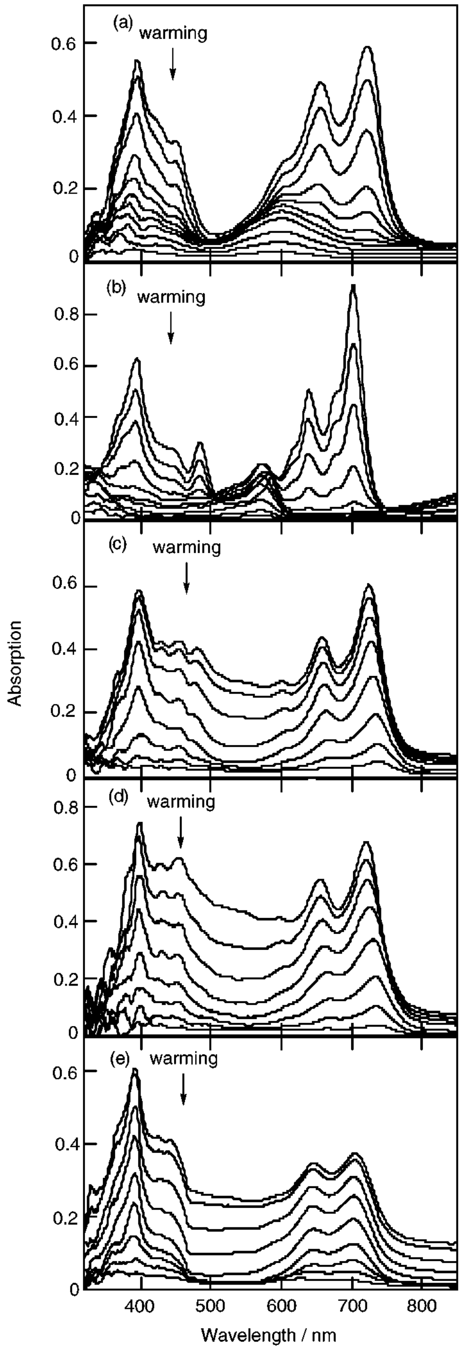

Figure 3. Absorption spectral changes of radical cations recorded immediately after γ-radiolyses of 3×10^{-2} M **3a** (a), 3×10^{-2} M naphthalene (b), 3×10^{-2} M **1a** (c), 1×10^{-2} M **2a** (d), and 1×10^{-2} M **6** (e) in butyl chloride rigid matrices at 77 K and after warming. Arrows show decrease in the peak upon warming. See the text for details.

butyl chloride rigid matrix at 77 K and upon warming below 90 K.[16] We have reinvestigated the γ-radiolysis of naphthalene in the butyl chloride rigid matrix at 77 K to compare it with those of **1a**−**3a**. The absorption peaks of the naphthalene radical cation at 400, 650, and 700 nm disappeared with increasing temperature, while new peaks appeared at 350 and 580 nm together with a shoulder absorption at 750−850 nm (Figure 3b). Since the intensities of new the peaks increased with the increasing concentration of naphthalene, the peaks are assigned to an intermolecular π-dimer radical cation of naphthalene. Since the chromophore of **3a**$^{\bullet+}$ is the naphthyl group, the peaks at 380 and 600 nm that appeared with the disappearance of **3a**$^{\bullet+}$ are assigned to the intermolecular π-dimer radical cation $(\mathbf{3a})_2^{\bullet+}$ between the two naphthyl groups of **3a** and **3a**$^{\bullet+}$ (Figure 3a). The peaks of **3a**$^{\bullet+}$ and $(\mathbf{3a})_2^{\bullet+}$ were broader in shape and observed at a longer wavelength than those of the naphthalene radical cation and π-dimer radical cation of naphthalene, respectively. This is probably attributable to the electron-withdrawing property of the P(O) group of the O−P(O)−O spacer in **1**−**3**.

The three peaks of **1a**$^{\bullet+}$ at 400, 680, and 720 nm and two broad bands in the region of 500−600 and 800−850 nm were observed after the γ-radiolysis of **1a** in the butyl chloride rigid matrix at 77 K (Figure 3c). The absorption spectrum of **1a**$^{\bullet+}$ was similar to that obtained during the laser flash photolysis of **1a** in oxygen-saturated acetonitrile. The absorption spectrum disappeared with no formation of a peak upon warming. The absorption spectrum and spectral changes were independent of the concentration of **1a**. The broad band in the region of 500−600 nm disappeared faster than the peaks of **1a**$^{\bullet+}$ at 400, 680, and 720 nm (Figure 3c). The broad band in the region of 500−600 nm is assigned to an intramolecular π-dimer radical cation of **1a**$^{\bullet+}$ with face-to-face interaction between the two naphthyl groups (π-dimer$^{\bullet+}$). Similar spectral changes were observed during the γ-radiolysis of **2a** in a butyl chloride rigid matrix at 77 K (Figure 3d). Consequently, it is found that the π-dimer$^{\bullet+}$ of **1a**$^{\bullet+}$ and **2a**$^{\bullet+}$ easily forms in the butyl chloride rigid matrices at 77 K. γ-Radiolysis of **6** in a butyl chloride rigid matrix at 77 K was also performed. The radical cation of **6** formed the π-dimer$^{\bullet+}$ for which an absorption band appeared in the region similar to the π-dimer$^{\bullet+}$ of **1a**$^{\bullet+}$ and **2a**$^{\bullet+}$ (Figure 3e).

Pulse Radiolyses at Room Temperature. A time-resolved spectroscopic study was performed with pulse radiolyses in 1,2-dichloroethane at room temperature because transient absorption of the radical cation is measured without absorption overlap of the other intermediates.

The transient absorption spectrum assigned to **1a**$^{\bullet+}$ with peaks at 400, 450, and 650 nm and the π-dimer$^{\bullet+}$ of **1a** with a weak peak in the region of 500−600 nm were immediately observed after an 8 ns pulse and decayed with the formation of new peaks at 480 and 520 nm. The new peaks were assigned to **4a**$^{\bullet+}$, since the absorption spectrum of **4a**$^{\bullet+}$ with peaks at 480 and 520 nm was observed during the pulse radiolysis of **4a** in 1,2-dichloroethane (Figure 4). On the other hand, the transient absorption spectrum of **3a**$^{\bullet+}$ with peaks at 390 and 440 nm decayed without the formation of any new peaks during the pulse radiolysis of 2.0×10^{-2} M of **3a**. The transient absorption spectrum of **3a**$^{\bullet+}$ was slightly different in shape and peak wavelength from that of **1a**$^{\bullet+}$ (Figure 4b).

In 1,2-dichloroethane, **1a**$^{\bullet+}$ and its π-dimer$^{\bullet+}$ disappeared by neutralization with chloride anion generated by the initial radiolytic processes. The initial concentrations of **1a**$^{\bullet+}$ chloride anion were measured to be 1.0×10^{-6} M. The decay of the transient absorption at 400, 450, and 650 nm followed a second-order rate with a rate constant of $k_N = 4.7 \times 10^{10}$ M^{-1} s^{-1}. Since the π-dimer$^{\bullet+}$ of **1a**$^{\bullet+}$ has absorptions at 400, 450, 500−600, and 650 nm, the increase in the peaks at 480 and 520 nm involves

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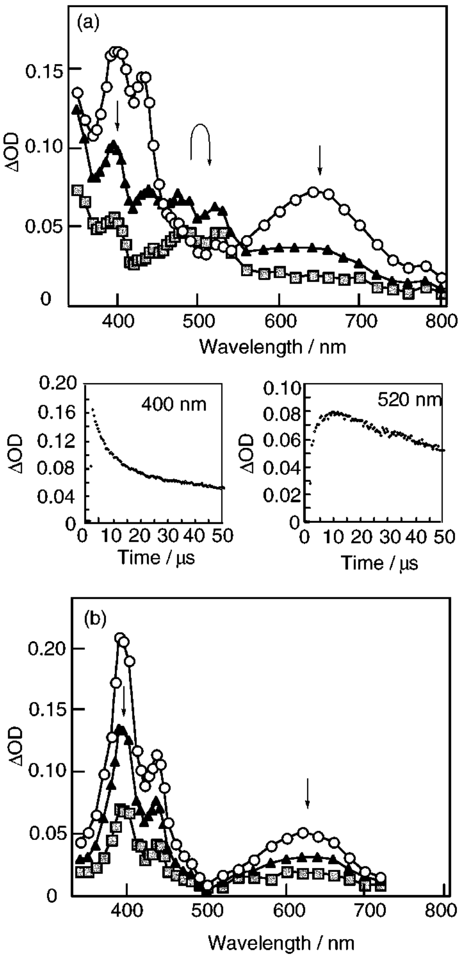

Figure 4. Transient absorption spectra observed immediately after the pulse (open circle), 5 μs after the pulse (solid triangle), and 20 μs after the pulse (gray square) during pulse radiolyses of 1.0 × 10^{-2} M **1a** (a) and 1.0 × 10^{-2} M **5a** (b) in 1,2-dichloroethane at room temperature. Attachments with (a) are the time profiles of transient absorptions at 400 and 520 nm.

the formation of $\mathbf{4a}^{\bullet+}$ and the decay of the π-dimer$^{\bullet+}$ of $\mathbf{1a}^{\bullet+}$. According to the mechanism, the time profile of the transient absorption at 520 nm was analyzed to give the rate constant of $k_r = 5.3 \times 10^5$ s^{-1}.

Discussion

Electron-Transfer Processes. The k_q values were calculated to be (1.6−2.1) × 10^9 M^{-1} s^{-1} on the basis of the Stern−Volmer analyses and τ_{DCA}. The k_q values are approximately equal to the diffusion-controlled rate constant of acetonitrile at room temperature ($k_{diff} = 2.0 \times 10^{10}$ M^{-1} s^{-1}). The free energy change, ΔG_{et}, is in the region of −14 to −24 kcal mol^{-1} (Table 1).[14] This indicates that the electron transfer from **1**−**3** to ^{1}DCA* occurs exergonically to give $\mathbf{1}^{\bullet+}$−$\mathbf{3}^{\bullet+}$ and DCA$^{\bullet-}$ at the diffusion-controlled rate.

The formation of the radical ions was confirmed by the transient absorption measurements with the laser flash photolysis. The electron transfer from **1a** to ^{1}DCA* immediately occurs to give $\mathbf{1a}^{\bullet+}$ and DCA$^{\bullet-}$ after irradiation of a 355 nm laser flash of the mixture of **1a** and DCA in an argon-saturated acetonitrile. The quantum efficiency of formation of the free radical ions from radical ion pairs was determined to be 0.77 from the measurement of the concentration of DMS$^{\bullet+}$.[11] The value is larger than $\phi_{\mathrm{MeONp}^{\bullet+}} = 0.43$ and 0.17 for the formation of the 1-methoxynaphthalene and 1,4-dimethoxynaphthalene radical cation (MeONp$^{\bullet+}$) from the radical ion pair MeONp$^{\bullet+}$/DCA$^{\bullet-}$.

Reactivity of the Radical Cations. $\mathbf{3a}^{\bullet+}$ with peaks at around 400 and 700 nm, having one naphthyl group, dimerized with **3a** to form an intermolecular π-dimer radical cation $(\mathbf{3a})_2^{\bullet+}$ above the **3a** concentrations of 3.0 × 10^{-2} M upon warming below 90 K (Figure 3a). Since $(\mathbf{3a})_2^{\bullet+}$ disappeared with no formation of the binaphthyl or binaphthyl radical cation, neutralization of $(\mathbf{3a})_2^{\bullet+}$ with chloride anion occurs at the rate constant of k_N. It is suggested that two **3a** are reproduced from the electron transfer from DCA$^{\bullet-}$ to $(\mathbf{3a})_2^{\bullet+}$ because of no product formation in the DCA-sensitized photoinduced electron-transfer reaction of **3a**.

On the other hand, the absorption bands at around 400 and 700 nm similar to those of $\mathbf{3a}^{\bullet+}$ and the additional broad absorption bands at 500−600 and 800−850 nm were observed independent of the concentration of **1a** during the γ-radiolysis of **1a** at 77 K (Figure 3c). These absorption bands are assigned to $\mathbf{1a}^{\bullet+}$ and its intramolecular dimer radical cation (π-dimer$^{\bullet+}$). The broad absorption bands at 500−600 and 800−850 nm disappeared faster than those at around 400 and 700 nm. The similar spectrum of the π-dimer$^{\bullet+}$ of $\mathbf{1a}^{\bullet+}$ was also immediately observed after the 8 ns electron pulse during the pulse radiolysis of **1a** in 1,2-dichloroethane at room temperature (Figure 4a). These results show that $\mathbf{4a}^{\bullet+}$ is eliminated from the π-dimer$^{\bullet+}$ of $\mathbf{1a}^{\bullet+}$ at $k_r = 5.3 \times 10^5$ s^{-1}.

The spectral change indicates that the equilibrium between $\mathbf{1a}^{\bullet+}$ and its π-dimer$^{\bullet+}$ is not attained after the irradiation in the *n*-butyl chloride rigid matrix at 77 K. Dissociation of the π-dimer$^{\bullet+}$ to $\mathbf{1a}^{\bullet+}$ predominantly occurs with increasing free volume in the matrix upon warming. The warming is not enough for the activation barrier for the formation of the binaphthyl radical cation from the π-dimer$^{\bullet+}$ to $\mathbf{1a}^{\bullet+}$. On the other hand, equilibrium is completely attained even for the electron pulse duration of 8 ns at room temperature. The π-dimer$^{\bullet+}$ with an internal energy greater than the activation barrier undergoes elimination of the binaphthyl radical cation.

It has been reported that the 1,3-di-1-naphthylpropane radical cation (DNP$^{\bullet+}$) forms an intramolecular π-dimer$^{\bullet+}$ in the photoinduced electron transfer with 1,2-dicyanobenzene (DCB) in acetonitrile.[10d] The transient absorption spectrum of this π-dimer$^{\bullet+}$ with the peak at 720 nm was observed during laser flash photolyses (308 nm). The broad absorption peaks of the π-dimer$^{\bullet+}$ of $\mathbf{1a}^{\bullet+}$ at 500−600 and 800−850 nm during the γ-radiolyses were different from that of π-dimer$^{\bullet+}$ of DNP$^{\bullet+}$. The difference is probably attributable to the difference in the spacers, O−P(O)−O and $(CH_2)_3$, between the two naphthyl groups in $\mathbf{1a}^{\bullet+}$ and DNP$^{\bullet+}$, respectively.[17]

Mechanism of the Photoinduced Electron-Transfer Reaction. The DCA-sensitized photoinduced elec-

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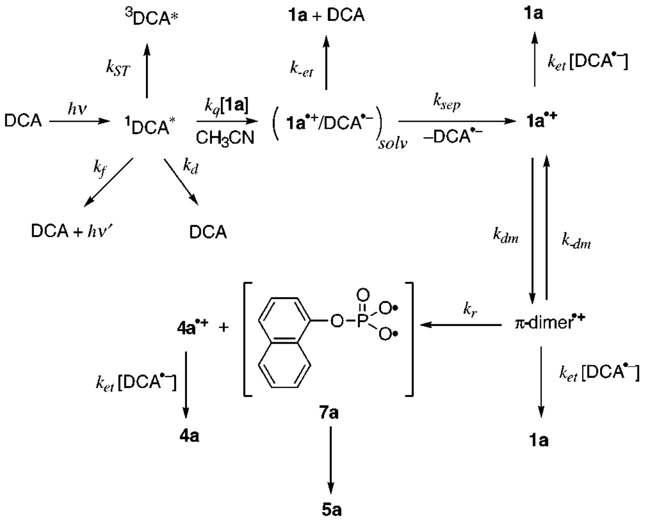
(17) The difference may also be attributable to the difference of the structures of the intramolecular p-dimer$^{\bullet+}$ of $\mathbf{1a}^{\bullet+}$ and DNP$^{\bullet+}$. The partially overlapped structure of two naphthyl groups has been reported for the π-dimer$^{\bullet+}$ of DNP$^{\bullet+}$.[10d] The full overlapped structure of two naphthyl groups may be supposed for the π-dimer$^{\bullet+}$ of $\mathbf{1a}^{\bullet+}$ because of the flexible O−P(O)−O chain. However, detailed experiments including measurement of the charge-resonance bands of the π-dimer$^{\bullet+}$ of $\mathbf{1a}^{\bullet+}$ and DNP$^{\bullet+}$ are necessary to assign the structures.

Scheme 2



tron transfer reaction of **1a** is explained by the mechanism as shown in Scheme 2. The electron transfer initially occurs from **1a** to ^{1}DCA* to form a radical ion pair, **1a**$^{•+}$/DCA$^{•-}$, at the diffusion-controlled rate. Solvent separation and back-electron transfer competitively occur in **1a**$^{•+}$/DCA$^{•-}$ to give **1a**$^{•+}$ and DCA$^{•-}$ at $k_{sep} = 5.0 \times 10^8$ s^{-1} [11] and **1a** and DCA at k_{-et}, respectively. Dimerization in **1a**$^{•+}$ occurs to reversibly form π-dimer$^{•+}$. The rate constant of $k_{dm} = 1.0 \times 10^8 - 1.0 \times 10^9$ s^{-1} was assumed because π-dimer$^{•+}$ was immediately observed after a 8 ns pulse during pulse radiolysis (Figure 4a).

Elimination of **4a**$^{•+}$ from the π-dimer$^{•+}$ occurs to give the intermediate **7a**, while electron transfer from DCA$^{•-}$ to π-dimer$^{•+}$ competitively occurs with recovery of **1a** and DCA. Electron transfer from DCA$^{•-}$ to **4a**$^{•+}$ occurs to give **4a** and DCA, while **7a** abstracts hydrogens from solvent to give **5a**. This mechanism is suggested by the high material balances for the formation of **4a** and **5a** and the lack of hydrogen donor molecules except for solvent molecules. Intermediacy of **7a** and formation of **5a** via the hydrogen abstraction from the solvent molecules have been already reported in the direct photolysis of **4a** in acetonitrile, methanol, ethanol, and cyclohexane.[6d]

The quantum efficiency of formation of the free radical ions described above ($\phi_{DMS^{•+}} = 0.77$) is represented in eq 1. The value of $k_{-et} = 1.5 \times 10^8$ s^{-1} was calculated

$$k_{sep}/(k_{sep} + k_{-et}) = 0.77 \qquad (1)$$

from k_{sep}.

The quantum yield of **4a** (= 0.0013) is represented in eq 2 where [**1a**] is the concentration of **1a** and k_{dm} and k_{-dm} denote the rate constants of the intramolecular dimerization of **1a**$^{•+}$ and the dissociation of π-dimer$^{•+}$ to **1a**$^{•+}$, respectively, on the basis of the quantitative forma-

$$\left(\frac{k_q[\mathbf{1a}]k_{sep}}{X\bullet(k_{-et} + k_{sep})} + \frac{k_{-dm}}{Y}\right)\frac{k_{dm}k_r}{Z\bullet Y} = 0.0013 \qquad (2)$$

$$X = \tau_{DCA}{}^{-1} + k_q[\mathbf{1a}]$$

$$Y = k_{et}[\mathrm{DCA}^{\bullet -}] + k_r + k_{-dm}$$

$$Z = k_{et}[\mathrm{DCA}^{\bullet -}] + k_{dm}$$

tion of **4a** from **4a**$^{•+}$ because of the high material balances (Table 1). The concentration of DCA$^{•-}$, [DCA$^{•-}$] = 2.9×10^{-5} M, was calculated using eq 1, $k_q = k_{et} = k_{diff} = 2.0 \times 10^{10}$ M^{-1} s^{-1} and [DCA] = 5.0×10^{-5} M. When the rate constant, $k_{dm} = 1.0 \times 10^8 - 10^9$ s^{-1}, was estimated, the rate constant, $k_{-dm} = 6.4 \times 10^8$ s^{-1}, was calculated. Therefore, the equilibrium constant, $K = k_{dm}/k_{-dm} = 0.16-1.6$, was determined.

On the basis of the quantum yields and the rate constants, branching ratios of the reaction pathways are estimated for the reactive intermediates such as ^{1}DCA*, **1a**$^{•+}$/DCA$^{•-}$, **1a**$^{•+}$, and the π-dimer$^{•+}$ as shown in Scheme 2. ^{1}DCA* reacts with **1a** to give **1a**$^{•+}$/DCA$^{•-}$ in 75% yield, which dissociates to give **1a**$^{•+}$ and DCA$^{•-}$ in 77% yield, **1a**$^{•+}$ reversibly gives π-dimer$^{•+}$ ($K = 0.16-1.6$), the elimination of **4a**$^{•+}$ from the π-dimer$^{•+}$ occurs to give an intermediate **7a** in 0.1−0.2% yield, and **4a**$^{•+}$ quantitatively gives **4a** through electron transfer with DCA$^{•-}$. Though the yield of **4a**$^{•+}$ from the π-dimer$^{•+}$ is very small, **4a**$^{•+}$ is selectively given from π-dimer$^{•+}$.

The reactions of **1b** and **2** are also explained by the similar mechanisms involving initial formation of the radical cations of **1b** and **2** (**1b**$^{•+}$ and **2**$^{•+}$), the formation of the π-dimer$^{•+}$ of **1b**$^{•+}$ and **2**$^{•+}$, the elimination of **4**$^{•+}$ to give **7**, and the formation of **4** and **5** as the final products. On the other hand, the DCA-sensitized photoinduced electron transfer reaction of **3** does not occur, although the electron transfer from **3** to ^{1}DCA* occurs to form **3**$^{•+}$ and DCA$^{•-}$. Since **3**$^{•+}$ has neither unimolecular nor bimolecular reactivities, **3** is completely recovered by the back-electron transfer from DCA$^{•-}$ to **3**$^{•+}$. It should be emphasized that the key intermediate is the π-dimer$^{•+}$ of two naphthyl groups formed in **1**$^{•+}$ and **2**$^{•+}$ having two and three naphthyl groups before the solvent separation of the radical ion pairs, **1**$^{•+}$/DCA$^{•-}$ and **2**$^{•+}$/DCA$^{•-}$.

Elimination of the binaphthyl radical cation does not occur in the π-dimer$^{•+}$ of DNP$^{•+}$ with a trimethylene spacer between the two naphthyl groups. Therefore, the electron-withdrawing character of the P(O) group of the O−P(O)−O spacer is responsible for the elimination of the binaphthyl radical cation. In other words, the O−P(O)−O spacer induces a unique reactivity of the π-dimer$^{•+}$ between the two naphthyl groups.[18]

Comparison of the Photoinduced Electron Transfer Reaction with Direct Photoreaction. We have compared the DCA-sensitized photoinduced electron transfer reaction with the direct photoreaction of **1** and **2** with respect to product formation. The quantum yield of **4** in the photoinduced electron-transfer reaction is approximately one-third of those in the direct photoreaction of **1** and **2**. Since efficiencies of the formation of **1a**$^{•+}$/DCA$^{•-}$ via the electron transfer from **1a** to ^{1}DCA* and the separation of **1a**$^{•+}$/DCA$^{•-}$ are sufficiently high (75 and 77%, respectively), the lower quantum yield of **4** is attributed to the dissociation of the π-dimer$^{•+}$ to **1a**$^{•+}$ at $k_{-dm} = 6.4 \times 10^8$ s^{-1} and the electron transfer with DCA$^{•-}$ at k_{et}[DCA$^{•-}$] = 5.8×10^5 s^{-1}. The energy gap between **1a**$^{•+}$ and the π-dimer$^{•+}$, which are in the ground states, is probably small because of the fast equilibrium between

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[18] The mechanism including a radical cation intermediate formed from rearrangement of one naphthyl group via fission of the *O*-naphthyl bond to the ipso position of another naphthyl group is not reasonable because **4a**$^{•+}$ is eliminated from the intramolecular π-dimer$^{•+}$ of **1a**$^{•+}$ and **4a** is the main product. If such radical cation would be formed, **4a**$^{•+}$ could not be eliminated, and several products such as isomers and/or addition products of **4a** could be formed from migration of naphthyl group and nucleophilic reactions of alcohols on the cationic center in the presence of alcohols.

1a$^{\bullet+}$ and the π-dimer$^{\bullet+}$. The dissociation of the π-dimer$^{\bullet+}$ to **1a**$^{\bullet+}$ results in the lower concentration of the π-dimer$^{\bullet+}$, which is a disadvantage of the photoinduced electron-transfer reactions of **1a** with respect to product formation.

The energy gap ($\Delta E = 12.4$ kcal mol^{-1}) between **1a** in the singlet excited state and the intramolecular excimer of **1a** is calculated from the difference in the emission peaks at $\lambda^{\mathrm{em}}{}_{\mathrm{max}} = 340$ and 400 nm, respectively. It is reasonably assumed that the energy gap between **1a**$^{\bullet+}$ and the π-dimer$^{\bullet+}$ is less than a few kcal mol^{-1}, since a fast equilibrium is attained between **1a**$^{\bullet+}$ and the π-dimer$^{\bullet+}$. Once the intramolecular excimer of **1a** is formed in the singlet excited **1a**, the intramolecular excimer of **1a** cannot dissociate to the monomeric excited state because of the large energy barrier. Therefore, the intramolecular excimer of **1a** reacts unimolecularly to give **4** and **5** or is deactivated to the ground state by solvent molecules. The deactivation of the intramolecular excimer of **1a** occurs at the rate constant of 7×10^7 s^{-1}, since the lifetime was measured to be 14 ns. Therefore, it is estimated from the yield of **4** that the elimination of **4** from the intramolecular excimer of **1a** occurs at the rate constant of the order of 10^6 s^{-1}. It is notable that elimination of **4** from the intramolecular excimer of **1a** occurs in a low yield in spite of the large rate constant of 10^6 s^{-1}.

On the other hand, the π-dimer$^{\bullet+}$ formed by the intramolecular dimerization of **1a**$^{\bullet+}$ reacts unimolecularly to give **4**$^{\bullet+}$ and **7** or is deactivated to **1a** by the electron transfer from DCA$^{\bullet-}$ to **1a**$^{\bullet+}$ at the rate constant (10^{10}–10^{11} M^{-1} s^{-1}) faster than the diffusion-controlled rate constant of the solvent because of the electrostatic property. The apparent rate constant of the deactivation is calculated to be on the order of 10^5–10^6 s^{-1} at [DCA$^{\bullet-}$] $= 2.9 \times 10^{-5}$ M. Therefore, the unimolecular reaction of π-dimer$^{\bullet+}$ competitively occurs to give **4**$^{\bullet+}$ and **7** at the rate constant of $k_{\mathrm{r}} = 5.3 \times 10^5$ s^{-1}.

Since several excited species such as the monomeric singlet excited state, excimer, and triplet excited state involve in the direct photoreactions of **1** and **2**, the corresponding reaction pathways occur to give several products depending on the experimental conditions.[6d] On the other hand, the π-dimer$^{\bullet+}$ is the key intermediate to give **4**$^{\bullet+}$, which quantitatively gives **4** in the DCA-sensitized photoinduced electron transfer reactions of **1** and **2**. Therefore, controlling the reaction pathways and selective formation of **4** can be easily accomplished in the DCA-sensitized photoinduced electron transfer reactions of **1** and **2** in comparison to the direct photoreaction. This is an advantage of the photoinduced electron-transfer reactions of **1** and **2** from the synthetic point of view.

Conclusions

The DCA-sensitized photoinduced electron transfer reactions of **1** and **2** occur to give **4** by the mechanism as shown in Scheme 2. An electron transfer from **1a** to ^{1}DCA* gives the radical ion pair **1a**$^{\bullet+}$/DCA$^{\bullet-}$ in 75% yield, which dissociates to **1a**$^{\bullet+}$ and DCA$^{\bullet-}$ in 77% yield, **1a**$^{\bullet+}$ reversibly gives the π-dimer$^{\bullet+}$ ($K = 0.16$–1.6), elimination of **4a**$^{\bullet+}$ from the π-dimer$^{\bullet+}$ selectively occurs at $k_{\mathrm{r}} = 5.3 \times 10^5$ s^{-1} to give an intermediate **7a**, and **4a**$^{\bullet+}$ quantitatively gives **4a** via electron transfer with DCA$^{\bullet-}$. The lower quantum yield of **4** is attributed to the reverse reaction from the π-dimer$^{\bullet+}$ to **1a**$^{\bullet+}$ at $k_{-\mathrm{dm}} = (1.4$–$5.3) \times 10^8$ s^{-1} when the rate constant of the dimerization, $k_{\mathrm{dm}} = 1.0 \times (10^8$–$10^9)$ s^{-1}, is assumed. The π-dimer$^{\bullet+}$ is the key intermediate for the elimination of **4**$^{\bullet+}$ in which the O–P(O)–O spacer linked to two naphthyl groups acts as in an important role because of the electron-withdrawing character of the P(O) group.

Experimental Section

Materials. The substrates **1**–**3** were prepared according to the method described in the literature.[19] The reaction products were isolated by silica gel column chromatography and analyzed by GC–MS and ^{1}H and ^{13}C NMR spectroscopies. Authentic samples were synthesized to identify the reaction products by GC and HPLC. The GC–MS and ^{1}H and ^{13}C NMR data of the materials were shown in our previous paper.[6d] Acetonitrile was dried using phosphorus pentoxide (P_2O_5) under distillation, and DCA was used after recrystallization from benzene.

General Methods. The photoirradiation was carried out using a 300 W medium-pressure Hg lamp with a 10 mm thick $BiCl_3$/HCl filter (cutoff $<$ 355 nm) at ambient temperature. The mixture solution was charged in a Pyrex tube with bubbling argon to purge off any dissolved air. Oxidation potentials (E^{ox}) of the substrates in dry acetonitrile (1.0×10^{-2} M) were measured by cyclic voltammetry using a potensiostat and function generator at a scan speed of 100 mV s^{-1}. The fluorescence spectra of DCA were measured at a concentration of 5×10^{-5} M in the presence and absence of **1**–**3** and recorded using a double-beam fluorescence spectrometer in the range of 400–700 nm. The fluorescence lifetime was measured by the single-photon counting method. Laser flash photolyses of the sample solutions were performed at room temperature by a flash at 355 nm (4 ns, 20 mJ pulse^{-1}) obtained by the third-harmonic oscillation from a Nd:YAG laser.[20] γ-Radiolyses of substrates in degassed butyl chloride at 77 K were performed in a 1.0 mm thick quartz cell using a ^{60}Co γ source; concentration of substrate was $(1$–$30) \times 10^{-3}$ M.[21] Pulse radiolyses of the sample solutions were performed at room temperature using an electron pulse (8 ns, 28 MeV, 0.7 kGy per pulse) obtained from a linear accelerator at Osaka University.[22] The initial concentrations of radical cations of the substrates and chloride anion generated during the pulse radiolyses in DCE at room temperature were measured to be 1.0×10^{-6} M according to the peak intensity of the radical cation of *trans*-stilbene at 480 nm (absorption coefficient, 6.5×10^4 M^{-1} cm^{-1})[22] generated under the present experimental conditions.

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