Photoinduced electron-transfer reactions of tri-1-naphthyl phosphate and di-1-naphthyl methylphosphonate sensitised by 9,10-dicyanoanthracene

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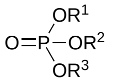
1,1′-Binaphthyl is formed by photoinduced electron-transfer reactions of tri-1-naphthyl phosphate and di-1-naphthyl methylphosphonate sensitised by 9,10-dicyanoanthracene in MeCN, while no reaction occurs in the case of mono-1-naphthyl and di- or tri-phenyl esters.

Photochemical reactions of organophosphorus compounds have been widely studied from the mechanistic and synthetic points of view.[1] Recently much attention has been paid to the photoreactivities of caged compounds of phosphates and phosphonates with an aryl substituent as a chromophore *in vivo*.[2] Radical cations of trivalent phosphorous compounds such as phosphines or phosphites generated in photoinduced electron-transfer reactions have been found to be oxidised by MeOH.[3] Although photoinduced electron-transfer reactions of organic compounds have been extensively investigated,[4,5] little is known about aryl phosphates and phosphonates. Electron-transfer reactions of aryl phosphates and phosphonates are of particular importance in relation to the caged compounds *in vivo*. We report here the photoinduced electron-transfer reactions of phosphates **1** and methylphosphonates **2** with aromatic substituents sensitised by 9,10-dicyanoanthracene.

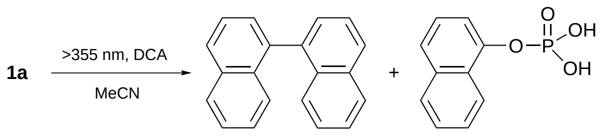


$O{=}P(OR^1)(OR^2)(OR^3)$

1a $R^1 = R^2 = R^3$ = 1-naphthyl
b $R^1 = R^2 = R^3$ = 4-methoxy-1-naphthyl
c $R^1 = R^2 = \text{Et}, R^3$ = 1-naphthyl
d $R^1 = R^2 = \text{Et}, R^3$ = 4-methoxy-1-naphthyl
e $R^1 = \text{H}, R^2 = R^3 = 4\text{-MeOC}_6\text{H}_4$
f $R^1 = \text{Me}, R^2 = R^3 = 4\text{-MeOC}_6\text{H}_4$

An argon-saturated MeCN solution containing of 5×10^{-5} M of 9,10-dicyanoanthracene (DCA) and 1×10^{-3} M of tri-1-naphthyl phosphate **1a** was irradiated with a medium-pressure Hg lamp using a $BiCl_3$–HCl filter (cutoff < 355 nm) for 1 h (conversion 15%) to give 1,1′-binaphthyl **3a** and 1-naphthyl phosphate **4a** with a 1 : 1 ratio and a qunatum yield of 0.0013 (Scheme 1). Similarly both **3a** and **4a** were formed as the main products in the photoreaction of a di-1-naphthyl methylphosphonate **2a** and DCA mixture.

4,4′-Dimethoxy-1,1′-binaphthyl **3b** was formed in the cases of tris(4-methoxy-1-naphthyl) phosphate **1b** and bis(4-methoxy-1-naphthyl) methylphosphonate **2b**, while no reaction occurred in the cases of mono-1-naphthyl (**1c**, **1d**) and diphenyl derivatives (**1e**, **1f**, **2c**, **2d**). These results show that the photoreaction occurs only in the compounds with two or three naphthyl substituents linked by an O–P(O)–O chain. Since fluorescence of ^{1}DCA* was completely quenched with **1** or **2** and the free-energy change of the quenching is exergonic with $\Delta G_{\text{et}} = -15$ or -25 kcal mol^{-1} (1 cal = 4.184 J), respectively, electron transfer proceeds from **1** or **2** to ^{1}DCA* to give radical cations of **1** or **2** ($\mathbf{1}^{\cdot+}$ or $\mathbf{2}^{\cdot+}$) and radical anion of DCA ($\text{DCA}^{\cdot-}$) at the diffusion-controlled rate.‡



3a **4a**

Scheme 1

Laser flash photolyses of a mixture of DCA and **1a** were performed to clarify the reaction mechanism of the formation of **3a** and **4a**.§ The transient absorption spectrum in the range of 430–750 nm with a peak at around 700 nm was observed at 20 ns after a 4 ns flash in argon-saturated MeCN (Fig. 1). The 700 nm peak was completely quenched, while an absorption in the range of 430–500 nm was observed even in oxygen-saturated MeCN. The 430–500 nm band disappeared in the presence of *trans*-4,4′-dimethoxystilbene (DMS) with formation of $\text{DMS}^{\cdot+}$.[5] The 700 nm band is assigned to $\text{DCA}^{\cdot-}$, while the 430–500 nm band is assigned to $\mathbf{1a}^{\cdot+}$. The assignments were confirmed by the measurement of $\mathbf{1a}^{\cdot+}$ formed during γ-radiolysis of **1a** in a butyl chloride rigid matrix at 77 K.¶ The quantum yield of $\mathbf{1a}^{\cdot+}$ formation was measured to be ϕ = 0.04–0.07 from that of $\text{DMS}^{\cdot+}$ fromation in the presence of DMS. The smaller value suggests that the back electron-transfer in the radical ion pair of $\text{DCA}^{\cdot-}$ and $\mathbf{1a}^{\cdot+}$ is significantly exergonic with $\Delta G_{-\text{et}} = -50$ kcal mol^{-1} and occurs more favourably than the solvent separation to give $\text{DCA}^{\cdot-}$ and $\mathbf{1a}^{\cdot+}$.

The decay of $\mathbf{1a}^{\cdot+}$ should correspond to the formation of **3a**. Unfortunately, the optical densities of the 430–500 nm band due to $\mathbf{1a}^{\cdot+}$ were too small to be analysed. Pulse radiolysis of **1a** in 1,2-dichloroethane at room temperature (Fig. 2) was performed to clarify the formation of **3a** from $\mathbf{1a}^{\cdot+}$.‖ The transient absorption spectrum assigned to $\mathbf{1a}^{\cdot+}$ with sharp bands at 400 and 430 nm and a broad band at 550–750 nm was observed

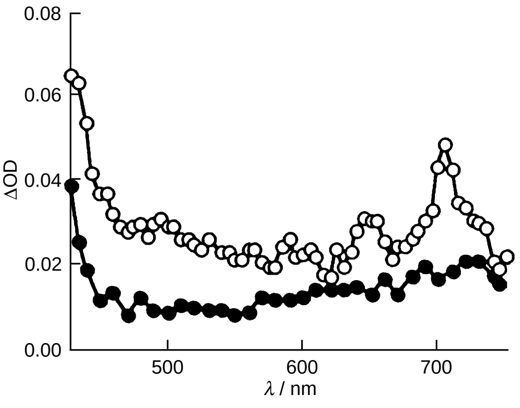
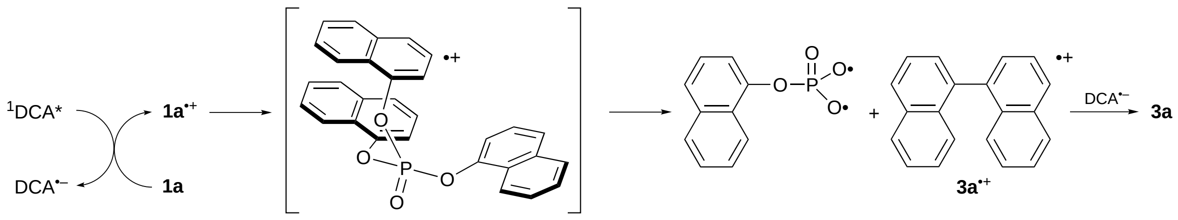


Fig. 1 Transient absorption spectra immediately after a flash during laser flash photolysis of **1a**–DCA in (○) argon-saturated and (●) oxygen-saturated MeCN



Scheme 2

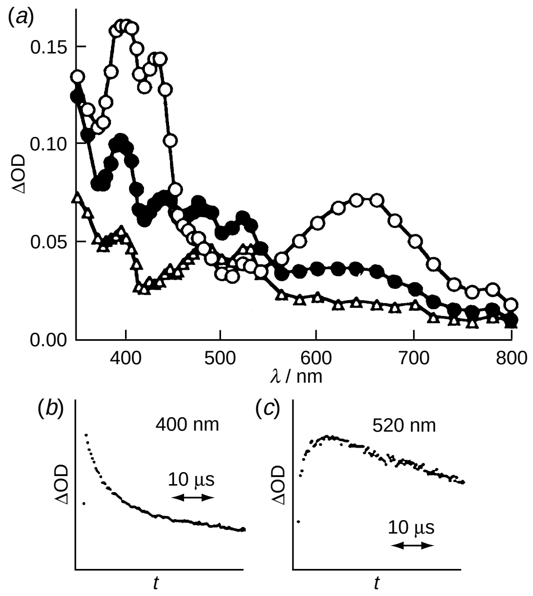


Fig. 2 (*a*) Transient absorption spectral changes during pulse radiolysis of **1a** in argon-saturated 1,2-dichloroethane: (○) immediately after the pulse, (●) 5 µs after the pulse, and (Δ) 20 µs after the pulse. Kinetic traces illustrating the time profiles of (*b*) ΔOD_{400} and (*c*) ΔOD_{520}.

immediately after an 8 ns pulse, and decayed with formation of new bands at 480 and 520 nm assigned to **3a**$^{\bullet+}$ at the first-order rate constant of $k = 8.9 \times 10^4$ s^{-1}.

On the other hand, the spectrum of **1c**$^{\bullet+}$ showed sharp bands at 390 and 440 nm and a broad band at 550–700 nm, was slightly different in the shape and peak wavelength from that for **1a**$^{\bullet+}$, and decayed without formation of any new bands. It is well known that naphthalene$^{\bullet+}$ dimerises with a neutral naphthalene to form a π-dimer radical cation with a 580 nm band at the equilibrium constant of $K = 520$ M^{-1} in PhCN,[6] and that 1,3-di-1-naphthylpropane$^{\bullet+}$ forms a stable intramolecular dimer radical cation.[7] Phosphate **1a** in the singlet excited state forms intramolecularly a face-to-face excimer between two naphthyl groups.[1c] Therefore, a face-to-face structure between two naphthyl groups is suggested to be present in **1a**$^{\bullet+}$, decomposing into **3a**$^{\bullet+}$.

Consequently, electron transfer from **1a** to ^{1}DCA* occurs to give **1a**$^{\bullet+}$ and DCA$^{\bullet-}$, **1a**$^{\bullet+}$ with the face-to-face structure between two naphthyl groups decomposes to **3a**$^{\bullet+}$ and the residue, and **3a** is finally formed as the stable product from the reduction of **3a**$^{\bullet+}$ with DCA$^{\bullet-}$ (Scheme 2).

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Footnotes

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‡ Since the Stern–Volmer constants, $k_q\tau$, in the fluorescence quenching of ^{1}DCA* by **1** and **2** were found to be 270–320 M^{-1} for **1** and **2**, $k_q = (1.6–2.1) \times 10^{10}$ M^{-1} s^{-1} was calculated to be approximately equal to the diffusion-controlled rate constant from the lifetime of ^{1}DCA*, $\tau = 14.9$ ns using the literature value (ref. 5). The oxidation potentials, $E^{ox}_{1/2}$, of **1** and **2** were measured by cyclic voltammetry at a platinum electrode in dry MeCN with 0.1 M Et_4NClO_4 as a supporting electrolyte. The free energy changes, ΔG_{et}, were calculated by using the Rehm–Weller equation (refs. 5 and 8).

§ Laser flash photolyses of the sample solutions were performed at room temperature by a flash at 355 nm (5 ns, 20 mJ pulse^{-1}) obtained by the third-harmonic oscillation from a Nd : YAG laser (ref. 9).

¶ γ-Radiolyses of the samples in degassed butyl chloride at 77 K were performed by a ^{60}Co γ source; concentration of substrate, 10^{-3} to 10^{-2} M (ref. 10).

‖ Pulse radiolyses of the sample solutions were performed at room temperature using an electron pulse (8 ns, 28 MeV) obtained from a linear accelerator at Osaka University (ref. 11).

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