

Photochemical Reactions of Coenzyme PQQ (Pyrroloquinolinequinone) and Analogues with Benzyl Alcohol Derivatives via Photoinduced Electron Transfer

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Abstract: Photochemical redox reactions of the trimethyl ester of coenzyme PQQ (PQQTME) with benzyl alcohol derivatives (ArCH₂OH), tetrahydrofuran, and 1,4-cyclohexadiene occur efficiently under visible light irradiation in MeCN to yield PQQTMEH₂ (reduced PQQTME in the quinol form) and the corresponding dehydrogenated products (ArCHO, furan, and benzene) quantitatively. A similar photochemical oxidation of benzyl alcohols also occurs with phenanthrolinequinone derivatives (PTQ), benzoquinolinequinone derivatives (BQQ), and phenanthrenequinone (PQ). PQQTME and the analogues are essentially nonfluorescent in MeCN, and the photochemical reaction of the *o*-quinones is retarded significantly in the presence of molecular oxygen. Transient absorption spectra of the triplet excited states of the *o*-quinones were detected in laser flash photolysis of the MeCN solutions. From the decay of T–T spectra were determined the lifetimes of the triplet excited states of the *o*-quinones. The quenching rate constants of the triplet excited states by benzyl alcohols agree with the observed rate constants of the photochemical reduction of the *o*-quinones with the same substrates determined from the saturated dependence of quantum yields on the benzyl alcohol concentrations. Such an agreement confirms that the photochemical reaction proceeds via the triplet excited state of the quinones. Dependence of the observed rate constants k_{obs} of the photochemical redox reaction on the one-electron oxidation potential E°_{ox} of the substrates as well as the results of kinetic deuterium isotopic study indicates that the photochemical redox reactions between the *o*-quinones and the substrates proceed via photoinduced electron transfer from the substrate to the triplet excited state of the *o*-quinone, followed by proton and hydrogen atom transfer to yield the quinol and the corresponding oxidation products. The transient absorption spectra of the radical ion pair formed in the photoinduced electron transfer have been detected successfully in laser flash photolysis of the *o*-quinone–benzyl alcohol systems.

Introduction

PQQ (pyrroloquinolinequinone) is a versatile *o*-quinone cofactor that was first isolated and identified from methanol dehydrogenase of methylotrophic bacteria in 1979.¹ Since then, much effort has been devoted to finding several kinds of quinone-containing enzymes (referred to as quinoproteins) from a variety of organisms of both bacterial and mammalian origins.² In addition to the enzymological importance, the growth stimulating activity for microorganisms,³ the pharmaceutical

activities,^{4–6} and the nutritional importance⁷ of PQQ itself have also been revealed to indicate that PQQ serves versatile functions in several living systems. Thus, recent attention has been focused on the chemistry of coenzyme PQQ to evaluate its biological

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(1) Salisbury, S. A.; Forrest, H. S.; Cruse, W. B. T.; Kennard, O. *Nature* **1979**, *280*, 843.

(2) The presence of PQQ itself in certain enzymes has been disproved, but instead amino acid derived coenzymes such as 6-hydroxydopa (TOPA), tryptophan tryptophylquinone (TTQ), and 2-alkylthiophenol derivative (Tyr-Cys) were found from bovine serum amine oxidase, methylamine dehydrogenase, and galactose oxidase, respectively. See: *Principles and Applications of Quinoproteins*; Davidson, V. L., Ed.; Marcel Dekker: New York, 1993.

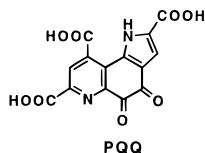
(3) (a) Ameyama, M.; Shinagawa, E.; Matsushita, K.; Adachi, O. *Agric. Biol. Chem.* **1984**, *48*, 2909. (b) Shima, M.; Yamamoto, H.; Ninomiya, K.; Kato, N.; Adachi, O.; Ameyama, M.; Sakazawa, C. *Agric. Biol. Chem.* **1984**, *48*, 2873. (c) Ameyama, M.; Shinagawa, E.; Matsushita, K.; Adachi, O. *Agric. Biol. Chem.* **1984**, *48*, 3099. (d) Ameyama, M.; Shinagawa, E.; Matsushita, K.; Adachi, O. *Agric. Biol. Chem.* **1985**, *49*, 699. (e) Ameyama, M.; Matsushita, K.; Shinagawa, E.; Hayashi, M.; Adachi, O. *BioFactors* **1988**, *1*, 51. (f) Adachi, O.; Okamoto, K.; Matsushita, K.; Shinagawa, E.; Ameyama, M. *Agric. Biol. Chem.* **1990**, *54*, 2751.

(4) (a) Watanabe, A.; Hobara, N.; Tsuji, T. *Curr. Ther. Res.* **1988**, *44*, 896. (b) Watanabe, A.; Hobara, N.; Ohsawa, T.; Higashi, T.; Tsuji, T.; Hiroshima, J. *Med. Sci.* **1989**, *38*, 49.

(5) Nishigori, H.; Yasunaga, M.; Mizumura, M.; Lee, J. W.; Iwatsuru, M. *Life Sci.* **1989**, *45*, 593.

(6) Hamagishi, Y.; Murata, S.; Kamei, H.; Oki, T.; Adachi, O.; Ameyama, M. *J. Pharmacol. Exp. Ther.* **1990**, *255*, 980.

(7) (a) Killgore, J.; Smidt, C.; Duich, L.; Romero-Chapman, N.; Tinker, D.; Reiser, K.; Melko, M.; Hyde, D.; Rucker, R. B. *Science* **1989**, *245*, 850. (b) Smidt, C. R.; Steinberg, F. M.; Rucker, R. B. *Proc. Soc. Exp. Biol. Med.* **1991**, *197*, 19.



functions at a molecular level. Thermal redox reactions of coenzyme PQQ with several biologically important substances such as alcohols,⁸ amines,⁹ amino acids,¹⁰ thiols,¹¹ and glucose¹² have been studied extensively to provide valuable insight into the biological functions of quinoproteins. Structure–reactivity relationships of coenzyme PQQ have also been investigated in detail by using several PQQ model compounds to reveal the structural uniqueness of coenzyme PQQ as compared to ordinary *o*-quinone compounds.^{13,14}

Photophysics and photochemistry of ubiquitous coenzymes such as flavins and NAD(P)H have so far been studied extensively.¹⁵ Although flavins have been believed to act as near-UV/blue-light photoreceptors,¹⁶ many photophysiological data of the pertinent blue-light photoreceptors cannot be explained by the exclusive action of flavins.¹⁷ Numerous processes in plants, fungi, and microorganisms are controlled by near-UV/blue-light receptors which may include unknown photoreceptors absorbing light between 300 and 500 nm.^{16,18} A new class of photopigments such as hypericin,¹⁹ blepharismine,²⁰ stentorin,¹⁹ and oxyblepharismine²¹ have recently been identified as photosensing chromophores and the photo-

physics and the photochemical reactions have merited increasing attention.^{22,23} However, there has been no report on the photophysics and photochemistry of coenzyme PQQ which absorbs light between 300 and 500 nm.

We report herein for the first time the photophysics and photoredox reactions of coenzyme PQQ and analogues which are found to be much stronger oxidants than flavins, providing valuable insight into the viability as a photoreceptor.²⁴ Extensive comparison of the photochemical redox reaction of PQQ with related heterocyclic *o*-quinones is also made to elucidate the common reaction mechanism of the photoredox reactions of the *o*-quinones.

Experimental Section

Materials. Trimethyl 4,5-dihydro-4,5-dioxo-1*H*-pyrrolo[2,3-*f*]quinoxaline-2,7,9-tricarboxylate (PQQTME), 1,7-phenanthroline-5,6-dione (1,7-PTQ), 4,7-phenanthroline-5,6-dione (4,7-PTQ), 1,10-phenanthroline-5,6-dione (1,10-PTQ), 1-aza-phenanthrene-5,6-dione (1-BQQ), and 4-aza-phenanthrene-5,6-dione (4-BQQ) were obtained from previous studies.²⁵ Spectrophotometric grade acetonitrile used as a solvent was purchased from Nacalai Tesque. α,α -Dideuterio-*p*-methoxybenzyl alcohol (*p*-MeOC₆H₄CD₂OH) was prepared from 4-methoxybenzoic acid by the reduction with LiAlD₄ according to the general procedures. Tris(2,2′-bipyridine)ruthenium dichloride hexahydrate, [Ru(bpy)₃]Cl₂·6H₂O (bpy = 2,2′-bipyridine), was obtained commercially from Aldrich. The oxidation of [Ru(bpy)₃]Cl₂ with lead dioxide in aqueous H₂SO₄ gives [Ru(bpy)₃]³⁺, which was isolated as the PF₆⁻ salt, [Ru(bpy)₃](PF₆)₃.²⁶ All other chemicals used in this study were commercial products of the highest available purity and were further purified by the standard methods, if necessary.²⁷

Product Analysis. Typically, a CD₃CN solution (0.7 mL) containing PQQTME (5.0 × 10⁻³ M) and benzyl alcohol (1.5 × 10⁻² M) in an NMR tube sealed tightly with a silicon rubber cap and Parafilm was deaerated by bubbling argon gas through it using a Teflon tube for 15 min. The solution was irradiated with a xenon lamp with UV-31 TOSHIBA color filter for 24 h. Since PQQTMEH₂ is hardly soluble in CD₃CN, it gradually precipitates with the progress of the reaction. Thus, the resulting aldehyde in the supernatant of the CD₃CN solution can be analyzed by ¹H NMR, and then the solvent was removed under reduced pressure to obtain PQQTMEH₂ as a brown solid. Identification of PQQTMEH₂ and the oxidation products (benzaldehyde derivatives) was performed by comparing the ¹H NMR spectra to those of the authentic samples.²⁸ Product analysis of the photooxidation of THF and 1,4-cyclohexadiene by PQQTME was carried out in a similar manner, and the oxidation products (furan and benzene) were detected

(8) (a) Itoh, S.; Kawakami, H.; Fukuzumi, S. *J. Am. Chem. Soc.* **1997**, *119*, 439. (b) Itoh, S.; Kawakami, H.; Fukuzumi, S. *Biochemistry* **1998**, *37*, 6562.

(9) (a) Ohshiro, Y.; Itoh, S.; Kurokawa, K.; Kato, J.; Hirao, T.; Agawa, T. *Tetrahedron Lett.* **1983**, *24*, 3465. (b) Itoh, S.; Kitamura, Y.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1907. (c) Sleath, P. R.; Noar, J. B.; Eberlein, G. A.; Bruce, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 3328. (d) Rodriguez, E. J.; Bruce, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 7947. (e) Mure, M.; Itoh, S.; Ohshiro, Y. *Chem. Lett.* **1989**, 1491. (f) Mure, M.; Itoh, S.; Ohshiro, Y. *Tetrahedron Lett.* **1989**, *30*, 6875. (g) Itoh, S.; Mure, M.; Ogino, M.; Ohshiro, Y. *J. Org. Chem.* **1991**, *56*, 6857. (h) Ohshiro, Y.; Itoh, S. *Bioorg. Chem.* **1991**, *19*, 169.

(10) (a) Itoh, S.; Kato, N.; Ohshiro, Y.; Agawa, T. *Tetrahedron Lett.* **1984**, *25*, 4753. (b) Mure, M.; Suzuki, A.; Itoh, S.; Ohshiro, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1608. (c) Itoh, S.; Mure, M.; Suzuki, A.; Muraio, H.; Ohshiro, Y. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1245.

(11) (a) Itoh, S.; Kato, N.; Ohshiro, Y.; Agawa, T. *Chem. Lett.* **1985**, 135. (b) Itoh, S.; Kato, N.; Mure, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 420.

(12) Itoh, S.; Mure, M.; Ohshiro, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1580.

(13) (a) Itoh, S.; Kato, J.; Inoue, T.; Kitamura, Y.; Komatsu, M.; Ohshiro, Y. *Synthesis* **1987**, 1067. (b) Itoh, S.; Inoue, T.; Fukui, Y.; Huang, X.; Komatsu, M.; Ohshiro, Y. *Chem. Lett.* **1990**, 1675. (c) Itoh, S.; Fukui, Y.; Ogino, M.; Haranou, S.; Komatsu, M.; Ohshiro, Y. *J. Org. Chem.* **1992**, *57*, 2788. (d) Itoh, S.; Fukui, Y.; Haranou, S.; Ogino, M.; Komatsu, M.; Ohshiro, Y. *J. Org. Chem.* **1992**, *57*, 4452.

(14) (a) Noar, J. B.; Rodriguez, E. J.; Bruce, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 7198. (b) Noar, J. B.; Bruce, T. C. *J. Org. Chem.* **1987**, *52*, 1942.

(15) (a) Heelis, P. F. *Chem. Soc. Rev.* **1982**, *11*, 15. (b) Fukuzumi, S.; Tanaka, T. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, pp 578–687. (c) Fukuzumi, S. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, CT, 1992; pp 67–175. (d) Fukuzumi, S.; Itoh, S. In *Advances in Photochemistry*; Neckers, D. C., Volman, D. H., von Büna, G., Eds.; Wiley: New York, 1998; Vol. 25, pp 107–172.

(16) Galland, P.; Senger, H. *J. Photochem. Photobiol. B* **1988**, *1*, 277.

(17) (a) Galland, P.; Senger, H. *Photochem. Photobiol.* **1988**, *48*, 811. (b) Galland, P.; Keiner, P.; Dörnemann, D.; Senger, H.; Brodhun, B.; Häder, D.-P. *Photochem. Photobiol.* **1990**, *51*, 675. (c) Galland, P.; Eslava, A. P.; Alvarez, M. I. *Photochem. Photobiol.* **1997**, *66*, 879.

(18) Lenci, F. In *Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; pp 1445–1449.

(19) Tao, N.; Orlando, M.; Hyon, J.-S.; Gross, M.; Song, P.-S. *J. Am. Chem. Soc.* **1993**, *115*, 2526.

(20) (a) Checucci, G.; Shoemaker, R. S.; Bini, E.; Cerny, R.; Tao, N.; Hyon, J.-S.; Gioffre, D.; Ghetti, F.; Lenci, F.; Song, P.-S. *J. Am. Chem. Soc.* **1997**, *119*, 5762, 9588. (b) Maeda, M.; Naoki, H.; Matsuoka, T.; Kato, Y.; Kotsuki, H.; Utsumi, K.; Tanaka, T. *Tetrahedron Lett.* **1997**, *38*, 7411.

(21) Spitzner, D.; Höfle, G.; Klein, I.; Pohlen, S.; Ammermann, D.; Jaenicke, L. *Tetrahedron Lett.* **1998**, *39*, 4003.

(22) (a) Song, P.-S.; Kim, I.-H.; Florell, S.; Tamai, N.; Yamazaki, T.; Yamazaki, I. *Biochim. Biophys. Acta* **1990**, *1040*, 58. (b) Cubeddu, R.; Ghetti, F.; Lenci, F.; Ramponi, R.; Taroni, P. *Photochem. Photobiol.* **1990**, *52*, 567. (c) Yamazaki, T.; Yamazaki, I.; Nishimura, Y.; Dai, R.; Song, P.-S. *Biochim. Biophys. Acta* **1993**, *1143*, 319. (d) Ghetti, F.; Checucci, G.; Lenci, F.; Heelis, P. F. *J. Photochem. Photobiol. B Biol.* **1992**, *13*, 315.

(23) (a) Angelini, N.; Quaranta, A.; Checucci, G.; Song, P.-S.; Lenci, F. *Photochem. Photobiol.* **1998**, *68*, 864. (b) Xia, G.; He, X.; Zhou, Y.; Zhang, M.; Shen, T. *J. Photochem. Photobiol. A Chem.* **1998**, *114*, 31. (c) Wells, T. A.; Losi, A.; Dai, R.; Scott, P.; Park, S.-M.; Golbeck, J.; Song, P.-S. *J. Phys. Chem.* **1997**, *101*, 366, 7460.

(24) A preliminary report on the photochemical reaction of PQQ has appeared: Itoh, S.; Komori, T.; Chiba, Y.; Fukuzumi, S.; Ishida, A.; Takamuku, S. *J. Chem. Soc., Chem. Commun.* **1996**, 465.

(25) Itoh, S.; Maruta, J.; Fukuzumi, S. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1429.

(26) DeSimone, R. E.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 2343.

(27) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Butterworth-Heinemann: Oxford, 1988.

(28) Itoh, S.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1911.

by ^1H NMR. The ^1H NMR measurements were performed using a JEOL JNM-GSX-400 (400 MHz) NMR spectrometer or a JEOL EX 270 (270 MHz) NMR spectrometer.

PQQTMEH₂ (in DMSO-*d*₆): δ 3.94 (s, 3H, $-\text{CH}_3$), 4.00 (s, 3H, $-\text{CH}_3$), 4.11 (s, 3H, $-\text{CH}_3$), 7.44 (d, 1H, $J = 2.0$ Hz, H-3), 8.47 (s, 1H, $-\text{OH}$), 8.54 (s, 1H, H-8), 10.29 (s, 1H, $-\text{OH}$), 12.17 (s, 1H, NH).

The photochemical oxidation of benzyl alcohols by other *o*-quinones was carried out in the same procedure, and the reduced products from the quinones were identified by comparing their ^1H NMR spectra with those of the authentic samples. The authentic sample of the quinol derivative was generated by the reduction of the corresponding quinone by methylhydrazine in CD₃CN.^{28,29}

1,7-PTQH₂: δ 7.58 (dd, 1H, $J = 4.3, 8.1$ Hz), 7.62 (dd, 1H, $J = 4.1, 8.1$ Hz), 8.60 (dd, 1H, $J = 1.6, 8.1$ Hz), 8.87 (dd, 1H, $J = 1.6, 4.3$ Hz), 8.93 (dd, 1H, $J = 1.8, 4.1$ Hz), 9.39 (dd, 1H, $J = 1.6, 8.1$ Hz).

4,7-PTQH₂: δ 7.64 (dd, 2H, $J = 4.6, 8.2$ Hz), 8.94 (dd, 2H, $J = 1.6, 4.6$ Hz), 9.02 (dd, 2H, $J = 1.6, 8.2$ Hz).

1-BQQH₂: δ 7.49–7.60 (m, 2H), 7.68 (t, 1H, $J = 6.9$ Hz), 8.23 (d, 1H, $J = 7.8$ Hz), 8.53 (d, 1H, $J = 8.1$ Hz), 8.80 (m, 1H), 9.14 (d, 1H, $J = 7.8$ Hz).

4-BQQH₂: δ 7.54 (dd, 1H, $J = 4.5, 8.5$ Hz), 7.58–7.72 (m, 2H), 8.28 (dd, 1H, $J = 1.2, 7.8$ Hz), 8.65 (dd, 1H, $J = 1.2, 7.8$ Hz), 8.86 (dd, 1H, $J = 1.4, 4.5$ Hz), 9.01 (dd, 1H, $J = 1.4, 8.5$ Hz).

PQH₂: δ 7.52 (dt, 2H, $J = 1.5, 7.5$ Hz), 7.60 (dt, 2H, $J = 1.5, 7.5$ Hz), 8.21 (dd, 2H, $J = 1.5, 7.5$ Hz), 8.67 (dd, 2H, $J = 1.5, 7.5$ Hz).

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)³⁰ was used for the quantum yield determination of the photooxidation of benzyl alcohol derivatives by the *o*-quinones. Typically, an MeCN solution (3.0 mL) containing PQQTME (1.5×10^{-4} M) and benzyl alcohol (9.7×10^{-3} to 2.9×10^{-1} M) was deaerated by bubbling argon gas through it using a teflon tube for 15 min in a 10-mm-square quartz cuvette sealed tightly with a silicon rubber cap and Parafilm. This solution was irradiated with monochromatized light of $\lambda = 360$ nm from a Shimadzu RF-5000 fluorescence spectrophotometer. Under the conditions of actinometry experiments, both the actinometer and PQQTME absorbed essentially all the incident light of $\lambda = 360$ nm. The light intensity of monochromatized light of $\lambda = 360$ nm was determined as 2.49×10^{-8} einstein s⁻¹ with the slit width of 20 nm. The photochemical reaction was monitored by using a Hewlett-Packard 8452A diode-array spectrophotometer. The quantum yields were determined from the decrease in absorbance due to PQQTME ($\lambda = 356$ nm, $\epsilon = 1.47 \times 10^4$ M⁻¹ cm⁻¹). The quantum yields of the photochemical reactions with other benzyl alcohol derivatives, THF, and 1,4-cyclohexadiene by PQQTME were determined in a similar manner.

In the case of 1,7-PTQ, 4,7-PTQ, 1-BQQ, 4-BQQ, and PQ, monochromatized light of $\lambda = 280$ nm was used for the photochemical redox reaction, and the light intensity of monochromatized light of $\lambda = 280$ nm was determined as 3.38×10^{-9} einstein s⁻¹ with the slit width of 20 nm. The progress of the reaction was followed by monitoring the formation of the quinol at its λ_{max} .

Laser Flash Photolysis. Typically, an MeCN solution containing PQQTME (1.0×10^{-4} M) was irradiated with a laser flash at room temperature. A flash at 355 nm was obtained by the third-harmonic oscillation from a Nd:YAG laser (Quantel Model Brilliant) which was operated by a large current pulse-power supply. The single laser flash has a diameter of 0.5 cm, 5 ns duration, 5 mJ pulse⁻¹, and incident photon number 1.4×10^{18} pulse⁻¹ cm⁻² measured by a pyroelectric power meter (Gentec ED-500). An almost collinear arrangement was used, such that the narrow laser beam passed through the central part of the irradiated volume. The probe beam was obtained from a 450 W Xe-lamp (Osram, XBO-450) which was also operated by a large current pulse-power supply. The probe beam was passed through an iris with a diameter of 0.2 cm, and sent into the sample solution with perpendicular intersection of the laser beam. In the meantime, the probe beam was arranged closely to the entrance side of the laser beam. Then

(29) For the mechanism of methylhydrazine reduction of PQQ, see: Mure, M.; Nii, K.; Inoue, T.; Itoh, S.; Ohshiro, Y. *J. Chem. Soc., Perkin Trans. 2* **1990**, 315.

(30) Hitchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, 235, 518.

the probe beam is focused to a computer-controlled monochromator (CVI Laser, Digikrom-240) by two lenses and four mirrors. The output of monochromator is monitored by a PMT (photomultiplier tube; Hamamatsu Photonix, R1417 or R2497). The signal from the PMT is recorded on a transient digitizer (Tektronix, 7912AD with plug-ins, 7A19 and 7B92A). Total system control is carried out with a microcomputer (Sharp, X-98000) which is connected to all measurement components with a GP-IB interface. The data processing was carried out by Igor Pro version 3.10 on a Macintosh personal computer. To avoid photolysis of sample solution by the probe beam, a suitable cutoff filter was used. An irradiation cell was placed in the beam of the linear accelerator and in front of the beam port with about 15 cm distance.

For the quenching experiments of the triplet excited state of PQQTME by 2,4-dimethoxybenzyl alcohol, the irradiation laser wavelength of PQQTME was 355 nm which excites PQQTME selectively. The solution was deoxygenated by bubbling argon gas through it for 30 min prior to the measurements. Relative intensities of the triplet-triplet absorption spectrum at maxima (420 nm) were measured for MeCN solutions containing PQQTME (5.0×10^{-5} M) and the alcohol at various concentrations. There was no change in the shape but there was a change in the lifetime of the T-T absorption spectrum by the addition of the alcohol. The Stern-Volmer relationship (eq 1) was obtained for the triplet lifetimes in the absence (τ_0) and presence of the substrate (τ) and the concentrations of the substrate [DH₂]. The observed quenching rate constants k_q were obtained from the slope of a linear plot of τ_0/τ and [DH₂] according to eq 1.

$$\tau_0/\tau = 1 + k_q\tau_0[\text{DH}_2] \quad (1)$$

For the quenching experiments of the triplet excited states of 1,7-PTQ and 4,7-PTQ (3.8×10^{-5} M), a 266 nm Nd:YAG laser was used to obtain the T-T absorption spectra and to perform the quenching experiments of the triplet excited states of the quinones (440 nm) by benzyl alcohol (9.7×10^{-4} to 4.9×10^{-3} M).

For the measurements of transient absorption spectra in the reactions of the triplet excited states of PQQTME and 4,7-PTQ with 2,4-dimethoxybenzyl alcohol (5.0×10^{-4} M) or benzyl alcohol (5.0×10^{-3} M) in MeCN, the PQQTME and 4,7-PTQ solutions (5.0×10^{-5} M) were excited by a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 532 nm with the power of 7 mJ. Since PQQTME and 4,7-PTQ in MeCN containing benzyl alcohols disappeared appreciably by each laser shot (532 nm; 7 mJ), the transient spectra were recorded using fresh solutions in each laser excitation. All experiments were performed at 295 K.

Phosphorescence Experiments. The phosphorescence spectra of the quinones (1.0×10^{-4} M) in 2-methyltetrahydrofuran were measured by irradiating with a xenon lamp using a capillary cell on a Hitachi 850 fluorescence phosphorescence spectrophotometer at 77 K.

Stopped-Flow Measurements. The transient absorption spectra of the radical cation of 2,4-dimethoxybenzyl alcohol were measured in the electron-transfer oxidation of 2,4-dimethoxybenzyl alcohol with [Ru(bpy)₃]³⁺ (bpy = 2,2'-bipyridine) using a UNISOKU RSP-601 stopped-flow rapid scan spectrophotometer equipped with the MOS-type high sensitive photodiode array under deaerated conditions. Gate time for the measurement was set at 5 ms. Typically, deaerated MeCN solutions of [Ru(bpy)₃]³⁺ and 2,4-(MeO)₂C₆H₃CH₂OH were transferred to the spectrophotometric cell by means of a glass syringe which had earlier been purged with a stream of argon.

Electrochemical Measurements. The second harmonic alternating current voltammetry (SHACV) and the cyclic voltammetry measurements of heterocyclic *o*-quinones and substrates were performed on a BAS 100B electrochemical analyzer in deaerated MeCN containing 0.10 M NBu₄ClO₄ as a supporting electrolyte at 298 K. The gold working electrode (BAS) was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to the Ag/AgNO₃ (0.01 M) reference electrode. The E_{red}^0 and E_{ox}^0 values (vs Ag/Ag⁺) are converted to those vs SCE by adding 0.29 V.³¹

(31) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non-aqueous Systems*, Marcel Dekker: New York, 1990.

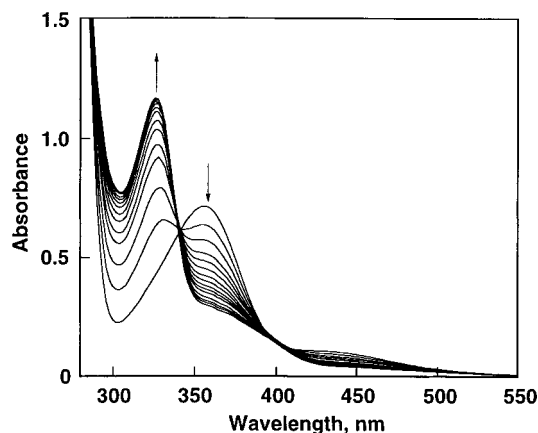
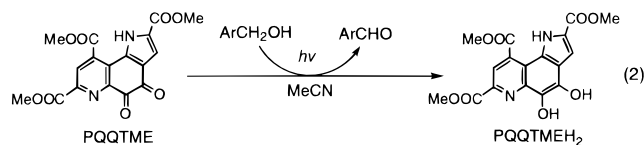


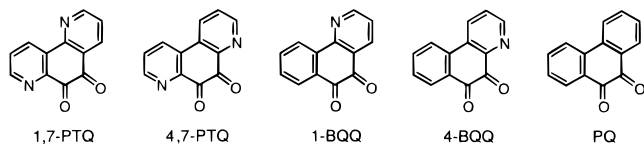
Figure 1. Spectral change observed in the photooxidation of *p*-MeOC₆H₄-CH₂OH (3.2×10^{-2} M) by PQQTME (5.1×10^{-5} M) in deaerated MeCN at 298 K under irradiation with a xenon lamp through a UV-31 TOSHIBA filter; 20 s time intervals.

Results and Discussion

Photochemical Redox Reactions of Coenzyme PQQ and the Analogues. Irradiation of a deaerated MeCN solution containing PQQTME (the trimethyl ester of coenzyme PQQ) and *p*-methoxybenzyl alcohol (ArCH₂OH, Ar = *p*-MeOC₆H₄) with a xenon lamp at 298 K results in formation of PQQTMEH₂ (reduced PQQTME in quinol form) and the corresponding aldehyde (ArCHO) as shown in eq 2. Figure 1 shows the spectral



change observed in the photochemical reaction of PQQTME (5.1×10^{-5} M) with *p*-methoxybenzyl alcohol (3.2×10^{-2} M). The decrease in absorbance at $\lambda_{\max} = 356$ nm due to the quinone is accompanied by the appearance of a new absorption band at $\lambda_{\max} = 326$ nm due to the quinol (PQQTMEH₂) with a clean isosbestic point at 342 nm.²⁸ The quantitative formation of PQQTMEH₂ and *p*-methoxybenzaldehyde in a 1:1 ratio was confirmed by the ¹H NMR spectra of the products in CD₃CN and DMSO-*d*₆ (see Experimental Section). The photochemical redox reaction of PQQTME also occurred with other benzyl alcohol derivatives (Ar = *p*-ClC₆H₄, C₆H₅, *p*-MeC₆H₄, 2,4-(MeO)₂C₆H₃), THF,³² and 1,4-cyclohexadiene to produce the corresponding oxidation products, ArCHO, furan, and benzene, respectively. The photochemical redox reaction of other *o*-quinones (PTQs, BQQs, and PQ) with ArCH₂OH also occurs



efficiently to produce the corresponding quinol and ArCHO quantitatively (see Experimental Section). It was confirmed that

(32) For the catalytic thermal oxidation of THF by oxygen, see: (a) Sen, A.; Lin, M.; Kao, L.-C.; Hutson, A. C. *J. Am. Chem. Soc.* **1992**, *114*, 6385. (b) Fazlur-Rahman, A. K.; Tsai, J.-C.; Nicholas, K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1334. (c) Aresta, M.; Fragale, C.; Quaranta, E.; Tommasi, I. *J. Chem. Soc., Chem. Commun.* **1992**, 315. (d) Hata, E.; Takai, T.; Mukaiyama, T. *Chem. Lett.* **1993**, 1513.

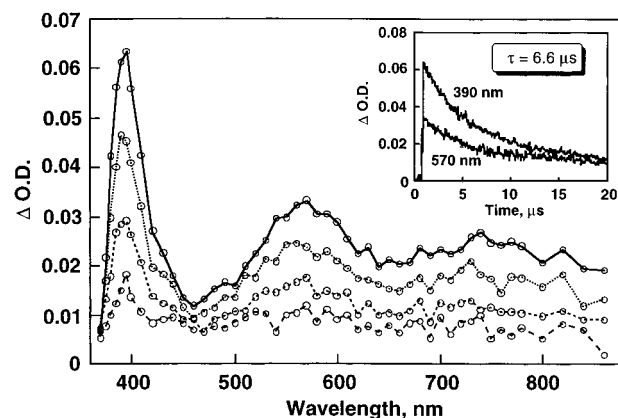


Figure 2. T–T absorption spectra of PQQTME obtained in the laser flash photolysis of a deaerated MeCN solution of PQQTME (5.0×10^{-5} M) at 298 K. Inset: Kinetic trace for the PQQTME triplet state decay at $\lambda = 390$ and 570 nm at 200 ns, 2.0 μ s, 6.0 μ s, and 14.0 μ s after laser excitation in deaerated MeCN at 298 K.

Table 1. T–T Absorption Maxima (λ_{\max}) and Lifetimes (τ_0) of the Triplet Excited State of Heterocyclic *o*-Quinones (3.8×10^{-5} to 7.5×10^{-5} M) in Deaerated MeCN at 298 K

heterocyclic <i>o</i> -quinone	λ_{\max} , nm	τ_0 , μ s
PQQTME	390	6.6
1,7-PTQ	440	4.3
4,7-PTQ	440	4.9
1-BQQ	440	2.5
4-BQQ	440	1.4
PQ	470	2.2

no thermal reaction occurred between the *o*-quinones and ArCH₂OH in the dark.

Excited States of PQQTME and Analogues. The photochemical reactions of the *o*-quinones are retarded significantly in the presence of dioxygen, which is a typical triplet quencher. The excitation of the absorption maximum band of an MeCN solution of each *o*-quinone results in no fluorescence.³³ These results indicate that the photochemical reaction of the *o*-quinones may proceed via the triplet excited state rather than the singlet excited state. Then, the direct detection of the triplet excited state of the *o*-quinones (³Q*) was carried out by laser flash photolysis. When PQQTME alone in deaerated MeCN was flashed with 355 nm laser light, a transient triplet–triplet (T–T) absorption spectrum having λ_{\max} at around 400 and 570 nm together with a broad band above 700 nm was observed as shown in Figure 2. The decay of each absorption obeyed first-order kinetics with an identical lifetime (τ_0) of 6.0 μ s (see the inset in Figure 2). Such a first-order decay suggests that a T–T annihilation process is negligible under the present experimental conditions. The transient triplet–triplet (T–T) absorption spectra of other quinones were also obtained by using a 266 nm laser light. The λ_{\max} values and the lifetimes (τ_0) obtained from the decay of the T–T absorption for the *o*-quinones are listed in Table 1. The λ_{\max} value of PQQ is 50 nm blue-shifted as compared to the values of PTQs and BQQs, whereas the λ_{\max} value of PQ is 30 nm red-shifted.³⁴

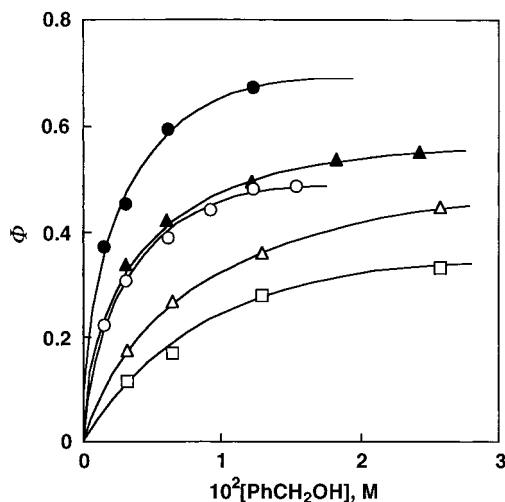
The triplet excitation energies (E_{0-0}) of the *o*-quinones are determined from the 0–0 band of phosphorescence of each *o*-quinone. The phosphorescence was monitored in 2-methyltetrahydrofuran glass at 77 K. The phosphorescence spectra

(33) Dekker, R. H.; Duine, J. A.; Frank, J.; Verwiel, P. E. J.; Westerling, J. *Eur. J. Biochem.* **1982**, *125*, 69.

(34) The blue shift of λ_{\max} of PQQTME as compared to the values of other *o*-quinones may be caused by the lower excitation energy of PQQTME than other *o*-quinones (see Table 3).

Table 2. Absorption Bands of Phosphorescence Peaks (λ_{0-0}), Triplet Excitation Energies (ΔE_{0-0}), One-Electron Reduction Potentials of the Ground States (E_{red}^0), and Triplet Excited States (E_{red}^{0*}) of the Heterocyclic *o*-Quinones

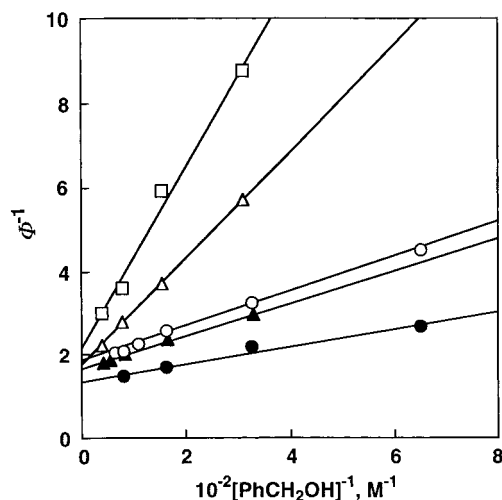
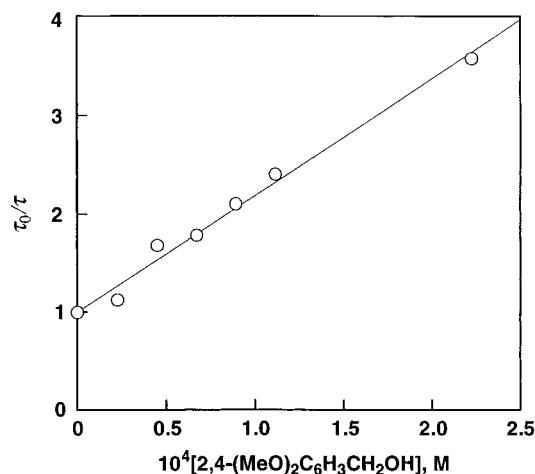
heterocyclic <i>o</i> -quinone	λ_{0-0} , nm	ΔE_{0-0} , eV	E_{red}^0 vs SCE, V	E_{red}^{0*} vs SCE, V
PQQTME	585	2.12	-0.53	1.59
1,7-PTQ	551	2.25	-0.53	1.72
4,7-PTQ	556	2.23	-0.52	1.71
1-BQQ	545	2.27	-0.62	1.65
4-BQQ	554	2.24	-0.62	1.62
PQ	549	2.26	-0.71	1.55

**Figure 3.** Dependence of quantum yields (Φ) on $[\text{PhCH}_2\text{OH}]$ for photooxidation of PhCH_2OH by heterocyclic *o*-quinones (2.2×10^{-4} to 3.5×10^{-4} M) (1,7-PTQ (○), 4,7-PTQ (●), 1-BQQ (△), 4-BQQ (▲), and PQ (□)) in deaerated MeCN at 298 K; monitored at $\lambda = 326$ (1,7-PTQ and 4,7-PTQ), 320 (4-BQQ), and 312 nm (1-BQQ and PQ).

exhibited vibrational progression (see Supporting Information) and the E_{0-0} values obtained from the λ_{0-0} values are listed in Table 2. The λ_{0-0} value of PQQTME (585 nm) is slightly blue-shifted as compared to that of riboflavin (610 nm).³⁵ The λ_{0-0} values of other *o*-quinones (549–556 nm) are further blue shifted as shown in Table 2.

The one-electron reduction potentials (E_{red}^{0*}) of triplet excited states of the *o*-quinones (${}^3\text{Q}^*$) can be obtained by adding the triplet excitation energy E_{0-0} to the one-electron reduction potentials (E_{red}^0) of the ground state *o*-quinones. The E_{red}^0 value of PQQTME (-0.53 V vs SCE) in MeCN has been reported previously.³⁶ The E_{red}^0 values of other *o*-quinones used in this study were determined by the cyclic voltammograms which give two reversible one-electron redox peaks corresponding to the $\text{Q}^{\bullet-}/\text{Q}$ and $\text{Q}^{2-}/\text{Q}^{\bullet-}$ couples, respectively. The E_{red}^0 and E_{red}^{0*} values thus determined are also listed in Table 2. The E_{red}^{0*} values of the triplet excited state of PQQTME (1.59 V vs SCE) and other *o*-quinones (1.55–1.72 V) are higher than that of the triplet excited state of riboflavin (1.41 V vs SCE).³⁷ This indicates that the triplet excited states of the *o*-quinones (${}^3\text{Q}^*$) act as stronger electron acceptors than that of riboflavin.

Quantum Yields. The quantum yields (Φ) for the photochemical redox reactions of ${}^3\text{Q}^*$ with benzyl alcohol derivatives were determined from a decrease in absorbance due to the quinone or an increase in absorbance due to the quinol using a

**Figure 4.** Plots of Φ^{-1} vs $[\text{PhCH}_2\text{OH}]^{-1}$ for photooxidation of PhCH_2OH by heterocyclic *o*-quinones (2.2×10^{-4} to 3.5×10^{-4} M) (1,7-PTQ (○), 4,7-PTQ (●), 1-BQQ (△), 4-BQQ (▲), and PQ (□)) in deaerated MeCN at 298 K.**Figure 5.** Stern–Volmer plot for quenching of ${}^3\text{PQQTME}^*$ by 2,4-(MeO) $_2\text{C}_6\text{H}_3\text{CH}_2\text{OH}$ in deaerated MeCN at 298 K.

ferrioxalate actinometer (see Experimental Section). The Φ value increases with an increase in the substrate concentrations, $[\text{DH}_2]$, to reach a limiting value (Φ_∞). Figure 3 shows typical examples for the photoreduction of *o*-quinones by benzyl alcohol (Supporting Information for other examples). Such a saturated dependence of Φ on $[\text{DH}_2]$ can be expressed by a double-reciprocal plot of Φ^{-1} vs $[\text{DH}_2]^{-1}$ according to

$$\Phi^{-1} = \Phi_\infty^{-1} [1 + (K_{\text{obs}}[\text{DH}_2])^{-1}] \quad (3)$$

where K_{obs} is the observed quenching constant of the triplet excited state, ${}^3\text{Q}^*$. From the linear plots of Φ^{-1} vs $[\text{DH}_2]^{-1}$ in Figure 4 are obtained the Φ_∞ and K_{obs} values (see Supporting Information for other examples). By using the τ_0 value of ${}^3\text{Q}^*$ listed in Table 1, the observed rate constants (k_{obs}) can be obtained from the K_{obs} values using the following relation, $K_{\text{obs}} = k_{\text{obs}}\tau_0$. The Φ_∞ and k_{obs} values are listed in Table 3.

The lifetimes of the triplet excited state of the *o*-quinones were shortened significantly by the presence of the benzyl alcohol derivatives. The Stern–Volmer plot (eq 1) is shown in Figure 5. From the slope is determined the quenching rate constant (k_q). The k_q values for the PQQTME–2,4-(MeO) $_2\text{C}_6\text{H}_3\text{CH}_2\text{OH}$, 1,7-PTQ– PhCH_2OH , and 4,7-PTQ– PhCH_2OH systems are determined as listed in Table 3. The k_q values

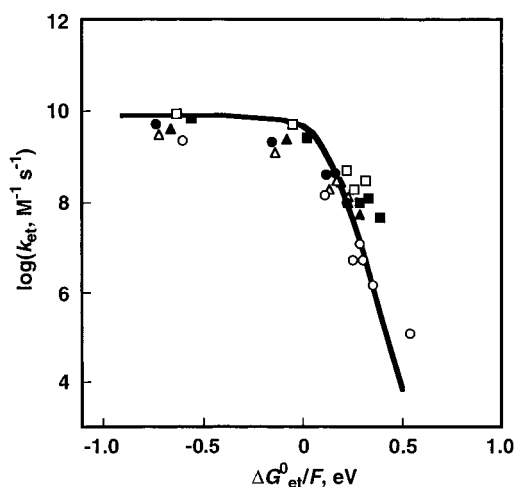
(35) Sun, M.; Moore, T. A.; Song, P.-S. *J. Am. Chem. Soc.* **1972**, *94*, 1730.

(36) Itoh, S.; Kawakami, H.; Fukuzumi, S. *J. Am. Chem. Soc.* **1998**, *120*, 7271.

(37) Seeley, G. R. *Photochem. Photobiol.* **1978**, *27*, 639.

Table 3. Free Energy Change of Electron Transfer (ΔG_{et}^0), Limiting Quantum Yields (Φ_{∞}), and Observed Rate Constants (k_{obs}) in the Photochemical Reactions of the Heterocyclic *o*-Quinones with Substrates in MeCN at 298 K

<i>o</i> -quinone	substrate	$\Delta G_{\text{et}}^0/F$, eV	Φ_{∞}	k_{obs} , M ⁻¹ s ⁻¹	k_{q} , M ⁻¹ s ⁻¹
PQQTME	2,4-(MeO) ₂ C ₆ H ₃ CH ₂ OH	-0.60	2.3×10^{-2}	2.3×10^9	2.0×10^9
	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	0.11	4.7×10^{-2}	1.4×10^8	
	<i>p</i> -MeC ₆ H ₄ CH ₂ OH	0.25	4.6×10^{-3}	5.2×10^6	
	<i>p</i> -ClC ₆ H ₄ CH ₂ OH	0.29	1.6×10^{-2}	1.2×10^7	
	C ₆ H ₅ CH ₂ OH	0.35	1.5×10^{-2}	1.4×10^6	
	1,4-cyclohexadiene	0.30	3.1×10^{-2}	5.0×10^6	
	THF	0.54	7.3×10^{-2}	1.2×10^5	
1,7-PTQ	2,4-(MeO) ₂ C ₆ H ₃ CH ₂ OH	-0.73	4.3×10^{-1}	5.1×10^9	1.1×10^8
	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	-0.15	4.9×10^{-1}	2.2×10^9	
	<i>p</i> -MeC ₆ H ₄ CH ₂ OH	0.12	4.4×10^{-1}	4.2×10^8	
	<i>p</i> -ClC ₆ H ₄ CH ₂ OH	0.16	4.4×10^{-1}	4.5×10^8	
	C ₆ H ₅ CH ₂ OH	0.22	5.5×10^{-1}	1.0×10^8	
4,7-PTQ	2,4-(MeO) ₂ C ₆ H ₃ CH ₂ OH	-0.72	3.7×10^{-1}	3.0×10^9	1.3×10^8
	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	-0.14	4.8×10^{-1}	1.2×10^9	
	<i>p</i> -MeC ₆ H ₄ CH ₂ OH	0.13	4.3×10^{-1}	1.9×10^8	
	<i>p</i> -ClC ₆ H ₄ CH ₂ OH	0.17	5.5×10^{-1}	3.1×10^8	
	C ₆ H ₅ CH ₂ OH	0.23	7.3×10^{-1}	1.3×10^8	
1-BQQ	2,4-(MeO) ₂ C ₆ H ₃ CH ₂ OH	-0.66	4.9×10^{-1}	4.2×10^9	1.3×10^8
	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	-0.08	5.4×10^{-1}	2.5×10^9	
	<i>p</i> -MeC ₆ H ₄ CH ₂ OH	0.19	3.9×10^{-1}	2.7×10^8	
	<i>p</i> -ClC ₆ H ₄ CH ₂ OH	0.23	4.4×10^{-1}	9.5×10^7	
	C ₆ H ₅ CH ₂ OH	0.29	5.7×10^{-1}	5.5×10^7	
4-BQQ	2,4-(MeO) ₂ C ₆ H ₃ CH ₂ OH	-0.63	6.7×10^{-1}	8.5×10^9	1.3×10^8
	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	-0.05	5.3×10^{-1}	5.2×10^9	
	<i>p</i> -MeC ₆ H ₄ CH ₂ OH	0.22	6.2×10^{-1}	5.3×10^8	
	<i>p</i> -ClC ₆ H ₄ CH ₂ OH	0.26	6.5×10^{-1}	1.9×10^8	
	C ₆ H ₅ CH ₂ OH	0.32	6.0×10^{-1}	3.1×10^8	
PQ	2,4-(MeO) ₂ C ₆ H ₃ CH ₂ OH	-0.56	5.1×10^{-1}	7.1×10^9	1.3×10^8
	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	0.02	4.2×10^{-1}	2.7×10^9	
	<i>p</i> -MeC ₆ H ₄ CH ₂ OH	0.29	3.7×10^{-1}	1.0×10^8	
	<i>p</i> -ClC ₆ H ₄ CH ₂ OH	0.33	3.0×10^{-1}	1.2×10^8	
	C ₆ H ₅ CH ₂ OH	0.39	4.6×10^{-1}	4.5×10^7	

**Figure 6.** Plots of $\log k_{\text{obs}}$ vs $\Delta G_{\text{et}}^0/F$ for oxidation of substrates by heterocyclic *o*-quinones (1,7-PTQ (○), 4,7-PTQ (●), 1-BQQ (△), 4-BQQ (◆), PQ (□), and PQQTME (■)) in deaerated MeCN at 298 K.

determined from the decay of the T–T absorption agree well with the observed rate constants (k_{obs}) determined from the dependence of Φ^{-1} on $[\text{DH}_2]^{-1}$. Such an agreement between k_{q} and k_{obs} strongly indicates the involvement of ${}^3\text{Q}^*$ as the reactive species in the photochemical reaction of the *o*-quinones.

Photoinduced Electron-Transfer Mechanism. The free energy change of photoinduced electron transfer from DH_2 to ${}^3\text{Q}^*$ (ΔG_{et}^0) is given by

$$\Delta G_{\text{et}}^0 = F(E_{\text{ox}}^0 - E_{\text{red}}^{0*}) \quad (4)$$

where E_{ox}^0 and E_{red}^{0*} are the one-electron oxidation potentials of DH_2 (Table 3)³⁸ and the one-electron reduction potential of

${}^3\text{Q}^*$ (Table 3), respectively. The $\log k_{\text{obs}}$ values in Table 3 including six different *o*-quinones are plotted against the ΔG_{et}^0 values in Figure 6, which exhibits a typical feature of the photoinduced electron-transfer process; the $\log k_{\text{obs}}$ value increases with a decrease in the ΔG_{et}^0 value to reach a plateau value corresponding to the diffusion rate constant ($1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) as the photoinduced electron transfer becomes energetically more favorable (i.e., more exergonic).^{39,40} The dependence of the activation free energy of photoinduced electron transfer ΔG^\ddagger on the free energy change of electron transfer to produce the radical ion pair (ΔG_{et}) has well been established as given by the Rehm–Weller free energy relation^{39,40}

$$\Delta G^\ddagger = (\Delta G_{\text{et}}/2) + [(\Delta G_{\text{et}}/2)^2 + (\Delta G_0^\ddagger)^2]^{1/2} \quad (5)$$

where ΔG_0^\ddagger is the intrinsic barrier that represents the activation free energy when the driving force of electron transfer is zero, i.e., $\Delta G^\ddagger = \Delta G_0^\ddagger$ at $\Delta G_{\text{et}} = 0$. The difference between ΔG_{et} for formation of the radical ion pair and ΔG_{et}^0 for formation of free radical ions is given by the work term w_{p} that is the energy required to bring the electron-transfer products, $\text{DH}_2^{+\bullet}$ and $\text{Q}^{\bullet-}$, to the mean separation distance of the radical ion pair. The w_{p} value for the opposite charges is taken as -0.1 eV .⁴¹ The ΔG^\ddagger values are related to the observed rate constant of electron transfer (k_{obs}) as given by

$$\Delta G^\ddagger = (2.3RT/F) \log[Z(k_{\text{obs}}^{-1} - k_{\text{diff}}^{-1})] \quad (6)$$

where Z is the collision frequency that is taken as 1×10^{11}

(38) Fukuzumi, S.; Kuroda, S. *Res. Chem. Intermed.* **1999**, 25, 789.(39) (a) Rehm, A.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, 73, 834. (b) Rehm, A.; Weller, A. *Isr. J. Chem.* **1970**, 8, 259.(40) Patz, M.; Mayr, H.; Maruta, J.; Fukuzumi, S. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1225.

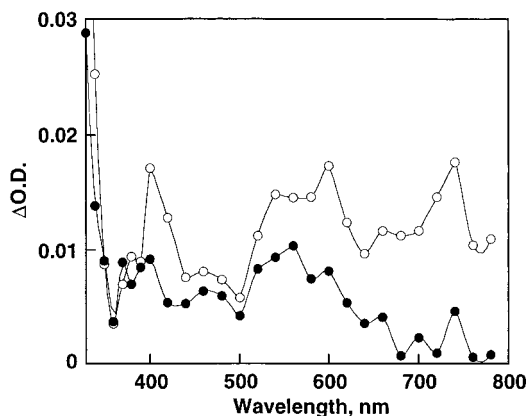


Figure 7. Transient absorption spectra observed in the photoreduction of PQQTME (5.0×10^{-5} M) with 2,4-(MeO) $_2$ C $_6$ H $_3$ CH $_2$ OH (5.0×10^{-4} M) at 250 ns (○) and 2.5 μ s (●) after laser excitation in deaerated MeCN at 298 K.

$M^{-1} s^{-1}$, F is the Faraday constant, and k_{diff} is the diffusion rate constant in MeCN ($2.0 \times 10^{10} M^{-1} s^{-1}$).³⁹ The best fit line for the plot of $\log k_{\text{obs}}$ vs ΔG_{et}^0 in MeCN shown by the solid line in Figure 6 gives the values of $\Delta G_{\text{et}}^{\ddagger}/F$ (0.1 eV) and w_p/F (-0.1 eV). All the data (32 k_{obs} values) in Table 3 fit the single correlation for the photoinduced electron transfer.⁴²

The occurrence of photoinduced electron transfer in the photochemical reaction of PQQTME with 2,4-dimethoxybenzyl alcohol has been confirmed by the laser flash photolysis study as follows. The transient absorption spectra in the visible region are observed by the laser flash photolysis of a deaerated MeCN solution containing 2,4-dimethoxybenzyl alcohol and PQQTME with 355 nm laser light as shown in Figure 7. The triplet-triplet absorption band of $^3\text{PQQTME}^*$ at 780 nm appearing immediately after nanosecond laser exposure decays in 1 μ s when the transient absorption bands at 390 and 570 nm are observed. These bands disappeared completely in 200 μ s. The absorption band at 570 nm in Figure 7 agrees with the reported absorption maximum due to the semiquinone radical anion of 1-methylated PQQTME.^{36,43}

To assign the absorption band at 390 nm, the transient absorption spectrum of the radical cation of 2,4-dimethoxybenzyl alcohol produced in the electron-transfer oxidation with $[\text{Ru}(\text{bpy})_3]^{3+}$ (bpy = 2,2'-bipyridine) was measured using a stopped-flow technique (see Experimental Section). Upon mixing a MeCN solution of $[\text{Ru}(\text{bpy})_3]^{3+}$ with 2,4-dimethoxybenzyl alcohol, the absorption bands at 450 and 390 nm appear instantly and only the latter band decayed to leave the absorption band due to $[\text{Ru}(\text{bpy})_3]^{2+}$. The difference spectrum between the initial and final spectra, exhibiting the absorption band at 390 nm due to the radical cation of 2,4-dimethoxybenzyl alcohol, is shown in Figure 8.⁴⁴ Thus, the absorption band at 390 nm in Figure 7 can be assigned to the radical cation of 2,4-dimethoxybenzyl alcohol.

The decay of the absorbance at 780 nm due to $^3\text{PQQTME}^*$ obeys pseudo-first-order kinetics, coinciding with the rise of

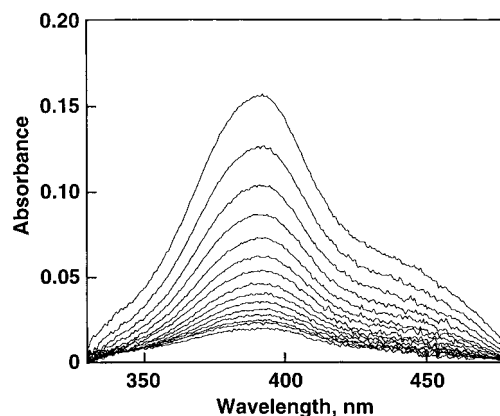


Figure 8. Transient absorption spectra observed in the electron-transfer oxidation of 2,4-(MeO) $_2$ C $_6$ H $_3$ CH $_2$ OH (5.0×10^{-3} M) by $[\text{Ru}(\text{bpy})_3]^{3+}$ (3.0×10^{-5} M) in MeCN at 298 K, 100 ms interval.

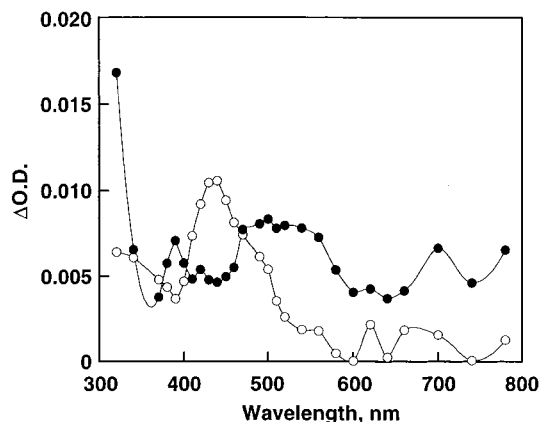


Figure 9. Transient absorption spectra observed in the photoreduction of 4,7-PTQ (5.0×10^{-5} M) with 2,4-(MeO) $_2$ C $_6$ H $_3$ CH $_2$ OH (5.0×10^{-4} M) at 250 ns (○) and 2.5 μ s (●) after laser excitation in deaerated MeCN at 298 K.

the absorbance at 570 nm due to $\text{PQQTME}^{\bullet-}$ (see Supporting Information). The rate constant for the electron transfer from 2,4-dimethoxybenzyl alcohol to $^3\text{PQQTME}^*$ is determined from the rise of the absorbance at 570 nm due to $\text{PQQTME}^{\bullet-}$ as $1 \times 10^9 M^{-1} s^{-1}$,⁴⁵ which agrees with the value determined from the dependence of Φ on the alcohol concentration (Table 3).

The occurrence of photoinduced electron transfer was also confirmed in the photochemical reaction of 4,7-PTQ with 2,4-dimethoxybenzyl alcohol as shown in Figure 9, where the transient absorption spectra due to the radical cation of 2,4-dimethoxybenzyl alcohol (390 nm) and the semiquinone radical anion, 4,7-PTQ $^{\bullet-}$ (480 nm),^{46,47} appear, accompanied by disappearance of the triplet-triplet absorption due to $^3\text{4,7-PTQ}^*$ (540 nm). Formation of 4,7-PTQ $^{\bullet-}$ was also confirmed in the photochemical reaction of 4,7-PTQ with benzyl alcohol (see Supporting Information).

The kinetic deuterium isotope effects on the quantum yields for the photochemical reactions were examined by using PQQTME, 4,7-PTQ, and 4-BQQ as the *o*-quinones, and benzyl alcohol, and *p*-methoxybenzyl alcohol as the substrates. The k_{obs} and Φ_{∞} values determined from the dependence of Φ on the substrate concentration are listed in Table 4. Essentially no

(41) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.

(42) Although there are some scatters in the correlation between $\log k_{\text{obs}}$ vs $\Delta G_{\text{et}}^0/F$, they may be attributed to the difference of the work term w_p being sensitive to the steric effects in the radical ion pair.

(43) The T-T absorption of $^3\text{PQQTME}^*$ at 570 nm shown in Figure 2 is overlapped with the absorption due to $\text{PQQTME}^{\bullet-}$ in the 250 ns spectrum in Figure 7.

(44) The transient absorption spectrum of the radical cation of 3,4-dimethoxybenzyl alcohol ($\lambda_{\text{max}} = 430$ nm) has been reported recently. The absorption maximum ($\lambda_{\text{max}} = 430$ nm) is red-shifted as compared to that of 2,4-dimethoxybenzyl alcohol radical cation. Bietti, M.; Baciocchi, E.; Steenken, S. *J. Phys. Chem. A* **1998**, *102*, 7337.

(45) The same value was obtained from the decay of the absorbance due to $^3\text{PQQTME}^*$ at 780 nm.

(46) Eckert, T. S.; Bruice, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 4431.

(47) The broad absorption at 480–550 nm is also observed in the transient absorption spectra in the photoreduction of 4,7-PTQ with PhCH $_2$ OH (see Supporting Information, S7) and it can be assigned to PTQ $^{\bullet-}$.

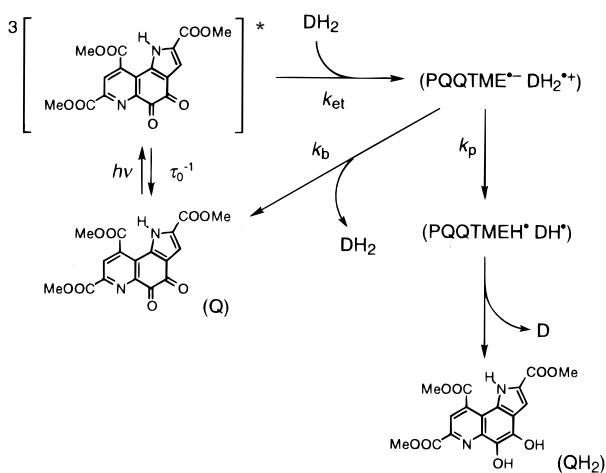
Table 4. Limiting Quantum Yields (Φ_∞), Observed Rate Constants (k_{obs}), and the Kinetic Isotope Effects ($\Phi_\infty^{\text{H}}/\Phi_\infty^{\text{D}}$, $k_{\text{obs}}^{\text{H}}/k_{\text{obs}}^{\text{D}}$) for the Photochemical Reactions of the Heterocyclic *o*-Quinones with Benzyl Alcohols in MeCN at 298 K

<i>o</i> -quinone	benzyl alcohol	Φ_∞	$\Phi_\infty^{\text{H}}/\Phi_\infty^{\text{D}}$	$k_{\text{obs}}, \text{M}^{-1} \text{s}^{-1}$	$k_{\text{obs}}^{\text{H}}/k_{\text{obs}}^{\text{D}}$
PQQTME	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	1.5×10^{-2}	1.6	1.4×10^6	1.0 ± 0.1
	$\text{C}_6\text{D}_5\text{CD}_2\text{OH}$	9.5×10^{-3}		1.4×10^6	
	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	4.7×10^{-2}		5.6×10^7	
4,7-PTQ	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	3.5×10^{-2}	1.3	5.6×10^7	1.0 ± 0.1
	<i>p</i> -MeOC ₆ H ₄ CD ₂ OH	4.8×10^{-1}		5.6×10^7	
4-BQQ	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	4.4×10^{-1}	1.1	5.6×10^7	1.0 ± 0.1
	<i>p</i> -MeOC ₆ H ₄ CD ₂ OH	5.3×10^{-1}		5.2×10^7	
	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	4.5×10^{-1}	1.2	5.4×10^7	1.0 ± 0.1

kinetic isotope effect is observed on the k_{obs} value (1.0 ± 0.1). However, the kinetic isotope effects (1.1–1.6) are observed on Φ_∞ .

The dependence of $\log k_{\text{obs}}$ on ΔG^0_{et} in Figure 6, direct detection of radical ions produced in the photoinduced electron-transfer reactions, and the absence of the kinetic isotope effect on k_{obs} strongly indicate that the reaction of ${}^3\text{Q}^*$ with the substrates (DH_2) proceeds via photoinduced electron transfer from DH_2 to ${}^3\text{Q}^*$ as shown in Scheme 1. The $\text{DH}_2^{\bullet+}$ such as

Scheme 1



benzyl alcohol radical cations produced in the photoinduced electron-transfer reactions are strong acids judging from the negative $\text{p}K_{\text{a}}$ values,^{15,38} while phenanthrolinequinone radical anions are known as strong bases ($\text{p}K_{\text{a}} = 8.0$).⁴⁸ Thus, proton transfer from $\text{DH}_2^{\bullet+}$ to $\text{Q}^{\bullet-}$ (k_{p}) may occur efficiently in competition with the back electron transfer from $\text{Q}^{\bullet-}$ to $\text{DH}_2^{\bullet+}$ (k_{b}) as shown in Scheme 1.⁴⁹ The subsequent facile hydrogen (electron and proton) transfer yields D and QH_2 .

By applying the steady-state approximation to the reactive intermediates, ${}^3\text{Q}^*$ and the radical ion pair in Scheme 1, the dependence of quantum yields on the substrate concentration $[\text{DH}_2]$ may be derived as shown in

$$\Phi = [k_{\text{p}}/(k_{\text{p}} + k_{\text{b}})]k_{\text{et}}\tau_0[\text{DH}_2]/(1 + k_{\text{et}}\tau_0[\text{DH}_2]) \quad (7)$$

where k_{et} is the rate constant of electron transfer from DH_2 to ${}^3\text{Q}^*$, k_{b} is the rate constant of the back electron transfer, and k_{p} is that of proton transfer from $\text{DH}_2^{\bullet+}$ to $\text{Q}^{\bullet-}$. The limiting quantum yield Φ_∞ corresponds to $k_{\text{p}}/(k_{\text{p}} + k_{\text{b}})$. Thus, the Φ_∞ values being smaller than unity in Table 3 and Table 4 may be ascribed to the competition of the proton-transfer step (k_{p}) with

(48) Evans, D. H.; Griffith, D. A. *J. Electroanal. Chem.* **1982**, *134*, 301.

(49) The small Φ_∞ values of PQQTME as compared with those of other *o*-quinones (Table 3) may be ascribed to the deprotonation of the pyrrole proton associated with the reduction of PQQTME,³⁶ which decelerates the proton transfer from $\text{DH}_2^{\bullet+}$.

the back electron-transfer process (k_{b}). When ArCH_2OH and THF in Table 3 is replaced by ArCD_2OH and THF-*d*₈, respectively, the kinetic deuterium isotope effects are observed on Φ_∞ as shown in Table 4. The observed kinetic deuterium isotope effects in Table 4 may be ascribed to those for proton transfer from $\text{DH}_2^{\bullet+}$ to $\text{Q}^{\bullet-}$ (k_{p}). The small kinetic deuterium isotope effects indicate that the proton transfer is a fast process with a small activation energy in each case. In contrast to this, an extraordinarily large kinetic isotope effect (e.g., $k_{\text{H}}/k_{\text{D}} = 61.5$) has been reported for hydride or hydrogen transfer from benzyl alcohol to *cis*-[$\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})$]²⁺ (py = pyridine) in MeCN.⁵⁰

The Φ_∞ values are rather constant irrespective of the difference in the E^0_{ox} values of benzyl alcohol derivatives. Such a constant dependence of Φ_∞ on the E^0_{ox} values suggests that the back electron-transfer process from $\text{Q}^{\bullet-}$ to $\text{DH}_2^{\bullet+}$ is not affected by the free energy change of electron transfer. Thus, the rate-determining step of the back electron transfer may be the intersystem crossing from the triplet radical ion pair formed initially to the singlet radical ion pair in which the back electron transfer occurs rapidly.

The coupling of electron transfer and proton transfer is a well-established alternative for the formal hydrogen atom transfer in an organic photochemical system,⁵¹ particularly in the case of photoreduction of flavins.^{15,37} Such a proton-coupled electron transfer has been suggested to play an important role in biological electron transfer.⁵² It is often difficult to determine whether the proton-coupled electron transfer is consecutive, i.e., electron transfer followed by proton transfer or vice versa, or a concerted process in one quantum mechanical tunneling event.⁵³ In the case of photooxidation of benzyl alcohol derivatives with the heterocyclic *o*-quinones, the photoinduced electron transfer process clearly precedes the proton-transfer step as demonstrated in this study.

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Supporting Information Available: Phosphorescence spectrum of a heterocyclic *o*-quinone (1-BQQ) (S1), dependence of the quantum yields (Φ) on $[\text{PhCH}_2\text{OH}]$ for photooxidation of PhCH_2OH by PQQTME (S2), plot of Φ^{-1} vs $[\text{PhCH}_2\text{OH}]^{-1}$

(50) (a) Lebeau, E. L.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 2174. (b) Roecker, L.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 746.

(51) (a) Lewis, F. D. *Acc. Chem. Res.* **1986**, *19*, 401. (b) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727. (c) Wagner, P. J.; Park, B. S. *Org. Photochem.* **1991**, *11*, 227. (d) Jones, G., II; Mouli, N. *J. Phys. Chem.* **1988**, *92*, 7174. (e) Cermenati, L.; Freccero, M.; Venturello, P.; Albin, A. *J. Am. Chem. Soc.* **1995**, *117*, 7869.

(52) (a) Okamura, M. Y.; Feher, G. *Annu. Rev. Biochem.* **1992**, *61*, 861. (b) Malmström, B. G. *Acc. Chem. Res.* **1993**, *26*, 332. (c) Ferguson-Miller, S.; Babcock, G. T. *Chem. Rev.* **1996**, *96*, 2889. (d) Hoganson, C. W.; Babcock, G. T. *Science* **1997**, *277*, 1953. (e) Cukier, R. I.; Nocera, D. G. *Annu. Rev. Phys. Chem.* **1998**, *49*, 337.

(53) Cukier, R. I. *J. Phys. Chem. A* **1999**, *103*, 5989.

(S3), dependence of the quantum yields on $[p\text{-MeC}_6\text{H}_4\text{CH}_2\text{OH}]$ for photooxidation of $p\text{-MeC}_6\text{H}_4\text{CH}_2\text{OH}$ by different *o*-quinones (S4), plots of Φ^{-1} vs $[p\text{-MeC}_6\text{H}_3\text{CH}_2\text{OH}]^{-1}$ (S5), decay of $^34,7\text{-PTQ}^*$ and rise of 4,7-PTQ radical anion observed in the photoreduction of 4,7-PTQ by PhCH_2OH (S6), transient absorp-

tion spectra observed in the photoreduction of 4,7-PTQ with PhCH_2OH (S7) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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