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Diels−Alder Reactions of Anthracenes with Dienophiles via Photoinduced Electron Transfer

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Photochemical Diels−Alder reaction of anthracene and its derivatives with dienophiles (*p*-benzoquinone and fumaronitrile) occurs in competition with the dimerization of anthracenes in chloroform at 298 K. The dependence of the quantum yields on the concentrations of dienophiles has revealed that the photochemical Diels−Alder reaction proceeds via electron transfer from the singlet excited states of anthracenes to dienophiles. The rates of photoinduced electron transfer are diffusion limited, agreeing with the largely negative free energy change of electron-transfer judging from the more negative one-electron oxidation potentials of the singlet excited states of anthracenes than the one-electron reduction potentials of dienophiles. The radical ion pair produced in the photoinduced Diels−Alder from the singlet excited states of anthracenes to *p*-benzoquinone and fumaronitrile has been detected as the transient absorption spectrum at 298 K with use of laser flash photolysis. The diradical intermediates prior to the Diels−Alder adduct formation following the photoinduced electron transfer have successfully been detected by ESR at 77 K under photoirradiation of chloroform solutions of anthracene derivatives and *p*-benzoquinones.

Introduction

Dimerization of anthracene and its derivatives is one of the oldest known photochemical reactions.[1] The photodimerization is known to occur via a singlet excimer intermediate.[2] The electronic structure of such an intermediate has been shown to be consistent with a structure where electron transfer occurs from one anthracene ring to the other.[3] On the other hand, the importance of the electron-transfer step via charge-transfer interactions between dienes and dienophiles in the transition state of Diels−Alder reactions has been reported.[4−6] The one-electron oxidation of one of the reacting species to the corresponding radical cation results in a significant decrease in the difference in the frontier orbital energies, which leads to an acceleration of the Diels−Alder reaction.[7−9] Such an oxidation can be achieved photochemically via photoinduced electron transfer with electron acceptors, resulting in photocyclodimerization of electron rich olefins.[10] Heterocyclodimers have also been attained between different olefins via the heterodimer radical cations.[11−13] Because the use of the photoexcited state enhances the electron donor or acceptor ability significantly, there has been considerable interest in photocycloadditions via photoinduced electron transfer as a new potentially important pathway for controlling synthetic processes which could not be exploited using a classical concerted pathway.[14−17] The radical ion pair formed in photoinduced electron transfer from anthracene to dienophiles has been detected by laser flash photolysis studies.[12b,13] However, the reaction mechanism of the Diels−Alder reactions via photoinduced electron transfer has yet to be fully understood. Although the C−C bond formation should occur in the radical ion pair to yield the Diels−Alder adduct, no reaction intermediates prior to the Diels−Alder adduct formation following the photoinduced electron transfer has so far been detected.

This study reports the photochemical Diels−Alder reactions of anthracenes with *p*-benzoquinone and fumaronitrile via photoinduced electron transfer from anthracenes to the dienophiles in competition with the photodimerization of anthracenes. We have succeeded in detecting not only the radical ion pair produced in the photoinduced electron transfer but also the biradical intermediate prior to formation of the Diels−Alder adduct. Such detection of intermediates together with the kinetic analysis of the photoinduced Diels−Alder reaction provides valuable insight into the stepwise bond formation in the Diels−Alder reaction via photoinduced electron transfer.

Experimental Section

Materials. Anthracene and its derivatives (9,10-dimethylanthracene, 9-methylanthracene, and anthracene) and fumaronitrile were obtained commercially. *p*-Benzoquinone and 2,5-dichloro-*p*-benzoquinone used as dienophiles were also obtained commercially and purified by the standard methods.[18] Tetrabutylammonium perchlorate used as a supporting electrolyte for the electrochemical measurements is commercially available. Spectral grade chloroform was obtained from Wako Pure Chemicals and was used without further purification. Acetonitrile used as a solvent was purified and dried by the standard procedure.[18]

Reaction Procedure. Typically, a [$^2H_1$]chloroform ($CDCl_3$) solution (0.8 cm^3) containing 9,10-dimethylanthracene (7.3×10^{-3} M) and *p*-benzoquinone (5.0×10^{-2} M) in a square quartz cuvette (1 mm i.d.) was deaerated by bubbling with argon gas for 5 min. The solution was irradiated with monochromatized light of $\lambda = 402$ nm from a xenon lamp of a Shimadzu RF-5000 spectrofluorophotometer with the slit width of 20 nm at 298 K for 1.8 h. The resulting solution was transferred to an NMR tube and analyzed by ^1H NMR spectroscopy. The ^1H NMR measurements were performed using a Japan Electron Optics JNM-GSX-400 (400 MHz) NMR spectrometer at 298 K. ^1H NMR ($CDCl_3$): Diels−Alder adduct of 9,10-dimethylanthracene with *p*-benzoquinone δ 1.95 (s, 6H), 2.77 (s, 2H), 5.96 (s, 2H), 7.09−7.19 (m, 6H), 7.33−7.38 (m, 2H). Diels−

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Alder adduct of 9,10-dimethylanthracene with fumaronitrile δ 2.12 (s, 6H), 2.93 (s, 2H), 7.20−7.38 (m, 8H).

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)[19] was used for the quantum yield determinations on the photodimerization of anthracenes and photochemical Diels−Alder reactions of anthracenes with *p*-benzoquinone and fumaronitrile. Typically, a chloroform ($CHCl_3$) solution (3.0 cm^3) containing 9,10-dimethylanthracene (2.0×10^{-4} M) and various concentrations of *p*-benzoquinone in a square quartz cuvette (10 mm i.d.) was deaerated by bubbling with argon gas for 8 min and sealed with rubber septum. The solution was irradiated with monochromatized light of $\lambda = 402$ nm (9,10-dimethylanthracene) or 389 nm (9-methylanthracene) from a xenon lamp of a Shimadzu RF-5000 spectrofluorophotometer with the slit width of 20 nm at 298 K. Under the conditions of actinometry experiments, both the actinometer and anthracenes absorbed essentially all of the incident light. The light intensities of monochromatized lights of $\lambda = 402$ and 389 nm with the slit width of 20 nm were determined as 1.52×10^{-5} and 1.38×10^{-5} einstein dm^{-3} s^{-1}, respectively. The photochemical reaction was monitored using a Hewlett-Packard 8452A diode-array spectrophotometer. The quantum yields were determined from the decrease in absorbance due to 9,10-dimethylanthracene ($\lambda_{max} = 402$ nm, $\epsilon_{max} = 7.2 \times 10^3$ M^{-1} cm^{-1}) and 9-methylanthracene ($\lambda_{max} = 389$ nm, $\epsilon_{max} = 6.7 \times 10^3$ M^{-1} cm^{-1}).

Fluorescence Quenching. Fluorescence measurements of anthracenes were performed on a Shimadzu RF-5000 spectrofluorophotometer. Fluorescence lifetimes of anthracenes were measured using a Horiba NAES-1100 time-resolved spectrophotometer. In the quenching experiments, the excitation wavelengths were selected as 402 and 389 nm for 9,10-dimethylanthracene and 9-methylanthracene. Relative fluorescence lifetimes were measured for deaerated $CHCl_3$ solutions containing anthracenes (2.0×10^{-5} M) and various concentrations of dienophiles (*p*-benzoquinone, fumaronitrile). The Stern−Volmer relationship (eq 1) was obtained between the ratio of the lifetime in the absence and presence of dienophiles (τ_0/τ) and [dienophile]

$$\tau_0/\tau = 1 + k_q\tau_0[\text{dienophile}] \qquad (1)$$

Electrochemical Measurements. Electrochemical measurements of anthracenes, *p*-benzoquinones, and fumaronitrile were performed on a BAS 100B electrochemical analyzer in deaerated $CHCl_3$ containing 0.10 M $NBu^n{}_4ClO_4$ as a supporting electrolyte at 298 K. The platinum working electrode (BAS) was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire (BAS). The measured potentials were recorded with respect to the Ag/$AgNO_3$ (0.01 M) reference electrode. The E^0_{ox} and E^0_{red} values (vs Ag/Ag^+) are converted to those vs SCE by adding 0.29 V.[20] The cyclic voltammograms of *p*-benzoquinone exhibit the reversible cathodic and anodic waves. Because the cyclic voltammograms of anthracenes and fumaronitrile show no cathodic wave and anodic wave, respectively, the one-electron oxidation and reduction potentials determined by second harmonic alternating current voltammetry (SHACV).[21]

Photophysical Measurements. Nanosecond transient absorption measurements were carried out using a Nd:YAG laser (Continuum, SLII-10, 4−6 ns fwhm) at 355 nm with the power of 10 mJ as an excitation source. Photoinduced events were estimated by using a continuous Xe-lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The transient spectra were recorded using fresh solutions in each laser excitation. All experiments were performed at 298 K.

SCHEME 1

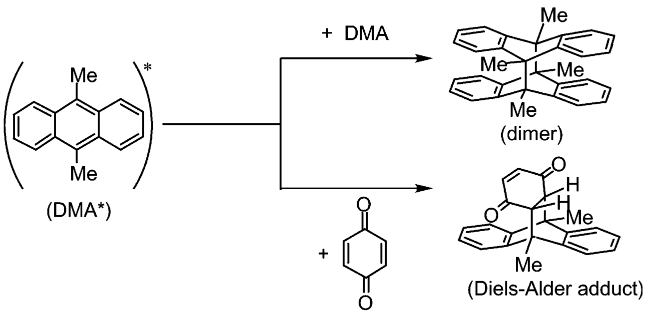


TABLE 1: Photochemical Diels−Alder Reaction of 9,10-Dimethylanthracene (8.3×10^{-3} M) with *p*-Benzoquinone (5.5×10^{-2} M) and Fumaronitrile (1.0×10^{-1} M) in Deaerated $CDCl_3$ at 298 K, Irradiated with Monochromatized Light of 402 nm from a Xenon Lamp

dienophile	irradiation time, h	yield of Diels−Alder adduct,[a] %
p-benzoquinone	1.8	65
fumaronitrile	1.8	80

[a] Determined by 400-MHz ^1H NMR analysis.

ESR Measurements. The ESR spectra of the biradical intermediate in the photoinduced Diels−Alder reactions were measured on a JEOL X-band spectrometer (JES-ME-LX). Typically, a $CHCl_3$ solution (1.0 cm^3) containing 9,10-dimethylanthracene (1.0×10^{-2} M) and *p*-benzoquinone (1.0×10^{-1} M) in an ESR tube (5 mm i.d.) was thoroughly degassed by successive freeze−pump−thaw cycles. The solution was irradiated with a xenon lamp at 77 K for 20 min, and the ESR spectrum of the solution was measured at 77 K. The ESR spectra were recorded under nonsaturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and signal-to-noise (*S*/*N*) ratio of the observed spectra. The *g* values and the zero-field splitting parameters (*D* and *E*) were calibrated using an Mn^{2+} marker.

Theoretical Calculations. Density-functional theory (DFT) calculations were performed on a COMPAQ DS20E computer. Geometry optimizations were carried out using the B3LYP functional and 6-31G basis set[22,23] with the unrestricted Hartree−Fock (UHF) formalism and the multiplicity TRIPLET as implemented in the Gaussian 98 program.[24]

Results and Discussion

Photochemical Diels−Alder Reaction of Anthracenes with Dienophiles. Irradiation of the absorption band ($\lambda_{max} = 402$ nm) of 9,10-dimethylanthracene (DMA) in $CHCl_3$ results in formation of the corresponding dimer. When *p*-benzoquinone is added to $CHCl_3$ solution of DMA, irradiation of the $CHCl_3$ solution with monochromatized light of $\lambda = 402$ nm results in a significant acceleration of the Diels−Alder reaction of DMA with *p*-benzoquinone in competition with the dimerization of DMA as shown in Scheme 1. The Diels−Alder reaction of DMA with fumaronitrile is also accelerated under irradiation of visible light of $\lambda = 402$ nm. The products are identified as the same as those in the thermal Diels−Alder reactions (see the Experimental Section),[25] and the yields are shown in Table 1.

TABLE 2: Limiting Quantum Yields ($\Phi_{D\infty}$) and Observed Rate Constants of Electron Transfer (k_{et}) for the Photochemical Diels−Alder Reactions of Anthracene Derivatives with Fumaronitrile (FN) and *p*-Benzoquinone (Q), Fluorescence Quenching Rate Constants (k_q) of the Fluorescence by Dienophiles, and Free Energy Change (ΔG^0_{et}) of Electron Transfer from the Singlet Excited State to Dienophiles in Deaerated CHCl$_3$ at 298 K

anthracene derivative	dienophile	$\Phi_{D\infty}$[a]	k_{et},[a] $M^{-1}\,s^{-1}$	k_q,[b] $M^{-1}\,s^{-1}$	ΔG^0_{et},[c] kcal mol^{-1}
MA	FN	9×10^{-3}	2.0×10^{10}	1.9×10^{10}	−15.0
DMA	FN	2×10^{-3}	2.0×10^{10}	1.8×10^{10}	−13.1
DMA	Q	5×10^{-3}	5.0×10^{10}	2.2×10^{10}	−35.3

[a] Determined from the plots of Φ^{-1} vs [dienophile]$^{-1}$ according to eq 4. [b] Determined from the Stern−Volmer plots for the fluorescence lifetime quenching. [c] Obtained from the $^1E^*_{ox}$ values of anthracenes (see Table 3) and E^0_{red} values of dienophiles (see Figure S4a and S4b for Q and FN, respectively) by using eq 2, respectively.

TABLE 3: One-Electron Oxidation Potentials (E^0_{ox}), the Conditions Used to Determine the E^0_{ox} Values, the Singlet Excitation Energies ($^1\Delta E_{0,0}$), and One-Electron Oxidation Potentials ($^1E^*_{ox}$) of the Singlet Excited States of Anthracene Derivatives in CHCl$_3$ at 298 K

anthracene derivatives	E^0_{ox} vs SCE, V	ac amplitude, mV	phase shift degree	$^1\Delta E_{0,0}$,[b] eV	$^1E^*_{ox}$ vs SCE, V
DMA	1.16	100	71/161	3.06	−1.90
MA	1.19	80	53/143	3.17	−1.98
An	1.27	70	54/144	3.25	−1.98

[a] Measured using a Ag/AgNO$_3$ (0.01 M) reference electrode and converted to the value vs SCE. All values obtained in deaerated CHCl$_3$ containing 0.10 M tetrabutylammonium perchlorate at 298 K using Pt working electrode and Pt wire auxiliary electrode at a scan rate of 4 mV s^{-1}, f (ac frequency) = 25 Hz. All solutions are 1.0 mM in anthracene concentration. [b] Determined from the absorption maximum and fluorescence maximum in CHCl$_3$. [c] Obtained by subtracting the $^1\Delta E_{0,0}$ values from the E^0_{ox} values.

The fluorescence of DMA in CHCl$_3$ at 298 K decays, obeying the first-order kinetics. Typical examples of single-exponential decay curves of DMA fluorescence in the presence of various concentrations of dienophiles are given in the Supporting Information S1, where the fluorescence lifetime decreases with an increase in the fumaronitrile concentration. The Stern−Volmer plots of the ratio of lifetime in the absence and presence of dienophile (S2), τ_0/τ vs [dienophile] (eq 1) afford the quenching rate constants (k_q) which are listed in Table 2. The k_q values are the same as the diffusion rate constant in MeCN (2.0×10^{10} M^{-1} s^{-1}).[26]

The photoexcitation of anthracenes may result in a significant decrease in the HOMO energies. The one-electron oxidation potentials (E^0_{ox}) of the singlet excited states of anthracenes are obtained by subtracting the zero-zero excitation energy ($^1\Delta E_{0,0}$) from the E^0_{ox} values of the ground states. The E^0_{ox} (vs SCE) values of the ground states of anthracenes in CHCl$_3$ were determined by the second-harmonic alternating current voltammograms (SHACV) (see the Supporting Information S3),[20] where symmetrical traces at phase angles differing by 90° are obtained around the intersection with the dc potential axis. The one-electron oxidation potential E^0_{ox} (vs Ag/0.01 M AgNO$_3$) can be readily determined as the intersection value. The E^0_{ox} values thus determined are converted to those vs SCE by adding 0.29 V[20] and listed in Table 3 together with the ac amplitudes and phase shifts.

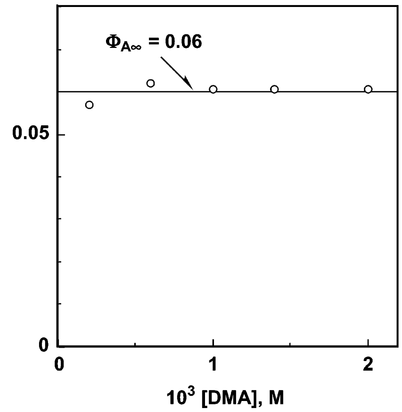


Figure 1. Dependence of the quantum yields (Φ) on [DMA] for the photodimerization of DMA in deaerated CHCl$_3$ at 298 K; excitation wavelength = 402 nm.

The E^0_{ox} values of anthracenes in CHCl$_3$ are ca. 0.1 V larger than those reported in MeCN,[27] because of the less solvation energy of the corresponding radical cations in the less polar solvent (CHCl$_3$) than MeCN. The E^*_{ox} values of the singlet excited states of anthracenes (* denotes the excited state) are also listed in Table 3 together with the $^1\Delta E_{0,0}$ values. The one-electron reduction potentials (E^0_{red} vs SCE) of *p*-benzoquinone and fumaronitrile in CHCl$_3$ were also determined to be −0.37 and −1.33 V by cyclic voltammogram and the second-harmonic alternating current voltammogram, respectively (S4).[20] As is the case of the E^0_{ox} values of anthracenes in CHCl$_3$, the E^0_{red} value of *p*-benzoquinone in CHCl$_3$ (−0.37 V) is by 0.13 V more positive than that (−0.50 V) in the more polar solvent, MeCN.[28]

The free energy change of electron transfer from the singlet excited states of anthracenes to dienophiles (ΔG^0_{et}) is obtained from the difference in the one-electron redox potentials by using eq 2, where F is the Faraday constant. The ΔG^0_{et} values

$$\Delta G^0_{et} = F(E^*_{ox} - E^0_{red}) \qquad (2)$$

are largely negative as listed in Table 2. In such a case, electron transfer from the singlet excited states of anthracenes to the dienophiles may be diffusion limited. This expectation agrees with the k_q values in Table 2. Thus, the fluorescence quenching may occur via electron transfer from the singlet excited states of anthracenes to the dienophiles.

The quantum yields (Φ) of the photochemical reaction of 9,10-dimethylanthracene (DMA) and 9-methylanthracene (MA) were determined from the decrease in absorbance due to DMA (λ_{max} = 402 nm, $\epsilon_{max} = 7.2 \times 10^3$ M^{-1} cm^{-1}) and MA (λ_{max} = 389 nm, $\epsilon_{max} = 6.7 \times 10^3$ M^{-1} cm^{-1}), respectively. In the absence of dienophile, the quantum yield corresponds to that of the photodimerization of anthracenes. The Φ_0 values in the absence of dienophile are constant irrespective of the concentrations of anthracenes as shown in Figure 1. In the presence of dienophiles, the Φ values decrease with an increase in concentrations of dienophiles to approach constant values as the Diels−Alder reaction of anthracenes with dienophiles becomes predominant as compared with the photodimerization as shown in Figure 2. Thus, the $\Phi_0 - \Phi$ values corresponds to the quantum yields for the photochemical Diels−Alder reactions of anthracenes and dienophiles.

The dependence of quantum yields on concentrations of dienophiles in Figure 2 may be explained by Scheme 2, where the reaction with *p*-benzoquinone (Q) is shown as the representative case. The mechanism of photodimerization of anthracenes is well established as shown in Scheme 2 in the absence of dienophile.[2] The photoexcitation of anthracenes

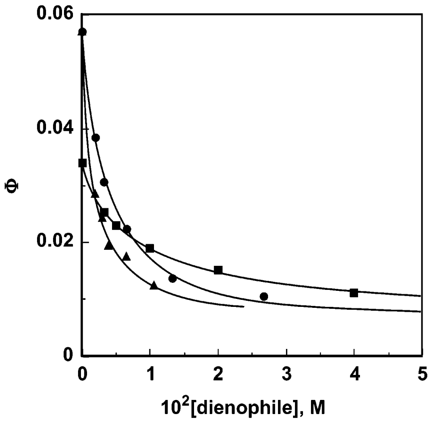
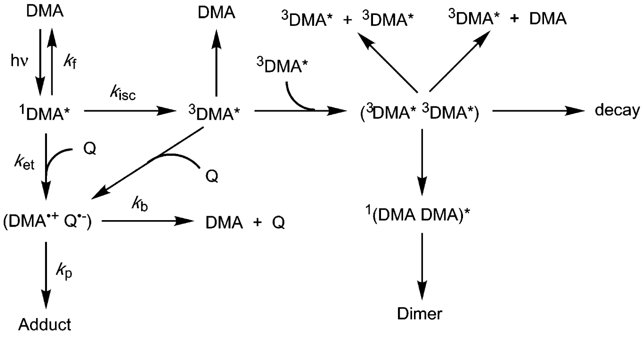


Figure 2. Dependence of the quantum yields (Φ) on [dienophile] for the photochemical reaction of DMA (2.0×10^{-4} M) with FN (●) and Q (▲) and MA (2.0×10^{-4} M) with FN (■) in deaerated MeCN at 298 K.

SCHEME 2



results in the formation of the singlet excited state ^{1}An*, which is converted to ^{3}An* by the intersystem crossing. The triplet−triplet annihilation leads to the singlet exciplex, which yields the anthracene dimer.

In the presence of dienophile, electron transfer (k_{et}) from ^{1}DMA* to dienophiles [*p*-benzoquinone (Q) and fumaronitrile (FN)] produces the radical ion pair ($DMA^{\bullet+}$ $Q^{\bullet-}$) or ($DMA^{\bullet+}$ $FN^{\bullet-}$), in competition with the intersystem crossing (k_{isc}) and the decay of the singlet excited state to the ground state (k_f).[29] The radical ion pair collapses to yield the Diels−Alder adduct (k_p) in competition with the back electron transfer from the radical anion ($Q^{\bullet-}$ or $FN^{\bullet-}$) to the radical cation ($DMA^{\bullet+}$). By applying the steady-state approximation to the reactive intermediates in Scheme 2, the quantum yield of the adduct formation (Φ_p) may be given by eq 3

$$\Phi_p = \Phi_\infty k_{et}\tau[\text{dienophile}]/(1 + k_{et}\tau[\text{dienophile}]) \qquad (3)$$

where k_{et} is the rateconstant of electron transfer from the singlet excited states of anthracenes to dienophiles, τ is the fluorescence lifetime in the absence of dienophile ($\tau^{-1} = k_f + k_{isc}$), and Φ_∞ corresponds to $k_p/(k_p + k_b)$; k_p and k_b are the rate constant of the adduct formation in the radical ion pair and that of back electron transfer from the dienophile radical anion to the anthracene radical cations, respectively. Because $\Phi_0 - \Phi = \Phi_p$, eq 3 is rewritten by eq 4

$$(\Phi_0 - \Phi)^{-1} = \Phi_\infty^{\ -1}\{1 + (k_{et}\tau[\text{dienophile}])^{-1}\} \qquad (4)$$

which predict a linear correlation between $(\Phi_0 - \Phi)^{-1}$ and $[\text{dienophile}]^{-1}$. The validity of eq 4 is confirmed by the linear plots in Figure 3. From the slopes and intercepts in Figure 3 are obtained the Φ_∞ and k_{et} values, which are listed in Table 2. The k_{et} values agree with the k_q values determined independently.[30] Such an agreement strongly supports the reaction mechanism shown in Scheme 2.

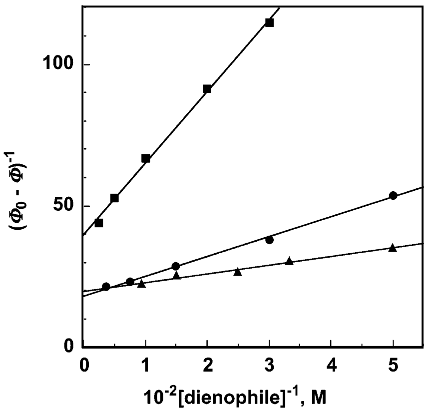


Figure 3. Double reciprocal plots of Figure 2.

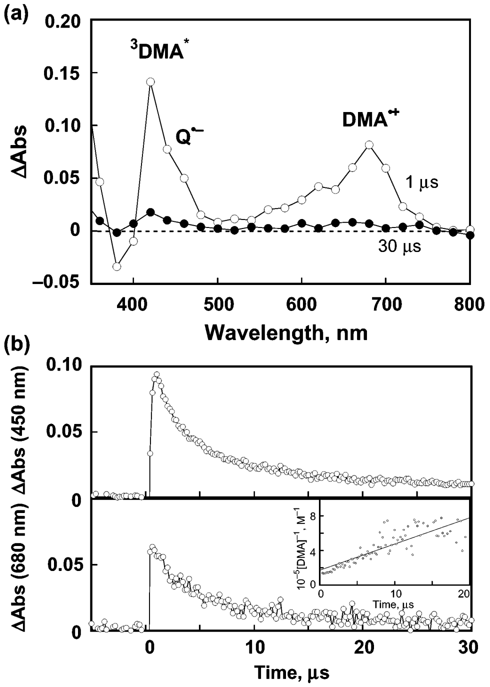


Figure 4. (a) Transient absorption spectrum observed in the photoreaction of DMA (1.0×10^{-4} M) with Q (5.0×10^{-3} M) at 1.0 (○) and 30 (●) *μ*s after laser excitation in deaerated MeCN at 298 K. (b) Decay time profile at 450 and 680 nm. Inset: second-order plot at 680 nm.

The transient absorption spectra of the radical ions produced in the photoinduced electron transfer from ^{1}DMA* to Q in Scheme 2 are observed by the laser flash photolysis of a deaerated acetonitrile (MeCN) solution of DMA and Q as shown in Figure 4a. The absorption bands at 420 and 450 nm are attributed to $Q^{\bullet-}$,[31] although the triplet−triplet absorption due to ^{3}DMA* is overlapped at 420 nm.[32] The absorption band at 680 nm is assigned to $DMA^{\bullet+}$.[33] Both absorption bands appear immediately after nanosecond laser exposure and decay at the same rate, obeying second-order kinetics as shown in Figure 4b. From the slope of a linear plot of $[DMA]^{-1}$ vs time (inset of Figure 4b) is obtained the decay rate constant as 2.9×10^{10} M^{-1} s^{-1} which is the diffusion-limited value in MeCN. The back electron transfer from $Q^{\bullet-}$ to $DMA^{\bullet+}$ is highly exergonic when the bimolecular rate constant should be diffusion-limited as observed experimentally (Figure 4b). The observed radical

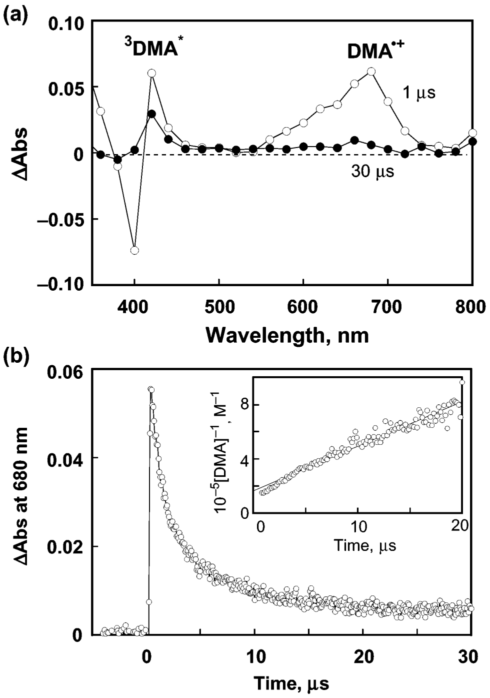


Figure 5. (a) Transient absorption spectra observed in the photoreaction of DMA (1.0×10^{-4} M) with FN (5.0×10^{-3} M) at 1.0 (○) and 30 (●) μs after laser excitation in deaerated MeCN at 298 K. (b) Decay time profile at 680 nm. Inset: second-order plot at 680 nm.

ions ($\mathrm{Q}^{\bullet-}$ and $\mathrm{DMA}^{\bullet+}$) are those escaped from the radical ion pair produced in the photoinduced electron transfer from ^{1}DMA* to Q. The generation of such free radical ions becomes much less efficient in $\mathrm{CHCl_3}$ because of the much smaller stabilization by solvation as compared to that in MeCN. Thus, no free radical ions have been observed in $\mathrm{CHCl_3}$ at the microsecond time scale. The back electron transfer and the C−C bond formation in $\mathrm{CHCl_3}$ may occur at the much faster time scale in the cage of the radical ion pair in Scheme 2.

The transeint absorption spectrum of $\mathrm{DMA}^{\bullet+}$ is also observed in photoinduced electron transfer from ^{1}DMA* to FN in MeCN as shown in Figure 5a, where the absoprtion band due to $\mathrm{FN}^{\bullet-}$ ($\lambda_{\max} = 380$ nm)[34] is overlapped with bleaching of DMA. The triplet−triplet absorption due to ^{3}DMA* also appears at 420 nm,[33]and the decay of ^{3}DMA* is much slower than the decay of $\mathrm{DMA}^{\bullet+}$ probably due to insufficient quenching of ^{1}An* by FN as compared with the quenching by Q. When DMA was replaced by anthracene (An), the transient absorption spectra of $\mathrm{An}^{\bullet+}$ ($\lambda_{\max} = 720$ nm)[32,34] and the triplet−triplet absorption due to ^{3}An* ($\lambda_{\max} = 420$ nm)[35] were also observed in photoinduced electron transfer from ^{1}An* to Q and FN (see the Supporting Information, S5 and S6, respectively).

Electron spin resonance (ESR) spectroscopy provides valuable information about an intermediate prior to the adduct formation following the photoinduced electron transfer from ^{1}DMA* to Q. When irradiation of $\mathrm{CHCl_3}$ solution of DMA and Q is carried out at 77 K, a typical triplet ESR signal is observed as shown in Figure 6. The small signal is also observed at $g = 4.0$ due to the $\Delta M_\mathrm{S} = 2$ transition. The observation of a "$\Delta M_\mathrm{S} = 2$" line in the region of $g = 4.0$ is the diagnostic marker for detection of the triplet state.[36] The zero-field splitting parameters D and E ($\cong 0$) are determined from the triplet signals and listed in Table 4. The triplet state may not result from the radical ion pair produced in the photoinduced electron transfer from ^{1}DMA* to Q, because the rapid back electron transfer would occur even in frozen media. The observed triplet state is stable at 77 K. The most likely candidate of such a stable triplet state at 77 K may be a biradical intermediate prior to formation of the Diels−Alder adduct.[37] The formation of the triplet radical under photoirradiation of the reactants in frozen media indicates that the biradical is formed from the reactants and not from the product. Thus, the C−C bond formation in the radical ion pair in Scheme 2 may occur in a stepwise manner: first the cation and anion parts are coupled to form the biradical and then the radical coupling (not the reversed order) occurs to yield the Diels−Alder adduct as shown in Scheme 3. However, a direct reaction pathway through the singlet radical ion pair or a concerted reaction pathway cannot be ruled out.

Because D depends on the distance between two electrons with parallel spins, the average distance of two spins can be evaluated from the D values. The distances between two electrons (R) for the biradicals generated from anthracene and

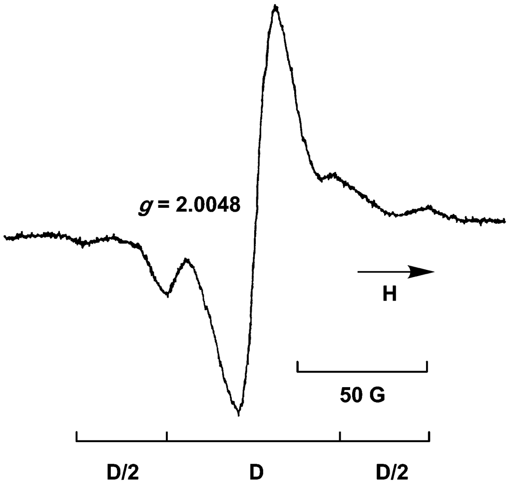
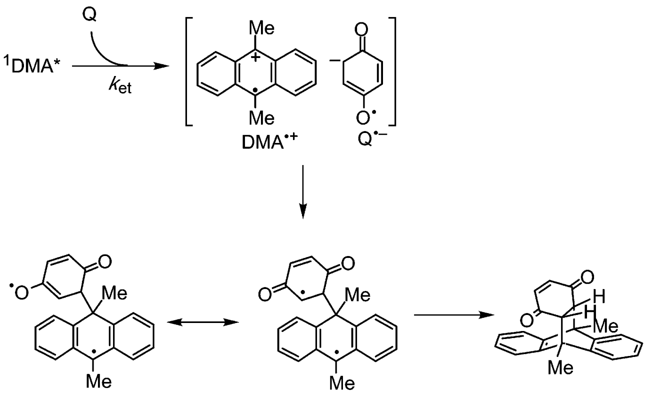


Figure 6. ESR spectrum of the triplet state observed by irradiation of a $\mathrm{CHCl_3}$ solution of DMA (1.0×10^{-2} M) and Q (1.0×10^{-1} M) at 77 K.

TABLE 4: ESR Parameters [*g* Value, Zero-Field Splitting Constant (*D*)] and the Distance (*R*) of the Two Unpaired Electrons of Triplet Biradicals Observed by Irradiation of a $\mathrm{CHCl_3}$ Solution of Anthracenes and *p*-Benzoquinones at 77 K

anthracene form (concentration, M)	*p*-benzoquinone form (concentration, M)	*g*	*D*, G	*R*, Å
An (1.9×10^{-2})	*p*-benzoquinone (1.0×10^{-1})	2.0046	67.8	7.4
DMA (1.0×10^{-2})	*p*-benzoquinone (1.0×10^{-1})	2.0048	68.3	7.4
DMA (1.2×10^{-2})	2,5-dichloro-*p*-benzoquinone (1.0×10^{-1})	2.0053	47.2	8.4

SCHEME 3



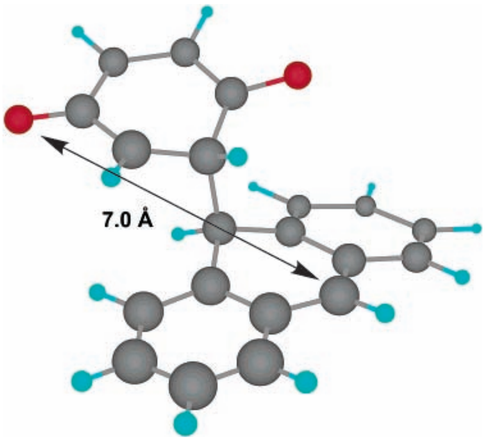


Figure 7. Optimized structure of the triplet birdical of anthracene with *p*-benzoquinone calculated by B3LYP/6-31G.

9,10-dimethylanthracene with *p*-benzoquinone and 2,5-dichloro-*p*-benzoquinone are also listed in Table 4. The *R* value of the biradical from anthracene with 2,5-dichloro-*p*-benzoquinone (8.4 Å) is larger than the other values (7.4 Å) because of the steric effect of the substituents on the quinone. The optimized structure of the biradical intermediate for the Diels−Alder adduct of anthrancene with *p*-benzouquinone is calculated by density-functional theory (DFT) using the B3LYP functional and 6-31G basis set,[22,23] as shown in Figure 7. The biradical structure is consistent with the ESR result.

In conclusion, the present study has indicated that photoinduced Diels−Alder reactions of anthracenes with *p*-benzoquinones proceed via electron transfer from the singlet excited states of anthracenes to *p*-benzoquinone, followed by the cation−anion coupling and the radical coupling to yield the Diels−Alder adducts.[37]

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Supporting Information Available: Fluorescence decay curves of DMA in the absence and presence of fumaronitrile (S1), Stern−Volmer plots (S2), second harmonic ac voltammogram (SHACV) of anthracenes (S3), cyclic voltammogram (CV) of *p*-benzoquinone and SHACV of fumaronitrile (S4), the transient absorption spectra of An$^{\bullet+}$ and ^{3}An* observed in photoinduced electron transfer from ^{1}An* to Q (S5) and FN (S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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