

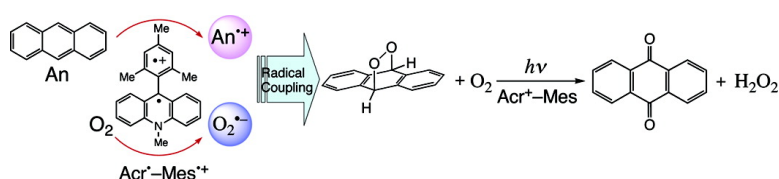
Article

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Photocatalytic Oxygenation of Anthracenes and Olefins with Dioxygen via Selective Radical Coupling Using 9-Mesityl-10-methylacridinium Ion as an Effective Electron-Transfer Photocatalyst

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Abstract: Visible light irradiation of the absorption band of 9-mesityl-10-methylacridinium ion (Acr^+-Mes) in an O_2 -saturated acetonitrile (MeCN) solution containing 9,10-dimethylantracene results in formation of oxygenation product, i.e., dimethylepidioxyanthracene ($\text{Me}_2\text{An-O}_2$). Anthracene and 9-methylantracene also undergo photocatalytic oxygenation with Acr^+-Mes to afford the corresponding epidioxyanthracenes under the photoirradiation. In the case of anthracene, the further photoirradiation results in formation of anthraquinone as the final six-electron oxidation product, via 10-hydroxyanthrone, accompanied by generation of H_2O_2 . When anthracene is replaced by olefins (tetraphenylethylene and tetramethylethylene), the photocatalytic oxygenation of olefins affords the corresponding dioxetane, in which the O–O bond is cleaved to yield the corresponding ketones. The photocatalytic oxygenation of anthracenes and olefins is initiated by photoexcitation of Acr^+-Mes , which results in formation of the electron-transfer state: $\text{Acr}^+-\text{Mes}^+$, followed by electron transfer from anthracenes and olefins to the Mes^{++} moiety together with electron transfer from the Acr^* moiety to O_2 . The resulting anthracene and olefin radical cations undergo the radical coupling reactions with $\text{O}_2^{\cdot-}$ to produce the epidioxyanthracene (An-O_2) and dioxetane, respectively.

Introduction

Although radical coupling reactions between radical cations and radical anions have profound fundamental and synthetic interest, the difficulty of generating such highly reactive species together had precluded the exploitation of such reactions until Amatore et al.¹ succeeded in generating an anthracene radical cation and a superoxide anion in close proximity with use of a pair of microband electrodes at the femtoliter scale. The radical cation and the radical anion combine chemically to form epidioxyanthracene (An-O_2) before reacting with the electrolyte solution.¹ However, any reactions on the femtoliter scale have no synthetic interest.

Alternatively radical cations and radical anions can be produced photochemically by photoexcitation of the charge-transfer complex between electron donors and acceptors.^{2–8} In particular, photoinduced cycloadditions via photoinduced electron transfer provide a new potentially important pathway for controlling synthetic processes which could not be exploited

using a classical concerted pathway.^{9–14} The radical ion pair formed in photoinduced electron transfer from anthracene to

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dienophiles has been detected by laser flash photolysis studies.^{15,16} However, the photoexcitation of dienes often results in formation of excimer intermediates which lead to the photoinduced dimerization, precluding the selective reactions between dienes and dienophiles.^{17–19} Thus, it is highly desired to use a photocatalyst which can catalyze cycloadditions via photoinduced electron transfer without involving the photoexcited states of substrates.

Radical cations and radical anions may also be formed using an electron donor–acceptor linked molecule, since the photoexcitation results in formation of a radical cation and anion pair which can oxidize and reduce substrates to generate radical cations and radical anions, respectively.^{20–24} Unfortunately, however, the lifetimes of charge-separated states of most donor–acceptor linked molecules reported so far were too short to be coupled with the oxidation and reduction of substrates.^{20–24} In this context, we have recently found that the photoexcitation of 9-mesityl-10-methylacridinium ion (Acr⁺–Mes) results in formation of the electron transfer state (Acr^{•+}–Mes^{•+}), which has an extremely long lifetime (e.g., 2 h at 203 K) and a high energy (2.37 eV).²⁵

We report herein that Acr⁺–Mes acts as an efficient electron-transfer photocatalyst for highly selective oxygenation of anthracenes with O₂ via selective radical coupling of anthracene radical cations and O₂^{•−} to produce epidioxyanthracenes under visible light irradiation. An-O₂ is further oxidized to anthraquinone, accompanied by generation of H₂O₂ under the photoirradiation. Epidioxyanthracenes, which are generally produced by the reactions of anthracenes with singlet oxygen (¹O₂), have merited significant interest in relation with reversible oxygen storage and as a species responsible for causing physiological damage.^{26,27} In the case of the present photocatalytic oxygenation of anthracenes, however, the epidioxyan-

thracenes are shown to be formed selectively by the radical coupling reactions of anthracene radical cations with O₂^{•−} rather than the reaction with ¹O₂. The radical coupling reaction is expanded to dioxetane formation, when anthracene is replaced by tetraphenylethylene or tetramethylethylene.

Experimental Section

Materials. Anthracene, 9-methylanthracene, 9,10-dimethylanthracene, tetraphenylethylene, and tetramethylethylene were purchased commercially. 9-Mesityl-10-methylacridinium ion (Acr⁺–Mes) was prepared by the reaction of 10-methylacridone in dichloromethane with mesitylmagnesium bromide, followed by addition of perchloric acid for the hydrolysis and sodium hydroxide for the neutralization, and then purified by recrystallization from methanol–diethyl ether. 9-Mesityl-10-methylacridinium (Acr⁺–Mes) perchlorate: Anal. Calcd for C₂₃H₂₂ClNO₄·0.15(H₂O): C, 66.63; H, 5.42; N, 3.38. Found; C, 66.44; H, 5.22; N, 3.49. ¹H NMR (300 MHz, CD₃CN, δ ppm) δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.93 (t, *J* = 9.0 Hz, 2H), 7.40 (s, 4H), 6.79 (s, 2H), 4.37 (s, 3H), 2.02 (s, 3H), 1.25 (s, 6H). Acetonitrile (MeCN) used as solvent was purified and dried by the standard procedure.²⁸ Deuterated [²H₃]acetonitrile (CD₃CN) and deuterated [²H₆]benzene (C₆D₆) were obtained from EURI SO-TOP, CEA, France, and used as received.

Reaction Procedure. Typically, a CD₃CN solution (0.6 mL) containing Acr⁺–Mes (1.0 × 10^{−3} M) and anthracene (1.0 × 10^{−2} M) in an NMR tube sealed with a rubber septum was saturated with oxygen by bubbling with oxygen through a stainless steel needle for 5 min. The solution was then irradiated with a xenon lamp (Ushio Optical ModelX SX-UID 500XAMQ) through a color filter glass (Asahi Techno Glass Y43) transmitting λ > 430 nm at room temperature. The irradiated solution was analyzed periodically by ¹H NMR spectroscopy. The ¹H NMR measurements were performed on a Japan Electron Optics JNM-AL300 (300 MHz) NMR spectrometer. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectra were measured on a Kratos Compact MALDI I (Shimadzu). Gas chromatographic analyses were performed on a Shimadzu GC-17A equipped with a DB-5MS column (Agilent Technologies, 30 m) and a mass spectrograph (Shimadzu QP-5050) as a detector. The products of the photooxygenation were determined by ¹H NMR, MALDI-TOF-MS, and GC–MS. 9,10-Dihydro-9,10-epidioxyanthracene (An-O₂): ¹H NMR (300 MHz, CD₃CN) δ 6.15 (s, 2H), 7.29–7.32 (m, 4H), 7.45–7.48 (m, 4H);²⁹ MALDI-TOF-MS *m/z* 211 (M⁺ calcd for C₁₄H₁₀O₂ 211.0). Anal. Calcd for C₁₄H₁₀O₂: C, 79.98; H, 4.79. Found: C, 79.96; H, 4.65. 9-Methyl-10-hydro-9,10-epidioxyanthracene: ¹H NMR (300 MHz, CD₃CN) δ 2.10 (s, 3H), 6.11 (s, 1H), 7.29–7.48 (m, 8H); MALDI-TOF-MS *m/z* 225 (M⁺ calcd for C₁₅H₁₂O₂, 225.1). Anal. Calcd for C₁₅H₁₂O₂·0.25H₂O: C, 79.15; H, 5.95. Found: C, 78.88; H, 6.27. 9,10-Dimethyl-9,10-epidioxyanthracene (Me₂An-O₂): ¹H NMR (300 MHz, CD₃CN) δ 2.09 (s, 6H), 7.31–7.34 (m, 4H), 7.44–7.48 (m, 4H);²⁷ MALDI-TOF-MS *m/z* 239 (M⁺ calcd for C₁₆H₁₄O₂, 238.1). Anal. Calcd for C₁₆H₁₄O₂·0.25H₂O: C, 79.15; H, 5.92. Found: C, 78.88; H, 6.27. Tetraphenylethylene dioxetane: ¹H NMR (300 MHz, CD₃CN) δ 7.16–7.22 (m, 12H), 7.26–7.31 (m, 8H). Tetramethylethylene dioxetane: ¹H NMR (300 MHz, CD₃CN) δ 1.32 (s, 12H). The isolation of the photocatalytic oxygenation product of dimethylanthracene in a preparative scale was performed using an O₂-saturated MeCN solution (20 mL) containing Acr⁺–Mes (8.2 mg, 2.0 × 10^{−5} mol) and dimethylanthracene (100 mg, 5.0 × 10^{−4} mol) in a Schlenk flask (20 mL) after the photoirradiation with a xenon lamp through a color filter glass transmitting λ > 430 nm for 6 h. After irradiation the solution was evaporated to dryness and purified by silica gel column chromatography

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(chloroform as an eluent) to afford Me₂An-O₂ as a white solid. The isolated yield of Me₂An-O₂ was determined as 80%. The amount of H₂O₂ was determined by titration by iodide ion by the following procedure.³⁰ An O₂-saturated MeCN solution (3.0 mL) of Acr⁺-Mes (1.0 × 10⁻⁴ M) and anthracene (1.0 × 10⁻⁴ M) was photoirradiated for 2 h, and the photoirradiated product mixture was treated with an excess amount of NaI. The amount of I₃⁻ formed was then determined by the visible spectrum ($\lambda_{\text{max}} = 361 \text{ nm}$, $\epsilon = 2.50 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).³¹

Quantum Yield Determination. Potassium ferrioxalate used as an actinometer was prepared according to the literature and purified by recrystallization from hot water.³² A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the photocatalytic oxygenation of anthracene and its derivatives with O₂. A square quartz cuvette (10 mm i.d.) which contained a MeCN solution (3.0 mL) of Acr⁺-Mes (2.0 × 10⁻⁴ M) and anthracene (3.0 × 10⁻⁵–7.0 × 10⁻⁴ M) was irradiated with monochromatized light of $\lambda = 430 \text{ nm}$ from a Shimadzu RF-5300PC fluorescence spectrophotometer. Under the conditions of actinometry experiments, both the actinometer and Acr⁺-Mes absorbed virtually all the incident light. The light intensity of monochromatized light of $\lambda = 430 \text{ nm}$ was determined as $5.5 \times 10^{-10} \text{ einstein s}^{-1}$ with an illumination bandwidth of 1 cm. The photochemical reaction was monitored by using a Hewlett-Packard 8453 photodiode array spectrophotometer. The quantum yields were determined from a decrease in absorbance due to anthracene ($\lambda = 376 \text{ nm}$, $\epsilon = 6.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 9-methylanthracene ($\lambda = 387 \text{ nm}$, $\epsilon = 6.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), and 9,10-methylanthracene ($\lambda = 398 \text{ nm}$, $\epsilon = 7.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). To avoid the contribution of light absorption of the products, only the initial rates were determined for determination of the quantum yields.

Electrochemical Measurements. Electrochemical measurements were performed on an ALS630B electrochemical analyzer in deaerated MeCN containing 0.1 M Bu₄NClO₄ (TBAP) as supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm²) and a platinum wire as the counter electrode. The Pt working electrode (BAS) was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/AgNO₃ (0.01 M) reference electrode. The second-harmonic alternating current voltammetry (SHACV) measurements were carried out with an ALS630B electrochemical analyzer in deaerated MeCN containing 0.1 M Bu₄NClO₄ (TBAP) as supporting electrolyte. All potentials (vs Ag/Ag⁺) were converted to values vs SCE by adding 0.29 V. All electrochemical measurements were carried out under an atmospheric pressure of Ar.

Theoretical Calculations. Density-functional theory (DFT) calculations were performed on a COMPAQ DS20E computer. Geometry optimizations were carried out using the Becke3LYP functional and 6-31G* basis set,^{33,34} with the unrestricted Hartree-Fock (UHF) formalism and as implemented in the Gaussian 98 program.³⁵ Graphical outputs of the computational results were generated with the Cerius² software program developed by Molecular Simulations Inc.

Laser Flash Photolysis. An argon or O₂-saturated MeCN solution containing anthracene (1.6 × 10⁻⁶ – 2.8 × 10⁻⁴ M) and Acr⁺-Mes (1.0 × 10⁻⁴ M) was excited by a Panther OPO pumped by Nd:YAG laser (Continuum, SLII-10, 4–6 ns fwhm) at $\lambda = 430 \text{ nm}$ with a power of 10 mJ per pulse. The transient absorption measurements were performed using a continuous xenon 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 at 298 K. The quantum yields of formation of the electron-transfer state (Acr⁺-Mes⁺) and anthracene radical cations upon laser photoexcitation were determined by comparing the transient absorption due to Acr⁺-Mes⁺ and anthracene radical cations with the triplet-triplet absorption of C₆₀ ($\lambda = 750 \text{ nm}$, $\epsilon = 1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) under the deaerated benzene solution of C₆₀ (1.8 × 10⁻³ M) as reported elsewhere.^{25,36,37}

ESR Measurements. An oxygen-saturated MeCN solution of Acr⁺-Mes (1.0 × 10⁻³ M) was irradiated at 233 K with a high-pressure mercury lamp (USH-1005D) through a water filter focusing at the sample cell in the ESR cavity. After the photoirradiation, the sample cell was immediately cooled to 123 K and the ESR spectra were taken on a JEOL JES-RE1XE under nonsaturating microwave power conditions. The magnitude of the modulation was chosen to optimize the resolution and the signal-to-noise ratio (*S/N*) of the observed spectra. The *g* values were calibrated using a Mn²⁺ marker.

O₂ Emission Measurements. An O₂-saturated CD₃CN solution containing Acr⁺-Mes (2.0 × 10⁻⁴ M) and Me₂An (1.0 × 10⁻² M) in a quartz cell (optical path length 10 mm) was excited at $\lambda = 400 \text{ nm}$ using a Cosmo System LVU-200S spectrometer. An O₂-saturated C₆D₆ solution containing C₆₀ (2.0 × 10⁻⁴ M) was also employed for comparison. A photomultiplier (Hamamatsu Photonics, R5509-72) was used to detect emission in the near-infrared region (band path 2 mm). For the emission lifetime measurements, O₂-saturated C₆D₆ solutions containing C₆₀ (2.0 × 10⁻⁴ M) in the presence of various concentrations of Me₂An were excited by the frequency-tripled output of Q-switched Nd:YAG laser at $\lambda = 355 \text{ nm}$ (Spectra Physics GCR-150-10) operating at 10 Hz. Typical pulse energies at sample were in the range 1–2 mJ. The emission was detected by a liquid nitrogen-cooled photomultiplier (Hamamatsu Photonics, R5509-72). The signal was captured and averaged by a digital storage oscilloscope (Tektronix TDS3032) and transferred to a PC for analysis.

Results and Discussion

Photocatalytic Formation of Epidioxyanthracenes. Visible light irradiation ($\lambda > 430 \text{ nm}$) of the absorption band of Acr⁺-Mes (1.0 × 10⁻³ M) in an O₂-saturated acetonitrile (MeCN) solution containing anthracenes (1.0 × 10⁻² M) results in formation of the oxygenation products, i.e., epidioxyanthracenes (eq 1). The yields of epidioxyanthracenes derived from 9,10-dimethylanthracene (Me₂An), 9-methylanthracene (MeAn), and anthracene (An) after 10 min photoirradiation are listed in Table 1. The photocatalytic oxygenation of Me₂An with O₂ in a preparative scale (100 mg, 5.0 × 10⁻⁴ mol) with Acr⁺-Mes (8.2 mg, 2.0 × 10⁻⁵ mol) was also performed to isolate dimethylepidioxyanthracene (80% yield, see Experimental Section). The lower yields of methylepidioxyanthracene (MeAn-

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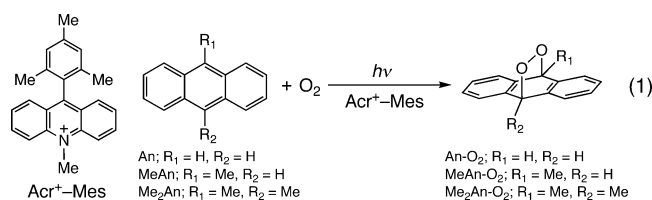
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Table 1. Product Yields and Quantum Yields (Φ_P) in Photocatalytic Oxygenation of Anthracenes with Oxygen in the Presence of Acr⁺-Mes (2.0×10^{-4} M) and Anthracenes (7.0×10^{-4} M), One-Electron Oxidation Potentials of Anthracenes, Rate Constants (k_{et}) of Electron-Transfer Oxidation of Anthracenes by Acr⁺-Mes⁺, Quantum Yields for Formation of Anthracene Radical Cations (Φ_R) under Ar, and Quantum Yields (Φ_R') under O₂ in the Presence of Acr⁺-Mes (1.0×10^{-4} M) and Anthracenes (2.8×10^{-4} M)

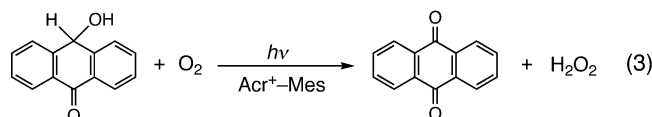
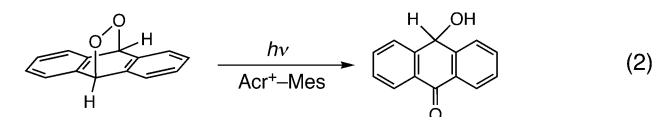
anthracene	product yield ^a (%)	Φ_P (%)	E°_{ox} (V)	k_{et} (M ⁻¹ s ⁻¹)	Φ_R (%)	Φ_R' (%)
Me ₂ An	99	30	1.05	1.4×10^{10}	66	86
MeAn	46	6	1.11	1.3×10^{10}	58	91
An	75	2	1.19	7.5×10^9	34	62

^a Determined by ¹H NMR after 10 min of photoirradiation. ^b vs SCE, taken from ref 39.



O₂) and epidioxyanthracene (An-O₂) as compared with Me₂An-O₂ result from the further photochemical reactions (vide infra).

In the case of anthracene, the An-O₂ is converted to 10-hydroxyanthrone³⁸ with the further photoirradiation ($\lambda > 430$ nm) of an O₂-saturated CD₃CN solution of An-O₂ and Acr⁺-Mes (eq 2). When the reaction is started from the isolated



An-O₂, no photochemical reaction has occurred without Acr⁺-Mes or no thermal reaction has taken place with Acr⁺-Mes. The photochemical reaction time profile of the photocatalytic oxygenation of An is examined by ¹H NMR as shown in Figure 1. After An-O₂ is converted to 10-hydroxyanthrone, the anthrone is further oxidized under prolonged photoirradiation to yield the final six-electron oxidation product, i.e., anthraquinone, which is accompanied by generation of H₂O₂ (eq 3). The yield of H₂O₂ was determined as 99% (see Experimental Section). The oxygenated final product of 9-methylanthracene (MeAn) was 10-hydroxy-10-methylanthrone as reported previously for the electron-transfer oxidation of MeAn.³⁸

In the case of Me₂An, the Me₂An-O₂ is stable under the photocatalytic conditions. This indicates that the photocatalytic conversion from An-O₂ to 10-hydroxyanthrone (eq 2) requires the migration of hydrogen. The further oxidation of 10-hydroxyanthrone (eq 3) also requires photoirradiation in the presence of Acr⁺-Mes (vide supra).

When ¹⁸O₂ is employed instead of ¹⁶O₂, ¹⁸O-labeled anthraquinone is produced as indicated by GC-MS (see Support-

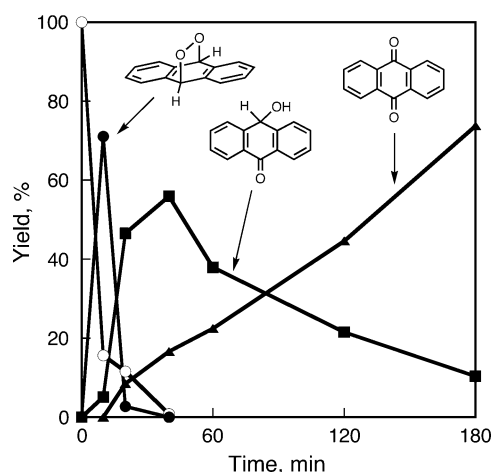


Figure 1. Photoirradiation time profile of the photooxygenation of anthracene (1.0×10^{-2} M) in the presence of Acr⁺-Mes (1.0×10^{-3} M) in O₂-saturated CD₃CN; anthracene (○), An-O₂ (●), 10-hydroxyanthrone (■), and anthraquinone (▲).

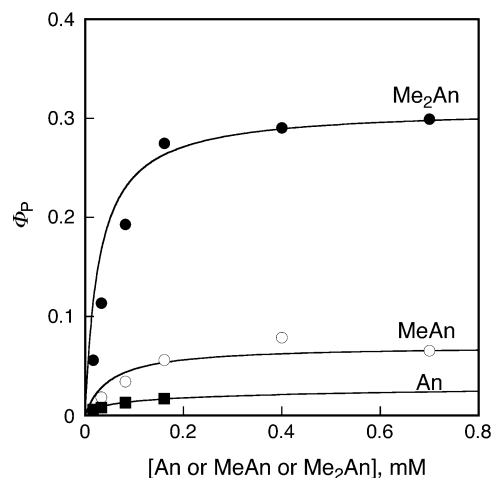


Figure 2. Dependence of the quantum yields (Φ_P) of formation of epidioxyanthracenes of Me₂An (●), MeAn (○), and An (■) on concentrations of anthracenes in photooxygenation of anthracenes in the presence of Acr⁺-Mes (2.0×10^{-4} M) in O₂-saturated MeCN.

ing Information Figure S1). This indicates that the two oxygen atoms of anthraquinone come from O₂.

The quantum yields (Φ_P) of formation of epidioxyanthracenes were determined from a decrease in absorbance due to anthracenes using an actinometer (see Experimental Section). The dependence of Φ_P on concentrations of anthracenes is shown in Figure 2. In each case, the Φ_P value increases with increasing concentration of anthracene or its derivative to reach a constant value ($> 10^{-4}$ M). Such a saturation behavior of Φ_P at the low concentration region indicates that the photooxygenation occurs via the long-lived electron-transfer state (Acr⁺-Mes⁺) produced by photoinduced electron transfer from the Mes moiety to the singlet excited state of the Acr⁺ moiety. The Φ_P values at a fixed concentration of anthracenes (7.0×10^{-4} M) are listed in Table 1. The photocatalytic oxygenation mechanism is discussed in the following section.

Photocatalytic Oxygenation Mechanism via Radical Coupling. To elucidate the photocatalytic oxygenation mechanism, the intermediate species are detected by laser flash photolysis experiments. Nanosecond laser excitation at 430 nm of a deaerated MeCN solution of Acr⁺-Mes results in formation

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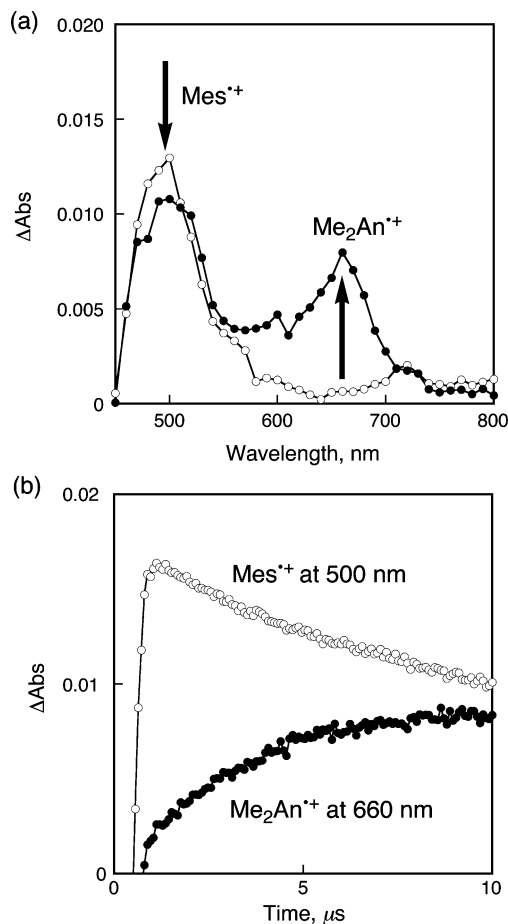


Figure 3. (a) Transient absorption spectra of Acr^+-Mes (1.0×10^{-4} M) in deaerated MeCN at 298 K taken at 15 μs after laser excitation at 430 nm in the absence (○) and presence (●) of Me_2An (5.0×10^{-5} M). (b) Absorbance time profiles at 500 nm due to Mes^+ (○) and at 660 nm due to Me_2An^+ (●).

of the electron-transfer state ($\text{Acr}^+-\text{Mes}^+$) via photoinduced electron transfer from the Mes moiety to the singlet excited state of the Acr^+ moiety.²⁵ The quantum yields for the formation of the electron-transfer state ($\text{Acr}^+-\text{Mes}^+$) has been previously determined as almost quantitative (98%).²⁵ Since the one-electron reduction potential of $\text{Acr}^+-\text{Mes}^+$ ($E_{\text{red}}^\circ = 1.88$ V vs SCE)²⁵ is more positive than the one-electron oxidation potential of Me_2An ($E_{\text{ox}}^\circ = 1.05$ V vs SCE),³⁹ electron transfer from Me_2An to the Mes^+ moiety in $\text{Acr}^+-\text{Mes}^+$ is energetically feasible. Thus, the addition of Me_2An to the MeCN solution of Acr^+-Mes and the laser photoirradiation result in formation of the Me_2An radical cation (Me_2An^+ ; $\lambda_{\text{max}} = 660$ nm)³⁸ with a concomitant decrease in the absorption band due to the Mes^+ moiety as shown in Figure 3a and b. It is important to note that the absorption band due to the Acr^+ moiety remains virtually the same in the absence of O_2 (Figure 3a). This indicates clearly that Me_2An^+ is formed by electron transfer from Me_2An to $\text{Acr}^+-\text{Mes}^+$ rather than by direct photoinduced electron transfer from Me_2An to the singlet excited state of the Acr^+ moiety in Acr^+-Mes . The rate of formation of Me_2An^+ increases with increasing concentration of Me_2An as shown in Figure 4a. The formation rate obeyed pseudo-first-order kinetics, and the pseudo-first-order rate constant (k_{obs}) increases linearly with

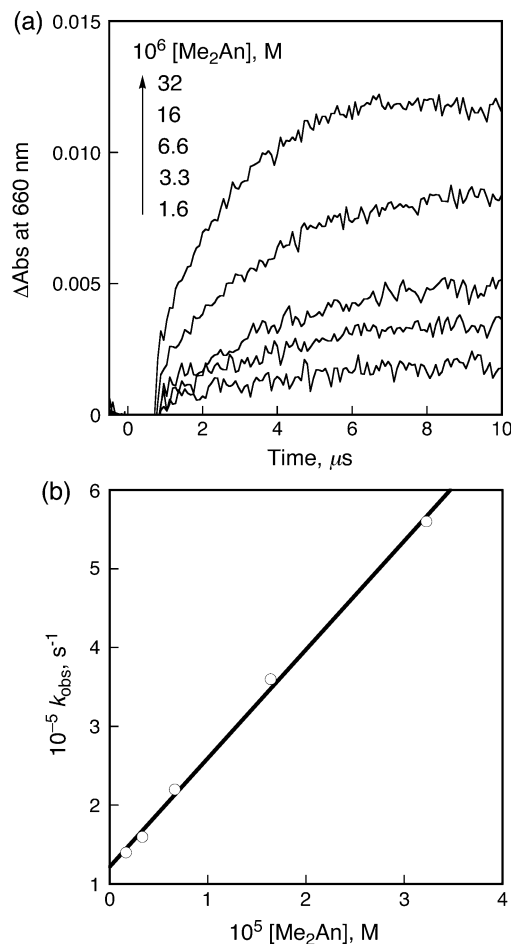


Figure 4. (a) Absorbance time profiles at 660 nm due to Me_2An^+ in the presence of various concentrations of Me_2An . (b) Plot of the pseudo-first-order rate constant (k_{obs}) for electron transfer from Me_2An to the Mes^+ moiety of $\text{Acr}^+-\text{Mes}^+$ vs $[\text{Me}_2\text{An}]$.

increasing concentration of Me_2An (Figure 4b). The second-order rate constant (k_{et}) of electron transfer from Me_2An to $\text{Acr}^+-\text{Mes}^+$ is determined from the slope of the linear plot in Figure 4b as $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is close to be the diffusion-limited value as expected from the exergonic electron transfer. Transient absorption spectra of radical cations of An and MeAn are also detected in the photoirradiation of Acr^+-Mes in the presence of An and MeAn (see Supporting Information Figure S2). The k_{et} values of anthracenes thus determined are also listed in Table 1, together with the one-electron oxidation potentials (E_{ox}°) of anthracenes.

The quantum yields (Φ_{R}) of formation of anthracene radical cations were determined from the transient absorption and the extinction coefficients using a comparative method (see Experimental Section). The dependence of Φ_{R} on concentrations of anthracenes is shown in Figure 5, where the Φ_{R} value becomes constant at a low concentration region of anthracene or its derivative ($>10^{-4}$ M) as in the case of the product quantum yields (Φ_{P}) in Figure 2. The quantum yields (Φ_{R}) at 2.8×10^{-4} M anthracenes are also listed in Table 1.

Although the absorption band due to the Acr^+ moiety remains virtually the same in the absence of oxygen (vide supra, see Figure 3a), the absorption band due to the Acr^+ moiety decays in the presence of O_2 by electron-transfer reduction from the Acr^+ moiety to O_2 . The decay of the transient spectrum at 500 nm due to the Acr^+ moiety obeys pseudo-first-order kinetics,

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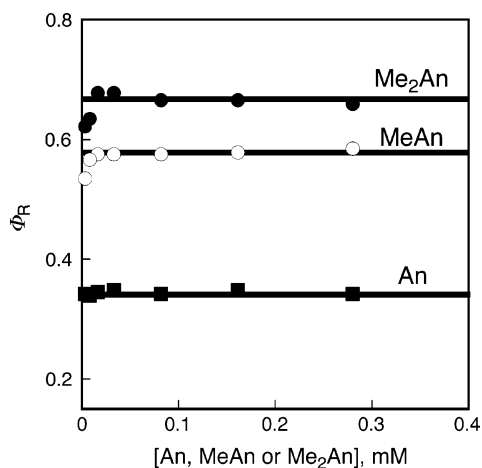


Figure 5. Dependence of the quantum yields (Φ_R) of formation of radical cations of Me₂An (●), MeAn (○), and An (■) on concentrations of anthracenes after laser photoexcitation at 430 nm of Acr⁺–Mes (1.0 × 10^{−4} M) in deaerated MeCN solution containing anthracenes.

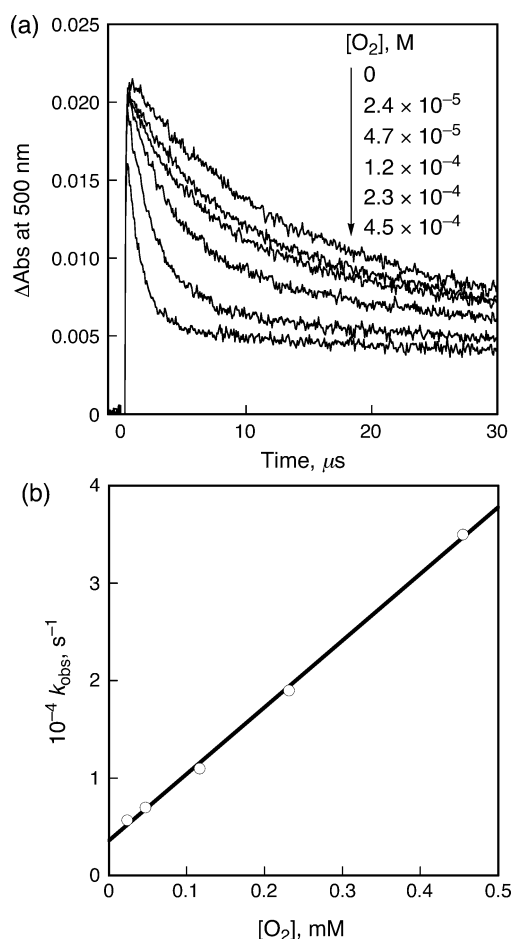


Figure 6. (a) Absorbance time profiles at 500 nm due to Acr^{*}–Mes^{**} in the presence of various concentrations of O₂ in MeCN containing Acr⁺–Mes (1.0 × 10^{−4} M). (b) Plot of the pseudo-first-order rate constant (k_{obs}) for electron transfer from the Acr^{*} moiety of Acr⁺–Mes^{**} to O₂ vs [O₂].

and the pseudo-first-order rate constant increases linearly with O₂ concentration (Figure 6a and b). The rate constant of electron transfer from the Acr^{*} moiety to O₂ (k'_{et}) was determined from the slope of Figure 6b as 6.8 × 10⁸ M^{−1} s^{−1}. The observed residual absorbance is attributed to the Mes^{**} moiety of Acr⁺–Mes^{**}, which decays at a prolonged reaction time by back electron transfer (BET) from O₂^{•−} to the Mes^{**} moiety of Acr⁺–

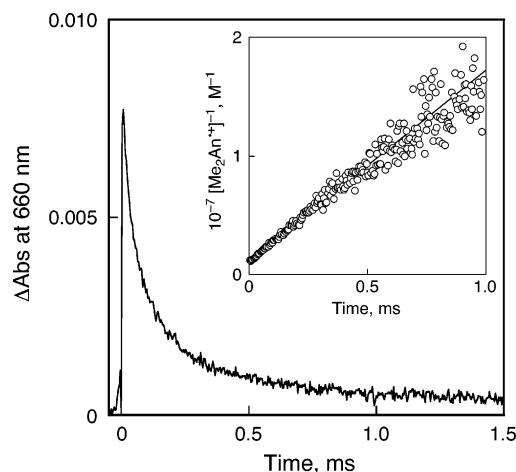


Figure 7. Decay time profile of absorbance at 660 nm due to Me₂An^{**} after laser excitation at 430 nm in an O₂-saturated MeCN solution containing Acr⁺–Mes (1.0 × 10^{−4} M) and Me₂An (1.0 × 10^{−3} M). Inset: Second-order plot.

Mes^{**}. Such a bimolecular decay obeys second-order kinetics. The formation of O₂^{•−} was confirmed by the ESR spectrum which was measured at 123 K immediately after the photoirradiation of an MeCN solution of Acr⁺–Mes (1.0 × 10^{−4} M) at 233 K ($g_{\parallel} = 2.1050$ and $g_{\perp} = 2.0032$, see Supporting Information Figure S3).^{40,41}

In the presence of both Me₂An and O₂, the quantum yields (Φ_R') of formation of anthracene radical cations were also determined from the transient absorption and the extinction coefficients using a comparative method, and the Φ_R' values at 1.0 × 10^{−3} M anthracenes are also listed in Table 1. The Φ_R' values of formation of anthracene radical cations in the presence of O₂ are larger than the corresponding Φ_R values in the absence of O₂. This indicates that electron transfer from the Acr^{*} moiety to O₂ prevents back electron transfer from the Acr^{*} moiety to anthracene radical cations, resulting in the increase in the Φ_R' values. The absorbance at 660 nm due to Me₂An^{**} decays obeying second-order kinetics. The second-order plot in Figure 7 affords the second-order rate constant as 1.7 × 10¹⁰ M^{−1} s^{−1} which is close to the diffusion-limited value in MeCN. The quantum yields of the formation of anthracene radical cations (Φ_R') in the presence of O₂ are significantly larger than those of the epidioxyanthracenes formation (Φ_P) (Table 1). This indicates that the back electron transfer from O₂^{•−} to anthracene radical cations to regenerate the reactant pair is also involved in the second-order decay of anthracene radical cations in addition to the radical coupling between anthracene radical cations and O₂^{•−} to afford the corresponding epidioxyanthracenes.

On the other hand, An–O₂ is known to be formed by the reaction of anthracene with ¹O₂.²⁶ To evaluate the contribution of the singlet oxygen pathway, the rate constant of the reaction of ¹O₂ with Me₂An was determined by emission decay rates of ¹O₂ ($\lambda_{\text{em}} = 1270$ nm)⁴² in the presence of various concentrations of Me₂An as 2.4 × 10⁵ M^{−1} s^{−1} (Figure 8a and b). This value is by far smaller than the second-order decay rate constant of Me₂An^{**} (1.7 × 10¹⁰ M^{−1} s^{−1}). It was confirmed that no singlet

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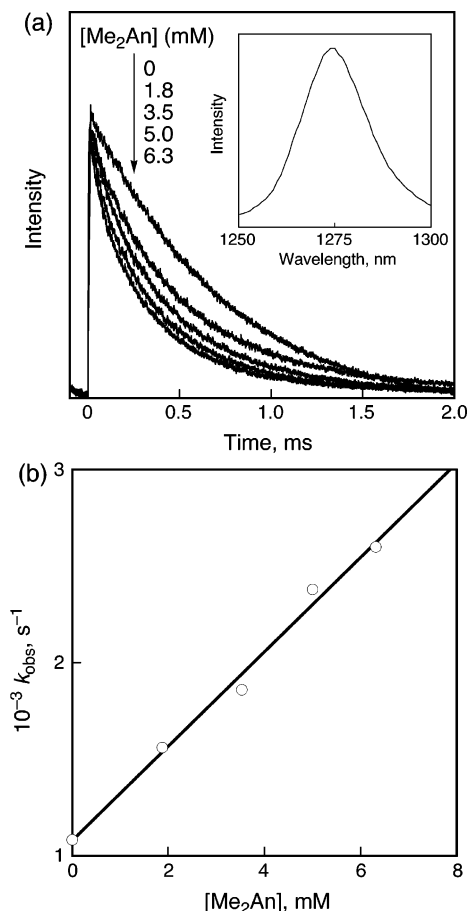


Figure 8. (a) Decay of emission intensity of singlet oxygen at 1270 nm generated by the laser irradiation ($\lambda = 355$ nm) of an O_2 -saturated C_6D_6 solution of C_{60} (2.0×10^{-4} M) containing various concentrations of Me_2An . Inset: Emission spectrum of singlet oxygen. (b) Plot of the pseudo-first-order decay rate constant for the emission quenching of the singlet oxygen by Me_2An vs $[Me_2An]$.

oxygen emission was observed during the photocatalytic oxygenation of Me_2An in an O_2 -saturated CD_3CN . Thus, it can be safely concluded that the $An-O_2$ is formed exclusively by the radical coupling between anthracene radical cation and $O_2^{\cdot-}$ (k_c) rather than the reaction of anthracene and 1O_2 as shown in Scheme 1. With regard to the radical coupling process, the fast radical coupling process being close to being diffusion-limited (vide infra) has precluded determining whether it is concerted or stepwise.

In order to elucidate the photocatalytic conversion of $An-O_2$ to 10-hydroxyanthrone (vide supra), we examined the laser flash photolysis of a deaerated MeCN solution of Acr^+-Mes in the presence of $An-O_2$. The addition of $An-O_2$ to a deaerated MeCN solution of Acr^+-Mes and laser photoirradiation result in appearance of a new absorption band at 650 nm together with an absorption band at 500 nm due to the Acr^* moiety as shown in Figure 9a. Virtually the same absorption band appears at 650 nm when $An-O_2$ is replaced by 10-hydroxyanthrone (Figure 9b). This indicates that $An-O_2$ radical cation, which is initially formed by electron transfer from $An-O_2$ to Acr^+-Mes^+ , is rapidly converted to 10-hydroxyanthrone radical cation within the

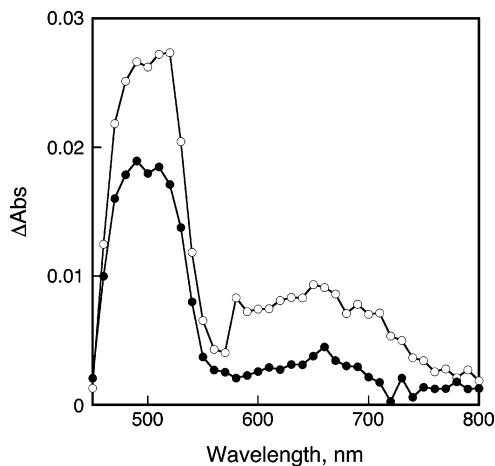
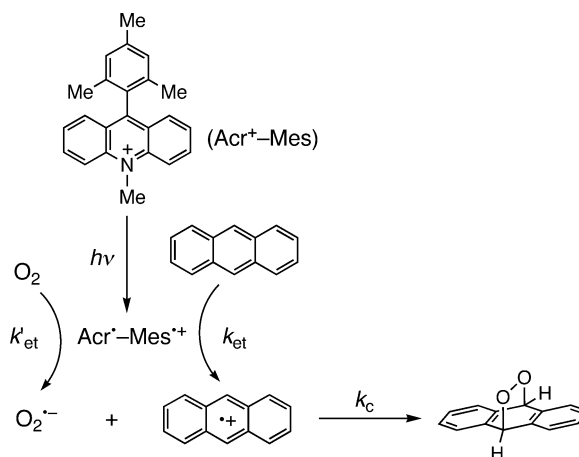


Figure 9. Transient absorption spectra of Acr^+-Mes (1.0×10^{-4} M) in deaerated MeCN at 298 K taken 20 μs after laser excitation at 355 nm in the presence of (O) $An-O_2$ (1.0×10^{-3} M) and (●) 10-hydroxyanthrone (3.3×10^{-4} M).

Scheme 1

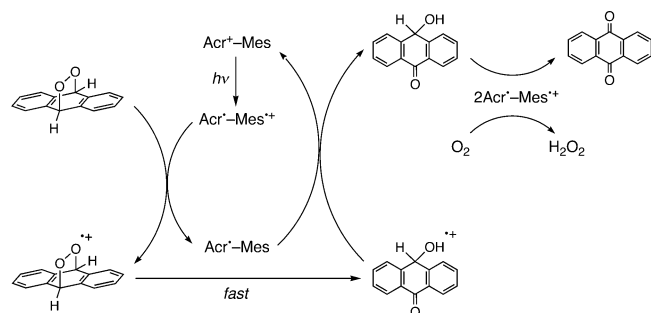


present time scale of the measurements. This is consistent with the redox potentials of $An-O_2$ determined by the CV and SHACV measurements (see Supporting Information Figure S4), since electron transfer from $An-O_2$ (E_{ox}^0 vs SCE = 2.05 V) to the Mes^+ moiety (E_{red}^0 vs SCE = 1.88 V) is thermodynamically much more favorable than that from the Acr^* moiety (E_{ox}^0 vs SCE = -0.57 V) to $An-O_2$ (E_{red}^0 vs SCE = -0.94 V). The rate of appearance of the absorption band at 650 nm due to 10-hydroxyanthrone obeys pseudo-first-order kinetics, and the pseudo-first-order rate constant (k_{obs}) increases linearly with increasing concentration of $An-O_2$ (see Supporting Information Figure S5). The second-order rate constant (k_{et}) of electron transfer from $An-O_2$ to the Mes^+ moiety of Acr^+-Mes^+ is determined from the slope of the linear plot of k_{obs} vs concentration of $An-O_2$ as 1.2×10^8 $M^{-1} s^{-1}$.

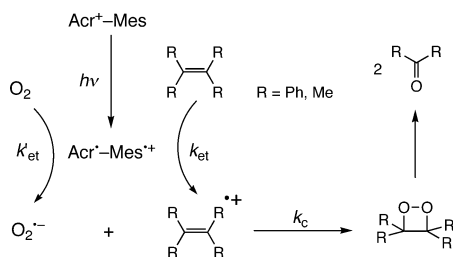
The mechanism of the photocatalytic conversion of $An-O_2$ to 10-hydroxyanthrone is shown in Scheme 2. The electron transfer from $An-O_2$ to the Mes^+ moiety of Acr^+-Mes^+ , produced upon photoexcitation of Acr^+-Mes , results in the O–O bond cleavage of $An-O_2$, followed by facile intramolecular hydrogen transfer to produce 10-hydroxyanthrone radical cation. This is supported by the DFT calculations using B3LYP/6-31G* basis set (see Experimental Section), which indicate that the 10-hydroxyanthrone radical cation is 60 $kcal\ mol^{-1}$ more stable than the $An-O_2$ radical cation. The back electron transfer from

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Scheme 2



Scheme 3



the Acr[•] moiety to 10-hydroxyanthrone radical cation affords 10-hydroxyanthrone, accompanied by regeneration of Acr⁺–Mes (Scheme 2).

The electron-transfer oxidation of 10-hydroxyanthrone by the mesitylene radical cation moiety of Acr[•]–Mes^{•+} results in the two-electron oxidation to yield anthraquinone by releasing two protons, whereas the two-electron reduction of O₂ by the acridinyl radical moiety of Acr[•]–Mes^{•+} with two protons yields H₂O₂ (Scheme 2).

Formation of Dioxetanes via Radical Coupling. The radical coupling reaction between the anthracene radical cation and O₂^{•-} to produce An–O₂ in Scheme 1 can be expanded to the dioxetane formation from olefins.^{43–46} Visible light irradiation ($\lambda > 430$ nm) to an O₂-saturated MeCN solution of Acr⁺–Mes (2.0 × 10⁻³ M) with tetraphenylethylene or tetramethylethylene (1.0 × 10⁻² M) results in formation of the corresponding radical cation and O₂^{•-}, followed by the radical coupling to afford the dioxetane as shown in Scheme 3. The products were analyzed by ¹H NMR (see Experimental Section). The irradiation time profiles are shown in Figure 10a and b, where tetraphenylethylene and tetramethylethylene are converted to the corresponding dioxetanes, in which the O–O bond is cleaved at a prolonged irradiation time to yield benzophenone and acetone, respectively.^{47–49}

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(49) The photocatalytic O–O bond cleavage of the dioxetane may proceed via electron transfer from the dioxetane to the Mes^{•+} moiety of Acr[•]–Mes^{•+} as in the case of An–O₂ (Scheme 2). However, the detailed mechanism has yet to be clarified.

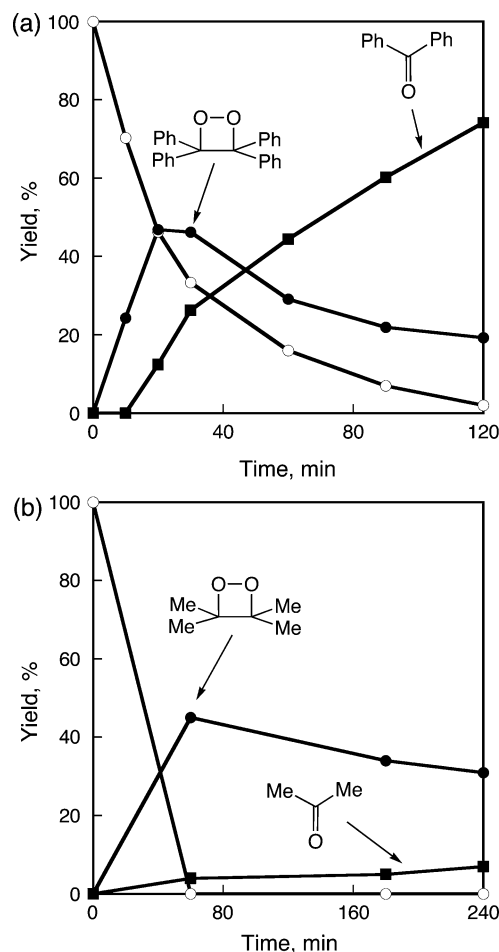


Figure 10. (a) Photoirradiation time profile of photooxygenation of tetraphenylethylene (1.0 × 10⁻² M) in the presence of Acr⁺–Mes (2.0 × 10⁻³ M) in O₂-saturated CD₃CN; tetraphenylethylene (○), tetraphenylethylene dioxetane (●) and benzophenone (■). (b) Photoirradiation time profile of photooxygenation of tetramethylethylene (1.0 × 10⁻² M) in the presence of Acr⁺–Mes (2.0 × 10⁻³ M) in O₂-saturated CD₃CN; tetramethylethylene (○), tetramethylethylene dioxetane (●) and acetone (■).

In conclusion, the use of Acr⁺–Mes as an electron-transfer photocatalyst in the presence of O₂ provides a convenient methodology to produce radical cations of electron donors of anthracenes and olefins as well as O₂^{•-}, which can combine together to yield the oxygenated products selectively in a preparative scale.

Acknowledgment. This work was partially supported by a Grant-in-Aid (No. 16205020) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: GC–MS spectra of anthraquinone (Figure S1), transient spectra of MeAn (Figure S2), ESR spectrum of O₂^{•-} produced in the electron transfer from Acr[•]–Mes^{•+} to O₂ (Figure S3), the CV of An–O₂ and Acr⁺–Mes (Figure S4), and a plot of the pseudo-first-order rate constant (*k*_{obs}) of formation of An–O₂ radical cation vs concentration of An–O₂ (Figure S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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