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Efficient Photocatalytic Oxygenation of Aromatic Alkene to 1,2-Dioxetane with Oxygen via Electron Transfer

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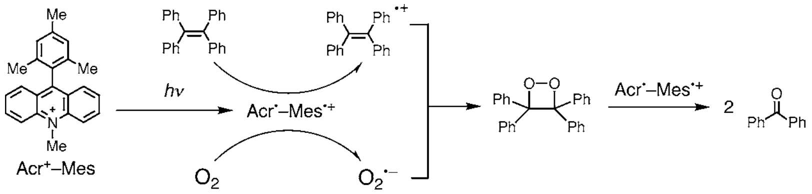
ABSTRACT



Photocatalytic oxygenation of tetraphenylethylene (TPE) with oxygen occurs efficiently via electron-transfer reactions of TPE and oxygen with a photogenerated electron transfer state of 9-mesityl-10-methylacridniium ion, followed by the radical-coupling reaction between TPE radical cation and $O_2^{•-}$ to produce 1,2-dioxetane selectively. The further photocatalytic cleavage of the O–O bond of dioxetane affords benzophenone as the final oxygenated product.

1,2-Dioxetanes have attracted considerable interest because of the key roles in chemiluminescence and bioluminescence,[1,2] which have a broad range of biological, chemical, and medical applications.[3−5] The most common preparation of 1,2-dioxetanes is through the formal [2 + 2] cycloaddition of singlet oxygen ($^1O_2$) to electron-rich alkenes.[6,7] Diastereoselective formation of dioxetanes has also been achieved by a chiral-axially induced [2 + 2] cycloaddition of $^1O_2$ with a chiral allylic alcohol and enecarbamates.[8−10] If alkenes are too electron poor to react with $^1O_2$, however, no oxygenated products were obtained. For example, it was reported that no products were formed in an oxygen-saturated acetonitrile solution of tetraphenylethylene (TPE) in the presence of $^1O_2$ sensitizers under photoirradiation.[11]

We report herein that the photocatalytic oxygenation of TPE with O_2 occurs efficiently with 9-mesityl-10-methylacridinium ion (Acr^+-Mes) via the radical coupling between TPE radical cation ($TPE^{•+}$) and $O_2^{•-}$, both of which were produced by electron-transfer reactions of TPE and O_2 with the photogenerated electron-transfer state of Acr^+-Mes ($Acr^•$-$Mes^{•+}$),[12] leading to successful isolation of the corresponding

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1,2-dioxetane.[13] It was confirmed that no oxygenation occurred in an O_2-saturated solution of TPE containing C_{60} or tetraphenylporphyrin as $^1O_2$ sensitizers instead of Acr^+-Mes under otherwise the same experimental conditions, i.e., photoirradiation time, concentration of TPE, and solvent.[14]

Visible light irradiation (λ > 430 nm) of the absorption band of Acr^+-Mes (2.0×10^{-3} M) in an O_2-saturated chloroform ($CHCl_3$) solution containing TPE (1.5×10^{-2} M) results in formation of the oxygenation products, i.e., dioxetane after 30 min irradiation by a 500 W xenon lamp. The photoirradiation time profiles are shown in Figure 1.

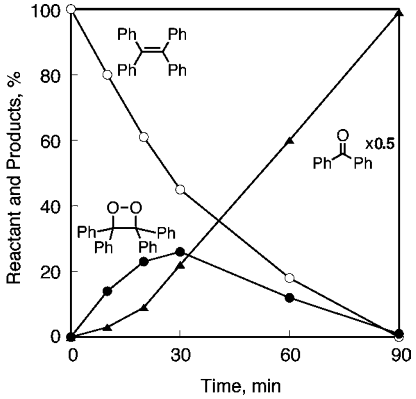

Figure 1. Photoirradiation time profiles of photooxygenation of TPE (1.5×10^{-2} M) in the presence of Acr^+-Mes (5.0×10^{-3} M) in O_2-saturated $CDCl_3$ (0.6 mL).

The dioxetane is converted to benzophenone quantitatively (199% based on the consumption of TPE) at prolonged irradiation time (Figure 1).

The photocatalytic oxygenation of TPE with O_2 on a preparative scale (60 mg, 1.8×10^{-4} mol) with Acr^+-Mes (3.8 mg, 8.7×10^{-6} mol) in chloroform (2.0 mL) was also performed to isolate the corresponding 1,2-dioxetane (27% yield) after 4 h of photoirradiation at 278 K. The dioxetane was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectra.[15,16] The purity of dioxetane was >99%, estimated by ^{1}H NMR (see the Supporting Information). Photooxygenation also occurred in MeCN; however, the rate is much slower than the case in $CHCl_3$. The product yield in MeCN was determined to be 156% after 2 h photoirradiation. The quantum yields (Φ) of the formation of the dioxetane were determined from the formation rate of benzophenone under irradiation of monochromatized light of $\lambda = 430$ nm. The Φ values were the same at different oxygen concentrations. The Φ value increases with an increase in concentration of TPE to approach a limitting value (Φ_∞) (Figure 2a).[17] The linear plot of Φ^{-1} and $[TPE]^{-1}$ in accordance with eq 1 is shown in Figure 2b. From the intercept in Figure 2b, the

$$\Phi^{-1} = \Phi_\infty^{-1}[1 + \text{const} \times [\text{TPE}]^{-1}] \qquad (1)$$

Φ_∞ value is determined as 17% in $CHCl_3$. The Φ_∞ value is also determined in MeCN as listed in Table 1.

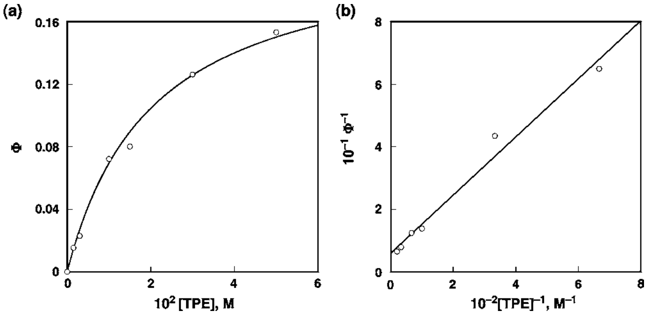

Figure 2. (a) Dependence of the quantum yield (Φ) of benzophenone on concentration of TPE for the Acr^+-Mes (5.0×10^{-3} M)-catalyzed photooxygenation of TPE in oxygen-saturated $CHCl_3$ at 298 K. (b) Plot of Φ^{-1} vs $[TPE]^{-1}$.

Table 1. Rate Constants of Electron Transfer (k_{et} and k'_{et}) and Radical Coupling (k_c), Limiting Quantum Yield (Φ_∞), and Product Yields of Benzophenone

	MeCN	$CHCl_3$
k_{et}, $M^{-1}\,s^{-1}$	7.2×10^8	2.5×10^9
k'_{et}, $M^{-1}\,s^{-1}$	6.8×10^8	3.8×10^8
k_c, $M^{-1}\,s^{-1}$	1.0×10^{10}	6.0×10^9
Φ_∞, %	2.2	17
product yield,[a] %	156[b]	199[c]

[a] Based on the consumption of TPE and determined from ^{1}H NMR. [b] After 2.0 h of photoirradiation. [c] After 1.5 h of photoirradiation.

Nanosecond laser excitation at 430 nm of a deaerated $CHCl_3$ solution of Acr^+–Mes results in formation of the electron-transfer state ($Acr^\bullet$–$Mes^{\bullet+}$) via photoinduced electron transfer from the Mes moiety to the singlet excited state

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[13] For the [4 + 2] cycloaddition of anthracene radical cation with $O_2^{\bullet-}$, see: Kotani, H.; Ohkubo, K.; Fukuzumi, S. *J. Am. Chem. Soc.* **2004**, *126*, 15999.

[14] Very slow reaction of TPE with $^1O_2$ has been reported. Rio, G.; Berthelot, J. *Bull. Chem. Soc. Fr.* **1969**, 3609.

[15] Typically, a chloroform solution (2 mL) containing Acr^+-Mes (3.8 mg, 8.7×10^{-6} mol) and TPE (60 mg, 1.8×10^{-4} mol) in a Schlenk flask with a rubber septum was saturated with oxygen by bubbling with oxygen through a stainless steel needle for 20 min. The solution was then irradiated with a 500 W xenon lamp (Ushio Optical ModelX SX-UID 500XAMQ) through a color filter glass (Asahi Techno Glass Y43) transmitting λ > 430 nm at 278 K. After 5 h of photoirradiation, the corresponding dioxetane was isolated by silica gel column chromatography (hexane/chloroform v/v 2/1) as a pale yellow solid (27% yield). The product is moisture sensitive. Tetraphenylethylene dioxetane: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14–7.18 (m, 12H), 7.22–7.28 (m, 8H); ^{13}C NMR (600 MHz, $CDCl_3$) δ 97.77 (C–O), 127.39, 127.57, 127.69, 140.16; IR(KBr) 956 (O–O), 1010 (C–O) cm^{-1}; mp 93–95 °C.

[16] *Caution! Dryness of dioxetane may result in explosion. All preparation should be handled with care and dioxane used only in small quantities.*

[17] A standard actinometer (potassium ferrioxalate) was used for the quantum yield determination of the photocatalytic oxygenation of TPE with O_2.

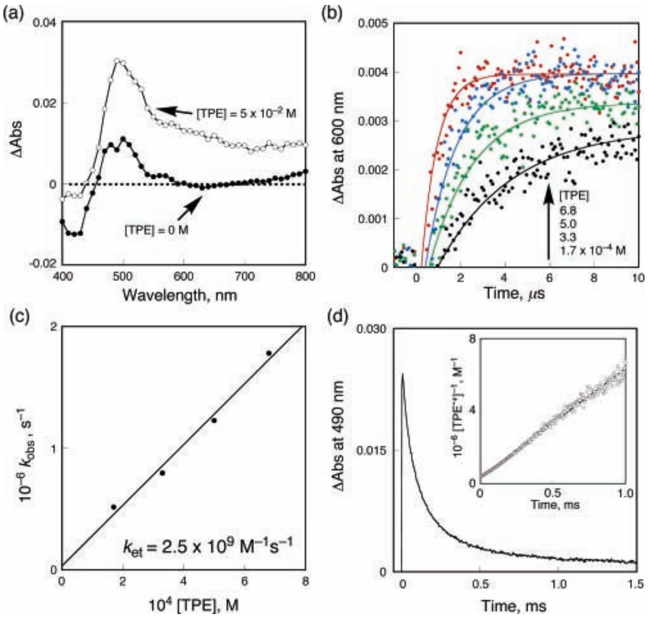
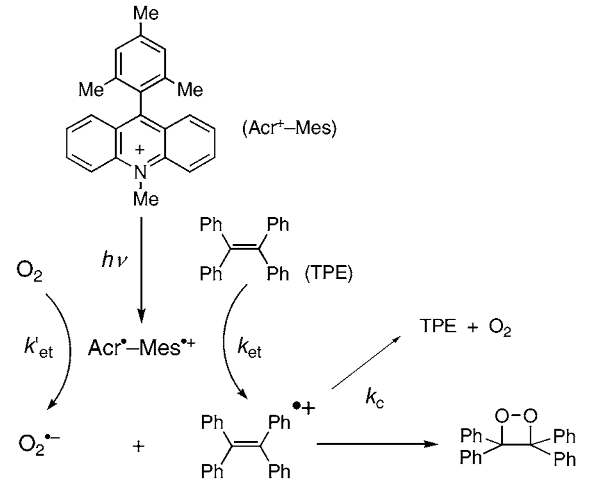


Figure 3. (a) Transient absorption spectra observed in photoinduced electron-transfer oxidation of TPE (0.05 M) with Acr$^+$-Mes (6.0×10^{-5} M) taken 2.0 μs after laser excitation at 430 nm in deaerated $CHCl_3$ at 298 K. (b) Time profiles at 600 nm with single-exponential curve. (c) Plot of pseudo-first-order rate constant (k_{obs}) vs concentration of TPE. (d) Decay time profile at 490 nm observed in photoinduced electron-transfer oxidation of TPE (0.05 M) with Acr$^+$-Mes (6.0×10^{-5} M) in O_2-saturated $CHCl_3$. Inset: second-order plot.

of the Acr$^+$ moiety as shown in Figure 3a (closed circles). Since the one-electron reduction potential of Acr$^•$−Mes$^{•+}$ (E_{red} = 1.88 V vs SCE)[12] is more positive than the one-electron oxidation potential of TPE (E_{ox} = 1.31 V vs SCE in $CHCl_3$),[18] electron transfer from TPE to the Mes$^{•+}$ moiety in Acr$^•$-Mes$^{•+}$ is energetically feasible. Thus, the addition of TPE to a $CHCl_3$ solution of Acr$^+$-Mes and the laser photoirradiation results in formation of TPE$^{•+}$ (λ_{max} = 490 nm, ϵ = 9800 M^{-1} cm^{-1})[19,20] as shown in Figure 3a (open circles). The formation rate of TPE$^{•+}$ obeyed pseudo-first-order kinetics, and the pseudo-first-order rate constant (k_{obs}) increases linearly with increasing concentration of TPE (Figure 3b,c). The second-order rate constant (k_{et}) of electron transfer from TPE to Acr$^•$-Mes$^{•+}$ is determined as 2.5×10^9 M^{-1} s^{-1} in $CHCl_3$, which is close to be the diffusion-limited value as expected from the exergonic electron transfer. The second-order rate constant of electron-transfer reduction of O_2 (k'_{et}) by the Acr$^•$ moiety was also determined as 3.8×10^8 M^{-1} s^{-1} in $CHCl_3$.

The formation of $O_2^{•-}$ was confirmed by ESR, which was measured in frozen $CHCl_3$ at 123 K after the photoirradiation of a chloroform solution of TPE (1.0×10^{-3} M) and Acr$^+$-Mes (1.0×10^{-4} M) at 233 K ($g_{\parallel}$ = 2.1050 and $g_{\perp}$ = 2.0032).[21] The transient absorption band of TPE$^{•+}$ decays second-order kinetics as shown in Figure 3d. The second-order rate constant (k_c) was determined as 6.0×10^9 M^{-1} s^{-1} which is close to the diffusion-limited value in $CHCl_3$.[22] The bimolecular process involves both the radical coupling between TPE$^{•+}$ and $O_2^{•-}$ to afford the corresponding dioxetane and the back electron transfer from $O_2^{•-}$ to TPE$^{•+}$ to regenerate the reactant pair (Scheme 1).

Scheme 1



Rate constants of electron transfer and the radical coupling, the quantum yields, and the product yields in MeCN and $CHCl_3$ are summarized in Table 1.

The E_{ox} and E_{red} values of the dioxetane were determined by second-harmonic ac voltammetry (SHACV) as 1.56 and −0.95 V vs SCE, respectively. The E_{ox} value is less positive than the E_{red} value (1.88 V vs SCE)[12] of the Mes$^{•+}$ moiety of Acr$^•$-Mes$^{•+}$, whereas the E_{ox} value of the Acr$^•$ moiety (−0.57 V vs SCE) is less negative than the E_{red} value of the dioxetane. In such a case, the dioxetane may be oxidized by Acr$^•$-Mes$^{•+}$ rather than by being reduced to produce the dioxetane radical cation, which undergoes the O−O bond homolysis to produce benzophenone and the radical cation as shown in Scheme 2. The benzophenone radical cation may be reduced by Acr$^•$-Mes to produce another benzophenone molecule, accompanied by regeneration of Acr$^+$-Mes (Scheme 2).

The thermal oxygenation reaction of TPE with oxygen has previously been proposed to proceed via radical chain processes as shown in Scheme 3.[23,24] The dioxetane is assumed to be produced by direct oxygenation of the

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(18) The electrochemical measurements were performed on a BAS 630B electrochemical analyzer in deaerated $CHCl_3$ containing 0.20 M Bu_4NClO_4 as a supporting electrolyte at 298 K.

(19) Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847.

(20) The concomitant decrease in the absorption band due to the Mes$^{•+}$ moiety of Acr$^•$-Mes$^{•+}$ is overlapped with an increase in the absorption band at 490 nm due to TPE$^{•+}$; see ref 13.

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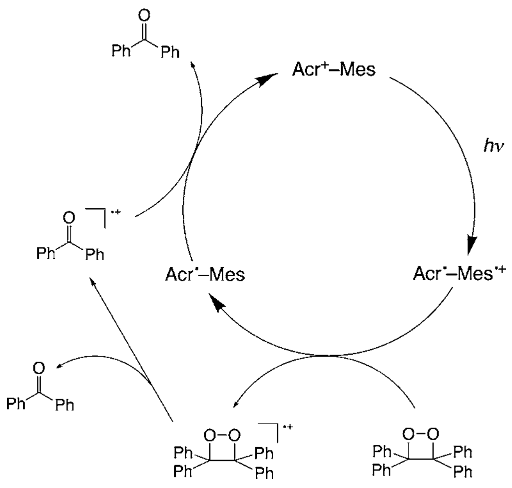
(22) Kavarnos, G. J. In *Fundamental of Photoinduced Electron Transfer*; Wiley-VCH: New York, 1993.

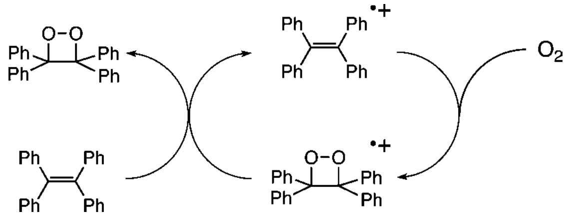
(23) (a) Nelsen, S. F.; Akaba, R. *J. Am. Chem. Soc.* **1981**, *103*, 2096. (b) Nelsen, S. F.; Kapp, D. L.; Akaba, R.; Evans, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 6863.

Scheme 2



dioxetane radical cation with O_2. However, the saturated dependence of Φ on [TPE] in Figure 2a (and also on $[O_2]$) indicates that such an electron-transfer radical chain process (Scheme 3) is not operative as the major pathway under the present photocatalytic reaction conditions. If the chain process in Scheme 3 were the major pathway, the Φ value would increase linearly with increasing concentration of TPE or O_2.

Scheme 3



The formation of the dioxetane radical cation was confirmed by ESR (electron spin resonance) measurements under photoirradiation at low temperature. A deaerated chloroform solution of Acr^+-Mes (3.7×10^{-2} M) with TPE dioxetane (3.0×10^{-3} M) was irradiated by a high-pressure Hg lamp at 223 K. The resulting ESR spectrum observed at 143 K is shown in Figure 4a, which exhibits anisotropic signals at $g_{||} = 2.020$ and $g_{\perp} = 2.004$. The isotropic g value (g_{iso}) is determined as 2.009 ± 0.001,[25,26] which agrees with the reported value of a dioxetane radical cation (2.0099).[27] The formation of TPE dioxetane radical cation was also confirmed by photoinduced electron-transfer oxidation of TPE dioxetane with the singlet excited state of 9,10-dicyanoanthracene ($^1E_{red}{}^* = 1.97$ V vs SCE) in frozen deaerated $CHCl_3$ at 143 K. The resulting ESR signal was virtually same as that shown in Figure 4a. The SOMO (singly occupied molecular orbital) of dioxetane radical cation involves O−O σ antibonding orbital (Figure 4b). This may be the reason for the facile cleavage of the O−O bond of the dioxetane radical cation.[28]

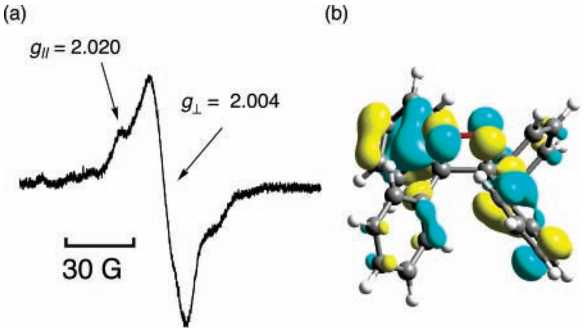


Figure 4. (a) ESR spectrum of TPE dioxetane radical cation observed under irradiation of a deaerated $CHCl_3$ solution containing TPE dioxetane (3.0×10^{-3} M) and Acr^+-Mes (3.7×10^{-2} M) at 223 K measured at 143 K (frozen). (b) The SOMO orbital of TPE dioxetane radical cation, calculated by the DFT method using the B3LYP/6-31G* basis set.

In conclusion, Acr^+-Mes acts as an efficient photocatalyst for the oxygenation of TPE with O_2, which proceeds via the radical coupling between $TPE^{\bullet+}$ and $O_2{}^{\bullet-}$ to yield the 1,2-dioxetane. The final product (benzophenone) is obtained from the O−O bond cleavage of the 1,2-dioxetane radical cation by the electron-transfer oxidation.

Acknowledgment. This work was partially supported by Grants-in-Aid (Nos. 16205020 and 17750039) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: ^{1}H NMR spectrum of TPE dioxetane. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Clennan, E. L.; Simmons, W.; Almgren, C. W. *J. Am. Chem. Soc.* **1981**, *103*, 2098.

(25) $g_{iso} = (g_{||} + 2g_{\perp})/3$.

(26) The ESR signal due to $Acr^\bullet$-Mes, which is more isotropic than the dioxetane radical cation,[12] may be overlapped with that of the dioxetane radical cation around $g = 2.004$.

(27) The isotropic g value of the dioxetane radical cation of adamantylidenadamantane has been reported as $g_{iso} = 2.0099$; see: Nelsen, S. F.; Kapp, D. L.; Gerson, F.; Lopez, J. *J. Am. Chem. Soc.* **1986**, *108*, 1027.

(28) C−O bond cleavage of dioxetane radical cation; see: Kamata, M.; Kaneko, J.; Hagiwara, J.; Akaba, R. *Tetrahedron Lett.* **2004**, *45*, 7423.