J. Phys. Chem. A **2003,** *107,* 4339−4346

Oxygenation of α-Methylstyrene with Molecular Oxygen, Catalyzed by 10-Methylacridinium Ion via Photoinduced Electron Transfer

Kyou Suga, Kei Ohkubo, and Shunichi Fukuzumi*

Department of Material and Life Science, Graduate School of Engineering, Osaka University,
CREST, Japan Science and Technology Corporation (JST), Suita, Osaka 565-0871, Japan

Received: January 27, 2003; In Final Form: March 14, 2003

Photooxygenation of α-methylstyrene with oxygen occurs efficiently in the presence of 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$) under visible light irradiation in oxygen-saturated acetonitrile (MeCN) to yield acetophenone as the main oxygenated product. No photoinduced oxygenation of α-methylstyrene occurs in the absence of $AcrH^+$ under otherwise the same experimental conditions. Little photodegradation of $AcrH^+$ occurs in the present photocatalytic system, which provides a clean method of photoinduced oxygenation reaction with molecular oxygen, alternate to the ene reaction of singlet oxygen. The photocatalytic oxygenation of α-methylstyrene with oxygen is shown to proceed via photoinduced electron transfer from α-methylstyrene to the singlet excited state of $AcrH^+$ ($^1AcrH^{+*}$) on the basis of the fluorescence quenching of $^1AcrH^{+*}$ by α-methylstyrene, the quantum yield determination, and the detection of radical intermediates by laser flash photolysis and ESR measurements.

Introduction

Photosensitized oxygenation of organic compounds with molecular oxygen has attracted considerable attention, since the development of catalytic oxygenation systems employing molecular oxygen, which is the cleanest and cheapest oxidant, is highly desired from the environmental and economical points of view.[1,2] The mechanisms of photosensitized oxygenation reactions have been the subject of intense research, since many reactive intermediates such as singlet oxygen ($^1O_2$), superoxide anion ($O_2^{\bullet-}$), and substrate radical cations are involved in the photosensitized oxygenation reactions and the role of reactive intermediates is different depending on the photocatalytic systems.[3−7] Singlet oxygen is normally produced by dye-sensitized photooxygenation,[3] and a variety of substrates are known to be oxygenated by the reactions with singlet oxygen.[4−7] However, a sensitizer for the formation of $^1O_2$ is often converted to $O_2^{\bullet-}$ by the photoinduced electron-transfer reactions in the presence of an electron donor and acceptor.[8−10] Both $O_2^{\bullet-}$ and $^1O_2$ can be formed under the same reaction conditions, resulting in a competition between two different types of oxidation reactions.[11,12] In some cases, $^1O_2$ can be reduced to $O_2^{\bullet-}$ by thermal and photoinduced electron transfer from electron donors.[12] Such a complex situation has precluded the exact delineation of the photooxygenation mechanism. In contrast, sensitizers such as 10-methylacridinium ion and 2,4,6-triphenylpyrylium ion are known to generate neither $^1O_2$ nor $O_2^{\bullet-}$.[13−17] This situation simplifies the mechanistic study on the photosensitized oxygenation reactions using these sensitizers.[13−16] Nonetheless, the detailed photocatalytic oxygenation mechanisms have yet to be fully understood because of the lack of information about the reactive intermediates.

We report herein that photooxygenation of α-methylstyrene with oxygen involving the cleavage of the carbon−carbon double bond occurs efficiently in the presence of 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$) under visible light irradiation in oxygen-saturated acetonitrile to yield acetophenone. The oxidative cleavage of alkenes to carbonyl compounds has been used as a useful synthetic tool in natural product synthesis.[18] The photocatalyst ($AcrH^+$) is found to be relatively stable under the photocatalytic conditions, as compared with other reported photosensitizers.[19,20] Thus, the present study provides a useful method of photoinduced double bond cleavage of alkenes with molecular oxygen under visible light irradiation. In addition, the detection of reactive intermediates in the photocatalytic oxygenation reaction by laser flash photolysis and ESR measurements as well as the kinetic study based on the quantum yield determination provides valuable insight into the mechanism of $AcrH^+$-photosensitized oxygenation of α-methylstyrene with oxygen.

Experimental Section

Materials. α-Methylstyrene, styrene, and acetophenone were obtained from Tokyo Kasei Kogyo Co., Ltd. *trans*-Stylbene and 1,1-diphenylethylene were obtained from Nacalai Tesque, Inc. 10-Methylacridinium iodide ($AcrH^+I^-$) was prepared by the reaction of acridine with methyl iodide in acetone, was converted to the perchlorate salt ($AcrH^+ClO_4^-$) by the addition of magnesium perchlorate to the iodide salt ($AcrH^+I^-$), and was purified by recrystallization from methanol.[21] Potassium ferrioxalate used as an actinometer was prepared according to the literature and purified by recrystallization from hot water.[22] Acetonitrile (MeCN) and propionitrile (EtCN) used as solvents were purified and dried by the standard procedure.[23] Deuterated [$^2H_3$]acetonitrile (CD_3CN, 99.8%) was obtained from EURI SOTOP, CEA, France, and used as received.

Reaction Procedure. Typically, an [$^2H_3$]acetonitrile (CH_3CN) solution (0.6 cm^3) containing $AcrH^+$ (1.0×10^{-2} M) and α-methylstyrene (3.0×10^{-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 mercury lamp through an acetophen-

---

* To whom correspondence should be addressed. E-mail: fukuzumi@ap.chem.eng.osaka-u.ac.jp.

10.1021/jp034213x CCC: $25.00

one−methanol filter transmitting $\lambda > 300$ nm light at room temperature. The irradiated solution was analyzed periodically by ^{1}H NMR spectroscopy. The ^{1}H NMR measurements were performed using a JEOL JMN-AL300 (300 MHz) NMR spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$). The products of the photoreaction of α-methylstyrene (3.0×10^{-2} M) with AcrH$^+$ (1.0×10^{-2} M) in oxygen-saturated CD$_3$CN (0.6 cm^3) were determined by ^{1}H NMR spectra. ^{1}H NMR (300 MHz, CD$_3$CN): acetophenone δ 2.56 (s, 3H), 7.4−8.0 (m, 5H); 2-(1-hydroxy-2-phenyl)propyl hydroperoxide δ 1.49 (s, 3H), 3.52 and 3.54 (asym, 2H).[24]

Quantum Yield Determination. A standard actinometer (potassium ferrioxalate)[22] was used for the quantum yield determination of the AcrH$^+$-photosensitized oxygenation of α-methylstyrene with oxygen. A square quartz cuvette (10 mm i.d.) which contained an acetonitrile solution (3.0 cm^3) of AcrH$^+$ (5.0×10^{-5} M) and α-methylstyrene (1.0×10^{-3} to 8.0×10^{-3} M) was irradiated with monochromatized light of $\lambda = 358$ nm from a Shimadzu RF-5300PC fluorescence spectrophotometer. Under the conditions of actinometry experiments, both the actinometer and AcrH$^+$ absorbed essentially all the incident light. The light intensity of monochromatized light of $\lambda = 358$ nm was determined as 2.53×10^{-9} einstein s^{-1} with the slit width of 20 nm, respectively. The photochemical reaction was monitored by using a Shimadzu UV-3100PC spectrophotometer. The quantum yields were determined from the disappearance of α-methylstyrene determined by GC as well as an increase in absorbance due to acetophenone ($\lambda = 278$ nm, $\epsilon = 1.1 \times 10^3$ M^{-1} cm^{-1}). The photochemical reaction was monitored using a Shimadzu GCMS-QP5000 mass spectrometer. The quantum yields were determined from the decrease in yield of α-methylstyrene. A 10-mm square quartz cuvette which contained an O$_2$-saturated MeCN solution (3.0 cm^3) of AcrH$^+$ ($0-1.5 \times 10^{-2}$ M) and α-methylstyrene (1.0×10^{-3} to 1.0×10^{-2} M) was irradiated with monochromatized light of $\lambda = 358$ nm using a Shimadzu spectrofluorophotometer (RF-5300PC). To avoid the contribution of light absorption of the products, only the initial rates were determined for determination of the quantum yields.

Fluorescence Quenching. Quenching experiments of the fluorescence of AcrH$^+$ by electron donors were performed using a Shimadzu RF-5300PC fluorescence spectrophotometer with the excitation wavelength 358 nm. The monitoring wavelength was that corresponding to the maximum of the emission band at 488 nm.[15] The solutions were deoxygenated by argon purging for 10 min prior to the measurements. Relative emission intensities were measured for MeCN solution containing AcrH$^+$ (5.0×10^{-5} M) with electron donors at various concentrations ($0-1.5 \times 10^{-2}$ M). There was no change in the shape, but there was a change in the intensity of the fluorescence spectrum by the addition of an electron donor. The Stern−Volmer relationship (eq 1) was obtained for the ratio of the emission intensities

$$I_0/I = 1 + K_{SV}[D] \tag{1}$$

in the absence and presence of electron donor (I_0/I) and the concentrations of quenchers [D]. The fluorescence lifetime τ of AcrH$^+$ is 37 ns in MeCN.[15] The observed quenching rate constants k_q ($=K_{SV}\tau^{-1}$) were obtained from the Stern−Volmer constants K_{SV} and the emission lifetimes τ (see Supporting Information Figure S1).

Electrochemical Measurements. The second harmonic ac voltammetry (SHACV)[25,26] measurements of olefins and styrenes were performed on a BAS 100B electrochemical analyzer in deaerated MeCN containing 0.10 M NBu$^n{}_4$ClO$_4$ 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°_{ox} values (vs Ag/Ag$^+$) are converted to those versus SCE by adding 0.29 V.[27]

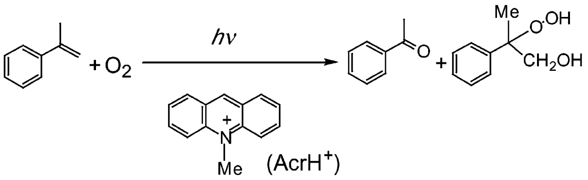
ESR Measurements. An O$_2$-saturated propionitrile solution of AcrH$^+$ (1.0×10^{-3} M) and α-methylstyrene (1.0×10^{-1} M) was irradiated at 193 K with a high-pressure mercury lamp (USH-1005D) through a water filter focusing at the sample cell in the ESR cavity. The ESR spectra were taken on a JEOL JES-RE1XE spectrometer and were recorded 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 and hyperfine splitting constants (hfs's) were calibrated using an Mn^{2+} marker.

Laser Flash Photolysis. The measurements of transient absorption spectra in the AcrH$^+$-photosensitized oxygenation of α-methylstyrene with oxygen were performed according to the following procedures. The Ar- or O$_2$-saturated MeCN solution containing α-methylstyrene (1.0×10^{-1} M) and AcrH$^+$ (5.0×10^{-5} M) was excited by an Nd:YAG laser (Continuum, SLII-10, 4−6 ns fwhm) at $\lambda = 355$ nm with the power of 30 mJ per pulse. 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.

Theoretical Calculations. Density-functional theory (DFT) and ZINDO calculations were performed on a COMPAQ DS20E computer. Geometry optimizations were carried out using the Becke3LYP functional and 6-311++G** or 3-21G* basis set[28,29] with the unrestricted Hartree−Fock (UHF) formalism and as implemented in the Gaussian 98 program.[30] The hfs values are evaluated from the spin density of each hydrogen multiplied by 506.82 G.

Results and Discussions

AcrH$^+$-Photosensitized Oxygenation of α-Methylstyrene with Oxygen. Irradiation of the absorption band of 10-methylacridinium perchlorate (AcrH$^+$ClO$_4^-$) in an O$_2$-saturated MeCN solution containing α-methylstyrene for 1.0 h gave a C−C double bond cleaved oxygenated product (acetophenone) as the major product in addition to 2-(1-hydroxy-2-phenyl)propyl hydroperoxide, as shown in eq 2. The products are identified by the ^{1}H NMR spectra (see Experimental Section). Formaldehyde (10% yield after 40 min photoirradiation) was also detected as the cleaved product, which was further oxidized under the present photocatalytic conditions. Figure 1 shows the time course of the photocatalytic reaction.[31] The hydroperoxide is formed initially but decomposes at prolonged reaction time, accompanied by an increase in the yield of acetophenone. Thus,



(2)

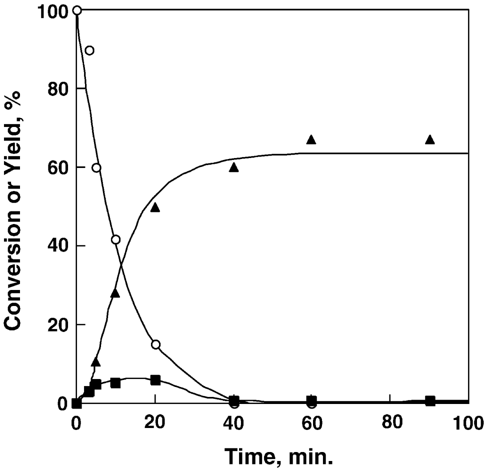


Figure 1. Time dependence of conversion of α-methylstyrene (○), and yields of acetophenone (▲) and 2-(1-hydroxy-2-phenyl)propyl hydroperoxide (■) in the photoinduced oxygenation of α-methylstyrene (3.0×10^{-2} M) in the presence of AcrH$^+$ (1.0×10^{-2} M) in oxygen-saturated acetonitrile at 298 K.

TABLE 1: Oxidation Potentials of Olefins ($E°_{ox}$), Free Energy Change of Photoinduced Electron Transfer ($\Delta G°_{et}$), and Fluorescence Quenching Rate Constants (k_q) of ^{1}AcrH^{+*} by Olefins in MeCN

olefin	$E°_{ox}$ vs SCE, V	$\Delta G°_{et}$, eV	$10^{-10}k_q$, M^{-1} s^{-1}
styrene	1.88	−0.44	2.0
1,1-diphenylethylene	1.82	−0.50	1.4
α-methylstyrene	1.82	−0.50	2.0
trans-stilbene	1.41	−0.91	2.0

the hydroperoxide is an intermediate product for the formation of the C−C double bond cleaved product, acetophenone.

After the photochemical reaction for 1.0 h, all α-methylstyrene molecules are consumed when the concentration of AcrH$^+$ remains largely the same as that before the photochemical reaction. Thus, AcrH$^+$ acts as an efficient and stable photocatalyst for the photoinduced oxygenation of α-methylstyrene with oxygen, in contrast with other photosensitizers employed for the photoinduced oxygenation of alkenes, which readily decompose under photoirradiation.[19,20]

Photoinduced Electron Transfer from Electron Donors to AcrH$^+$. Irradiation of the absorption band of AcrH$^+$ results in fluorescence at 488 nm in MeCN.[15] The fluorescence of the singlet excited state of AcrH$^+$ (^{1}AcrH^{+*}) is known to be quenched efficiently by a variety of aromatic electron donors via electron transfer from aromatic electron donors to ^{1}AcrH^{+*} in MeCN.[17] The fluorescence of ^{1}AcrH^{+*} is also quenched by a variety of olefins including α-methylstyrene. The quenching rate constants k_q are determined from the slopes of the Stern−Volmer plots and the lifetime of the singlet excited state ^{1}AcrH^{+*} (see Supporting Information, S1). The k_q values thus obtained are summarized in Table 1.

The free energy change of photoinduced electron transfer from electron donors to ^{1}AcrH^{+*} ($\Delta G°_{et}$ in eV) is given by eq 3 ,[32] where e is the elementary charge and $E°_{ox}$ and $E°_{red}$* are

$$\Delta G°_{et} = e(E°_{ox} - E°_{red}*) \tag{3}$$

the one-electron oxidation potentials of electron donors and the one-electron reduction potential of ^{1}AcrH^{+*} ($E°_{red}* = 2.32$ V vs SCE),[15] respectively. Since the $E°_{ox}$ values of various olefins in MeCN have been determined in this study (see Experimental Section), the $\Delta G°_{et}$ values are given from eq 3, as listed in Table 1. Judging from the exergonic nature of the photoinduced electron transfer ($\Delta G°_{et} \ll 0$), the photoinduced electron transfer is expected to occur at the diffusion-limited rate,[33,34] as observed experimentally (Table 1).

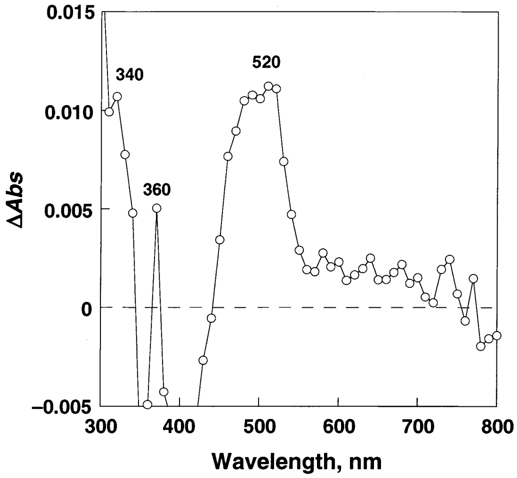


Figure 2. (a) Transient absorption spectrum observed by photoexcitation of a deaerated MeCN solution of AcrH$^+$ (5.0×10^{-5} M) and α-methylstyrene (1.0×10^{-1} M) at 40 μs after laser excitation at 298 K.

Detection of Reactive Intermediates. The occurrence of photoinduced electron transfer from α-methylstyrene to ^{1}AcrH^{+*} is confirmed by the laser flash photolysis experiments. Laser flash excitation (355 nm from an Nd:YAG laser) of AcrH$^+$ (5.0×10^{-5} M) in deaerated MeCN solution containing α-methylstyrene affords transient absorption bands at $\lambda_{max} = 340$ and 360 nm due to α-methylstyrene radical cation[35] and at $\lambda_{max} = 520$ nm due to AcrH$^•$,[15,17,36] as shown in Figure 2. Both absorption bands appear immediately after nanosecond laser exposure and decay at the same rate, obeying second-order kinetics, as shown in Figure 3. From the slope of the linear plot of ΔAbs^{-1} versus time in Figure 3b and the ϵ_{max} value (7400 M^{-1} cm^{-1})[36] is obtained the decay rate constant as 7.0×10^9 M^{-1} s^{-1}. The bimolecular decay of AcrH$^•$ may be ascribed to the back electron transfer from AcrH$^•$ to α-methylstyrene radical cation.

When oxygen was introduced to the AcrH$^+$−α-methylstyrene system, the absorption band at 360 nm due to α-methylstyrene radical cation disappeared and instead a new absorption band appeared at the long wavelength region at $\lambda_{max} = 680$ nm, as shown in Figure 4. The absorbance at 680 nm decreases with decreasing oxygen concentration. Thus, the absorption band at 680 nm is attributed to the intermediate product derived from the reaction of α-methylstyrene radical cation with oxygen. Oxygen is expected to add to the β-position of α-methylstyrene radical cation to produce the peroxyl radical cation, judging from the largest spin density (0.54) at the β-position of the radical cation, obtained by the density functional calculation at the Becke3LYP/6-311++G** level, as shown in Figure 5a (see Experimental Section).

Dioxetane intermediates are often isolated in the photooxygenation of sterically hindered olefins such as adamantylideneadamantane and its derivatives.[37,38] Thus, it is reasonable to assign the new absorption band at $\lambda_{max} = 680$ nm due to the dioxetane radical cation (**1**) derived from the peroxyl radical cation (Scheme 1).[39]

The absorption band at 680 nm decays obeying first-order kinetics (Figure 6a), in contrast with the absorption band at 520 nm due to AcrH$^•$, which decays obeying second-order kinetics (Figure 6b). When water is added to the oxygen-saturated MeCN solution of AcrH$^+$ (5.0×10^{-5} M) and α-methylstyrene (1.0 ×

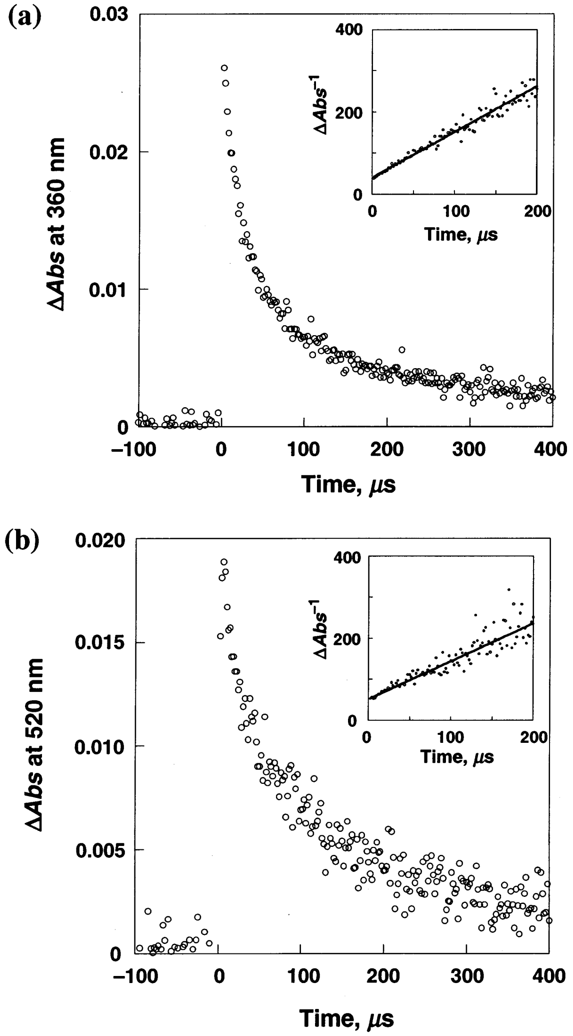


Figure 3. Decay time profiles of absorbance at (a) 360 nm and (b) 520 nm observed by photoexcitation of a deaerated MeCN solution of $AcrH^+$ (5.0×10^{-5} M) and α-methylstyrene at 298 K. Inset: Second-order plot.

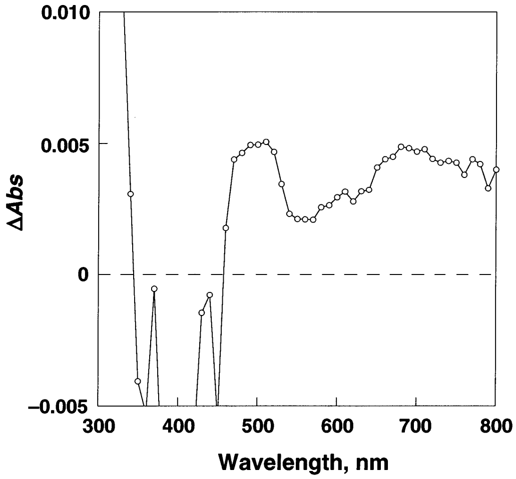


Figure 4. Transient absorption spectrum observed by photoexcitation of a oxygen-saturated MeCN solution ($[O_2] = 1.3 \times 10^{-2}$ M) of $AcrH^+$ (5.0×10^{-5} M) and α-methylstyrene (1.0×10^{-1} M) at 40 μs after laser excitation at 298 K.

10^{-1} M), the decay rate of the absorption band at 680 nm increases linearly with increasing H_2O concentration (Supporting Information Figure S2), whereas the decay of $AcrH^\bullet$ at 520 nm remains virtually the same (Supporting Information Figure S3). This indicates that the dioxetane radical cation reacts with H_2O to produce the species which has no absorption in the long wavelength region.

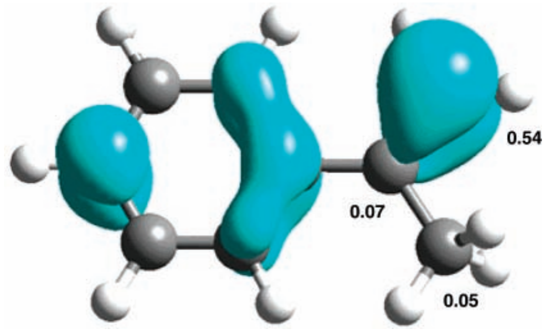


Figure 5. Spin distribution and spin density of α-methylstyrene radical cation obtained by DFT calculation using the B3LYP/6-311++G** basis set.

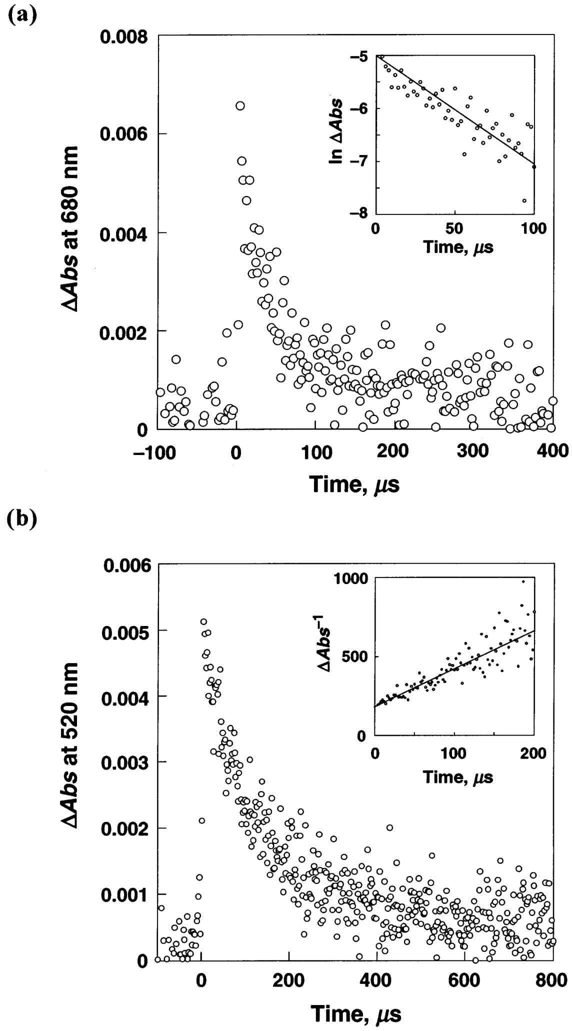
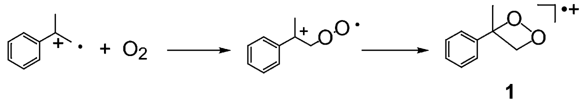


Figure 6. Decay time profiles of absorbance at (a) 680 nm and (b) 520 nm observed by photoexcitation of an oxygen saturated MeCN solution of $AcrH^+$ (5.0×10^{-5} M) and α-methylstyrene (1.0×10^{-1} M) at 298 K. Insets: First- and second-order plots.

SCHEME 1



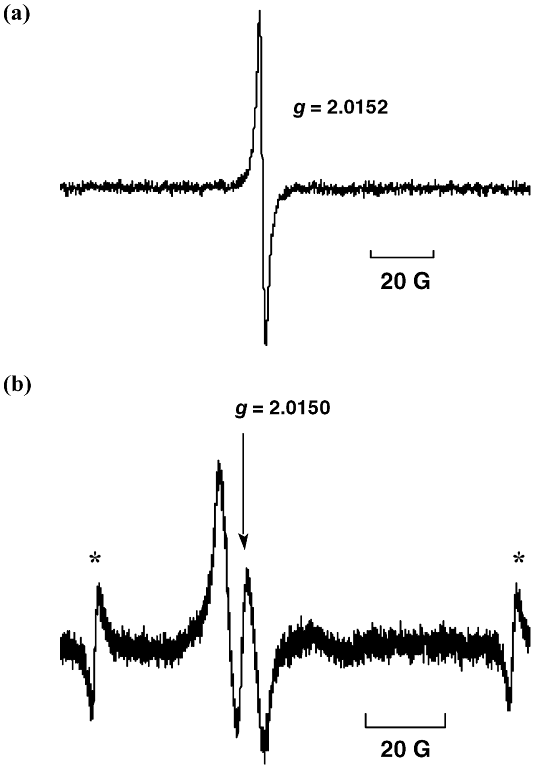


Figure 7. ESR spectra observed under photoirradiation of an oxygen-saturated EtCN solution of $AcrH^+$ (1.0×10^{-3} M) containing (a) α-methylstyrene (1.0×10^{-1} M) and (b) styrene (1.0×10^{-1} M) at 193 K.

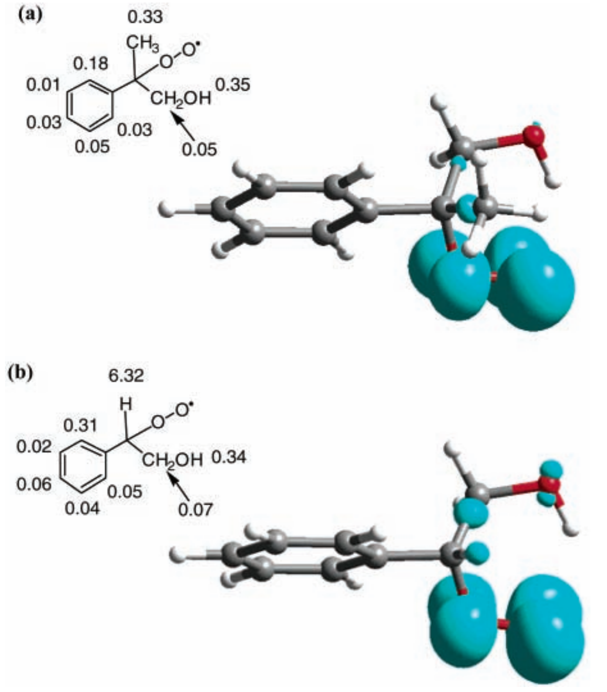


Figure 8. Spin distribution and a_H values (in gauss) of (a) the hydroxylated peroxyl radical (**2**) derived from α-methylstylene and (b) that from styrene, obtained by the DFT calculation using the B3LYP/3-21G* basis set. The hfs values are evaluated from the spin density of each hydrogen multiplied by 506.82 G.

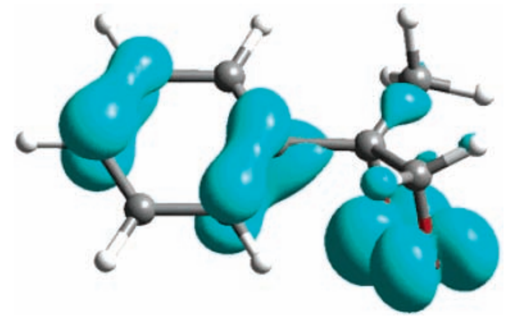
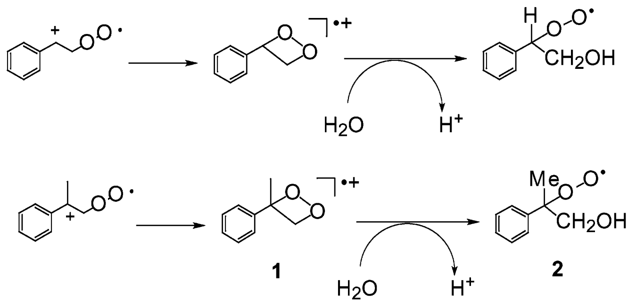


Figure 9. Spin distribution of the dioxetane radical cation (**1**), obtained by DFT calculations using the B3LYP/3-21G* basis set.

SCHEME 2



To obtain further insight into the reactive intermediates in the $AcrH^+$-photosensitized oxygenation of α-methylstyrene with oxygen, the ESR spectrum of an oxygen-saturated propionitrile (EtCN) solution containing $AcrH^+$ (1.0×10^{-3} M) and α-methylstyrene (1.0×10^{-1} M) was measured under photoirradiation of visible light at low temperatures. Figure 7a shows the detected ESR spectrum under such conditions.

The ESR spectrum consists of a single isotropic signal with the g value of 2.0152 showing no detectable hyperfine structure. This ESR feature is in good agreement with that of tertiary alkylperoxyl radicals.[40,41] The absence of the proton hyperfine structure suggests the observed peroxyl radical is attributed to neither the peroxyl radical cation nor the dioxetane radical cation in Scheme 1, since the peroxyl radical cation would exhibit the hyperfine splitting due to the β-proton and since the dioxetane radical cation (**1**) has a quite different g value (2.0099) than that of the complexed hyperfine structure.[42] When α-methylstyrene is replaced by styrene, the ESR spectrum obtained under the same experimental conditions as those for the case of α-methylstyrene exhibits a doublet signal which corresponds to the hyperfine structure due to one proton (Figure 7b). The observed hfs value ($a_H = 6.1$ G) is in the range 2−8 G reported for secondary alkylperoxyl radicals.[43] This indicates that oxygen is added to the α-position of styrene in the peroxyl radical. Thus, the peroxyl radical cation in which oxygen is added to the β-position is cyclized to give the dioxetane radical cation (Scheme 1), and the C−O bond is cleaved by the reaction with water to generate the hydroxylated peroxyl radical (**2**) that is observed in ESR spectroscopy, as shown in Scheme 2. The DFT calculation of **2** using the Becke3LYP/3-21G* basis set shown in Figure 8a indicates the estimated largest a_H value (0.33 G) is smaller than the observed line width, in agreement with the observation of no hyperfine structure of **2** in Figure 7a. The same DFT calculation of the hydroxylated peroxyl radical derived styrene (Figure 8b) affords the a_H value of 6.32 G, which agrees with the experimental value in Figure 7b ($a_H = 6.1$ G).

The spin distribution of the dioxetane radical cation (**1**) in Figure 9 indicates that the spin is delocalized over the molecule, in contrast with the case of **2** in Figure 8a, where the spin density of **2** is localized mainly on oxygen atoms.

Quantum Yield Determination. The quantum yields (Φ_p) of the $AcrH^+$-photosensitized oxygenation reaction of α-methylstyrene with O_2 were determined from the product formation rate under irradiation of monochromatized light of $\lambda_{max} = 358$

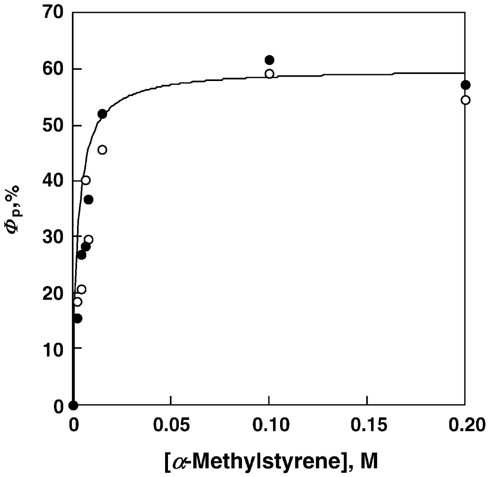
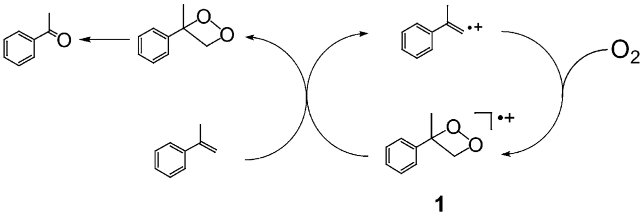


Figure 10. Dependence of the quantum yield (Φ_p) on the concentration of α-methylstyrene for the $AcrH^+$-catalyzed photooxygenation of α-methylstyrene in oxygen- (○) or air- (●) saturated MeCN at 298 K.

SCHEME 3



nm (see Experimental Section).[44] The Φ_p values increase with an increase in concentration of α-methylstyrene [S] to reach a limiting value ($\Phi_p = 0.62$) in accordance with eq 4 , as shown

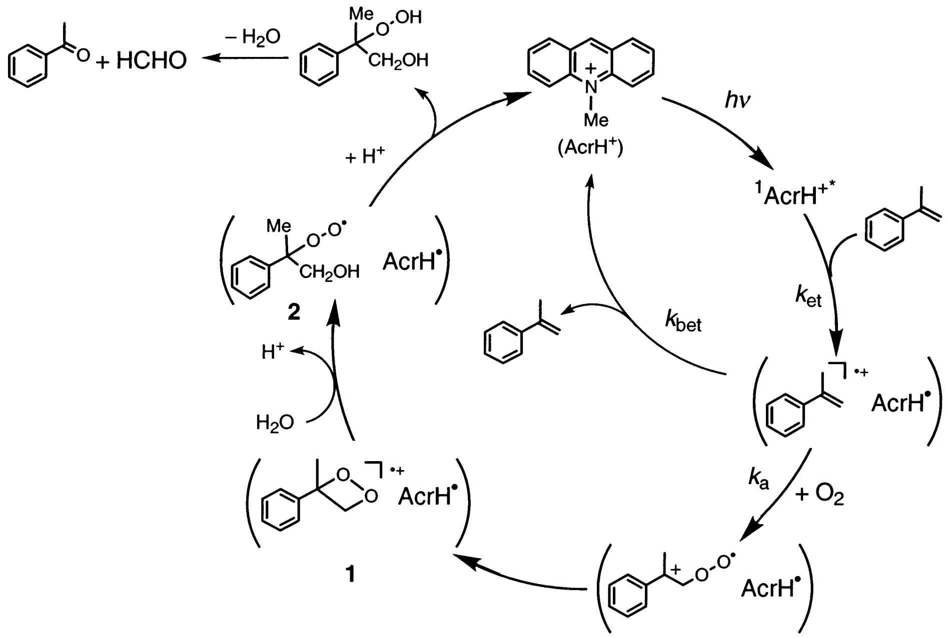
$$\Phi_p = \Phi_{p\infty} K_{obs}[S]/(1 + K_{obs}[S]) \qquad (4)$$

in Figure 10. It should be noted that the Φ_p values are virtually the same irrespective of the difference in O_2 concentration (Figure 10). The observed saturated dependence of Φ_p on [S] is well reproduced assuming that $K_{obs} = k_q\tau$, obtained from the fluorescence quenching of $^1AcrH^{+*}$ by α-methylstyrene, as indicated by Figure 10, where the calculated results using the $k_q\tau$ value (4.1×10^2 M^{-1}) in eq 4 (solid line) agree with the experimental results. Such agreement indicates that the photocatalytic reaction proceeds via photoinduced electron transfer from α-methylstyrene to $^1AcrH^{+*}$.

It has recently been reported that the same type of oxygenation of α-methylstyrene, involving the cleavage of the carbon−carbon double bond to yield acetophenone, as that of the present photocatalytic reaction proceeds at a high temperature (90 °C) with neither catalyst nor photoactivation although no reaction occurs at room temperature.[45] The thermal oxygenation reaction of α-methylstyrene with oxygen is proposed to proceed via radical chain processes, as shown in Scheme 3.[38b,46,47] The α-methylstyrene radical cation is assumed to be produced by direct electron transfer from α-methylstyrene to oxygen in the presumed charge-transfer complex between them.[45] However, the saturated dependence of Φ_p on concentration of α-methylstyrene in Figure 10 indicates that such an electron-transfer radical chain process (Scheme 3) is not operative as the major pathway in the present photocatalytic reaction. If the chain process in Scheme 3 is the major pathway, the Φ_p value would increase linearly with increasing concentration of α-methylstyrene.

Photocatalytic Mechanism. On the basis of the above results, the reaction mechanism for the $AcrH^+$-photosensitized oxygenation of α-methylstyrene is summarized, as shown in Scheme 4. The reaction is started by photoinduced electron transfer (k_{et}) from α-methylstyrene to the singlet excited state ($^1AcrH^{+*}$) to give the radical cation−acridinyl radical pair ($PhC(Me){=}CH_2^{\bullet+}$ $AcrH^\bullet$). This process occurs at the diffusion-limited rate, as indicated by the fluorescence quenching of $^1AcrH^{+*}$ with α-methylstyrene (Table 1). The formation of α-methylstyrene radical cation and acridinyl radical is detected as the transient absorption spectra in the absence of oxygen (Figure 2). In the presence of oxygen, oxygen is added to α-methylstyrene radical cation to give the peroxyl radical cation, which may be converted to the more stable form, that is the dioxetane radical cation (**1**), as detected as the transient absorption band at λ_{max} = 680 nm (Figure 4). The decay of the absorption band due to the dioxetane radical cation is accelerated by the presence of

SCHEME 4



water (Supporting Information Figure S2). This indicates that water is added to the dioxetane radical cation to give the hydroxylated peroxyl radical (**2**), which is detected by ESR (Figure 7a). The back electron transfer from acridinyl radical to the peroxyl radical gives the corresponding hydroperoxide, which is detected as an intermediate product (Figure 1), accompanied by regeneration of $AcrH^+$ (Scheme 4). The hydroperoxide decomposes to yield the final product, acetophenone. Formaldehyde formed together with the hydroperoxide decomposes under the present photocatalytic conditions (vide supra).

According to Scheme 4, the quantum yield is expressed by eq 5, where k_a is the rate constant of addition of O_2 to

$$\Phi_p = [k_a[O_2]k_{et}\tau/(k_a[O_2] + k_{bet})][S]/(1 + k_{et}\tau[S]) \qquad (5)$$

α-methylstyrene radical cation and k_{bet} is the back electron transfer from $AcrH^\bullet$ to α-methylstyrene radical cation. This equation agrees with the experimental result (eq 4). The limiting quantum yield Φ_∞ is then expressed by eq 6, where the

$$\Phi_{p\infty} = k_a[O_2]k_{et}\tau/(k_a[O_2] + k_{bet}) \qquad (6)$$

competition between the rate of oxygen addition (k_a) and the back electron transfer (k_{bet}) determines the limiting quantum yield. Since the observed quantum yield is indepent of O_2 concentration (vide supra), the rate of addition of O_2 to α-methylstyrene radical cation may be much faster than the back electron-transfer process (k_{ET}): $k_a[O_2] \gg k_{bet}$. In such a case, the limiting quantum yield would be unity. In fact, the observed limiting quantum yield determined from the acetophenone formation (60 ± 5%) corresponds to the quantum yield of the reactant conversion (97 ± 8%).

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research Priority Area (No. 11228205) from the Ministry of Education, Science, Culture and Sports, Japan.

Supporting Information Available: Stern−Volmer plot for the fluorescence quenching of $AcrH^+$ by olefins (S1), plot of the decay rate constant of absorbance at 680 nm versus $[H_2O]$ (S2), and decay time profile of absorbance at 520 nm in oxygen-saturated MeCN containing 0.50 M H_2O (S3). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Fox, M. A In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part D, p 1. (b) Gilbert, A.; Baggott, J. In *Essentials of Molecular Photochemistry*; Blackwell Scientific Publications: Oxford, 1991.

(2) (a) Sheldon, R. A. *J. Chem. Technol. Biotechnol*. **1997**, *68*, 381. (b) Sheldon, R. A. *Chem. Ind. (London)* **1997**, 12. (c) *Oxygenases and Model Systems*; Funabiki, T., Ed.; Kluwer: Dordrecht, 1997.

(3) (a) Foote, C. S. *Acc. Chem. Res*. **1968**, *1*, 104. (b) Kearns, D. R. *Chem. Rev*. **1971**, *71*, 395. (c) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419. (d) Foote, C. S.; Clennan, E. L. Properties and Reactions of Singlet Oxygen. In *Active Oxygen in Chemistry*; Foote, C. S., Valentine, J. S., Greenberg, A., Liebman, J. F., Eds.; Chapman and Hall: New York, 1995; pp 105−140.

(4) (a) Bellus, D. *Adv. Photochem*. **1979**, *11*, 105. (b) Gorman, A. A. *Adv. Photochem*. **1992**, *17*, 217. (c) Lissi, E. A.; Encinas, M. V.; Lemp, E.; Rubio, M. A. *Chem. Rev*. **1993**, *93*, 699. (d) Adam, W.; Prein, M. *Acc. Chem. Res*. **1996**, *29*, 275.

(5) (a) Sheu, C.; Foote, C. S. *J. Am. Chem. Soc*. **1995**, *117*, 474. (b) Sheu, C.; Foote, C. S. *J. Am. Chem. Soc*. **1995**, *117*, 6439. (c) Adam, W.; Saha-Möller, C. R.; Schönberger, A. *J. Am. Chem. Soc*. **1996**, *118*, 9233. (d) Raoul, S.; Cadet, J. *J. Am. Chem. Soc*. **1996**, *118*, 1892. (e) Singleton, D. A.; Hang, C.; Szymanski, M. J.; Meyer, M. P.; Leach, A. G.; Kuwata, K. T.; Chen, J. S.; Greer, A.; Foote, C. S.; Houk, K. N. *J. Am. Chem. Soc*. **2003**, *125*, 1319.

(6) (a) Duarte, V.; Gasparutto, D.; Yamaguchi, L. F.; Ravanat, J.-L.; Martinez, G. R.; Medeiros, M. H. G.; Mascio, P. D.; Cadet, J. *J. Am. Chem. Soc.* **2000**, *122*, 12622. (b) Greer, A.; Vassilikogiannakis, G.; Lee, K.-C.; Koffas, T. S.; Nahm, K.; Foote, C. S. *J. Org. Chem.* **2000**, *65*, 6876. (c) Bobrowski, M.; Liwo, A.; Oldziej, S.; Jeziorek, D.; Ossowski, T. *J. Am. Chem. Soc.* **2000**, *122*, 8112. (d) Adam, W.; Peters, K.; Peters, E.-M.; Schambony, S. B. *J. Am. Chem. Soc.* **2000**, *122*, 7610. (e) Cermola, F.; Lorenzo, F. D.; Giordano, F.; Graziano, M. L.; Iesce, M. R.; Palumbo, G. *Org. Lett.* **2000**, *2*, 1205. (f) Abdel-Shafi, A. A.; Wilkinson, F. *J. Phys. Chem. A* **2000**, *104*, 5747. (g) Bernstein, R.; Foote, C. S. *J. Phys. Chem. A* **1999**, *103*, 7244.

(7) (a) Yoshioka, M.; Sakuma, Y.; Saito, M. *J. Org. Chem.* **1999**, *64*, 9247. (b) Dussault, P. H.; Schultz, J. A. *J. Org. Chem.* **1999**, *64*, 8419. (c) Toutchkine, A.; Clennan, E. L. *J. Org. Chem.* **1999**, *64*, 5620. (d) Mori, H.; Ikoma, K.; Isoe, S.; Kitaura, K.; Katsumura, S. *J. Org. Chem.* **1998**, *63*, 8704. (e) Stratakis, M.; Orfanopoulos, M.; Foote, C. S. *J. Org. Chem.* **1998**, *63*, 1315. (f) Nojima, T.; Ishiguro, K.; Sawaki, Y. *J. Org. Chem.* **1997**, *62*, 6911. (g) Ishiguro, K.; Hayashi, M.; Sawaki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7265. (h) Fukuzumi, S.; Tanii, K.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1989**, 2103.

(8) Gollnick, K.; Schnatterer, A. *Photochem. Photobiol.* **1986**, *43*, 365.

(9) Lewis, F. D. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, Chapter 4.

(10) Hickerson, R. P.; Prat, F.; Muller, J. G.; Foote, C. S.; Burrows, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 9423.

(11) (a) Cao, Y.; Zhang, B. W.; Ming, Y. F.; Chen, J. X. *J. Photochem.* **1987**, *38*, 131. (b) Santamaria, J. *Tetrahedron Lett.* **1981**, *22*, 4511. (c) Steichen, D. S.; Foote, C. S. *Tetrahedron Lett.* **1979**, *20*, 4363.

(12) Foote, C. S. *Tetrahedron* **1985**, *41*, 2221.

(13) (a) Akaba, R.; Aihara, S.; Sakuragi, H.; Tokumaru, K. *J. Chem. Soc., Chem. Commun.* **1987**, 1262. (b) Akaba, R.; Sakuragi, H.; Tokumaru, K. *J. Chem. Soc., Perkin Trans. 2* **1991**, 291. (c) Akaba, R.; Kamata, M.; Itoh, H.; Nakao, A.; Goto, S.; Saito, K.; Negishi, A.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1992**, 33, 7011. (d) Akaba, R.; Kamata, M.; Koike, A.; Mogi, K.; Kuriyama, Y.; Sakuragi, H. *J. Phys. Org. Chem.* **1997**, *10*, 861.

(14) (a) Miranda, M. A.; Garcia, H. *Chem. Rev.* **1994**, *94*, 1063. (b) García, H.; Miranda, M. A.; Mojarrad, F.; Sabater, M.-J. *Tetrahedron* **1994**, *50*, 8773.

(15) Fujita, M.; Ishida, A.; Takamuku, S.; Fukuzumi, S. *J. Am. Chem. Soc.* **1996**, *118*, 8566.

(16) Ohkubo, K.; Fukuzumi, S. *Org. Lett.* **2000**, *2*, 3647.

(17) Fukuzumi, S.; Ohkubo, K.; Suenobu, T.; Kato, K.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **2001**, *123*, 8459.

(18) (a) Haines, A. H. *Methods for the Oxidatin of Organic Compounds*; Academic Press: London, 1985. (b) Baucherel, X.; Uziel, J.; Juge, S. *J. Org. Chem.* **2001**, *66*, 4504.

(19) Bhalerao, U. T.; Sridhar, M. *Tetrahedron Lett.* **1993**, *34*, 4341.

(20) (a) Mori, T.; Takamoto, M.; Tate, Y.; Shinkuma, J.; Wada, T.; Inoue, Y. *Tetrahedron Lett*. **2001**, *42*, 2505. (b) Mori, T.; Takamoto, M.; Wada, T.; Inoue, Y. *Helv. Chim. Acta* **2001**, *84*, 2693.

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

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

(23) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Elmsford, 1988.

(24) Ogata, Y.; Sawaki, Y.; Shimizu, H. *J. Org. Chem.* **1978**, *43*, 1760.

(25) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamental and Applications*; John Wiley & Sons: New York, 2001; Chapter 10, pp 368−416.

(26) The SHACV method provides a superior approach to directly evaluating the one-electron oxidation potentials in the presence of a follow-up chemical reaction, relative to the better-known dc and fundamental harmonic ac methods: (a) Bond, A. M.; Smith, D. E. *Anal. Chem.* **1974**, *46*, 1946. (b) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344.

(27) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non-aqueous Systems*; Mercel Dekker: New York, 1970.

(28) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(29) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(30) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz,

P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(31) The maximum yield of acetophenone is 63% at 100% conversion of α-methylstyrene. It was confirmed that there was no epoxide or the ene product,[20] although there remain unidentified products.

(32) Fukuzumi, S.; Tanaka, T. *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, p 578.

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

(34) (a) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(35) Andrew, L.; Harvey, J. A.; Kelsall, B. J.; Duffey, D. C. *J. Am. Chem. Soc.* **1981**, *103*, 6415.

(36) (a) Poulos, A. T.; Hammond, G. S.; Burton, M. E. *Photochem. Photobiol.* **1981**, *34*, 169. (b) Peters, K. S.; Pang, E.; Rudzki, J. *J. Am. Chem. Soc.* **1982**, *104*, 5535.

(37) Schaap, A. P.; Faler, G. R. *J. Am. Chem. Soc.* **1973**, *95*, 3381.

(38) (a) Barton, D. H. R.; Leclerc, G.; Magnus, P. D.; Menzics, I. D. *J. Chem. Soc., Chem. Commun.* **1972**, 447. (b) Nelsen, S. F.; Akaba, R. *J. Am. Chem. Soc.* **1981**, *103*, 2096. (c) Nelsen, S. F.; Kapp, D. L.; Akaba, R.; Evans, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 6863.

(39) The absorption maximum λ_{max} of the dioxetane radical cation (**1**) is calculated as $\lambda_{\mathrm{max}} = 833$ nm by the ZINDO method by using optimized structures by the B3LYP/3-21G* level, whereas the corresponding λ_{max} value of the peroxyl radical cation is significantly blue-shifted ($\lambda_{\mathrm{max}} = 550$ nm). Although the ZINDO method cannot predict the absolute λ_{max} values accurately, the calculation indicates that the absorption band of **1** is significantly red-shifted due to the ring closure in **1**, in agreement with the experimental observation in Figure 4.

(40) (a) Ingold, K. U.; Morton, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 3400. (b) Bennett, J. E.; Brown, D. M.; Mile, B. *Trans. Faraday Soc.* **1970**, *66*, 386.

(41) (a) Fukuzumi, S.; Ono, Y. *J. Phys. Chem.* **1976**, *80*, 2973. (b) Fukuzumi, S.; Ono, Y. *J. Chem. Soc., Perkin Trans. 2* **1977**, 622. (c) Fukuzumi, S.; Ono, Y. *J. Phys. Chem.* **1977**, *81*, 1895.

(42) Nelsen, S. F.; Kapp, D. L.; Gerson, F.; Lopez, J. *J. Am. Chem. Soc.* **1986**, *108*, 1027.

(43) Bennett, J. E.; Summers, R. *J. Chem. Soc., Faraday Trans. 2* **1973**, *10*, 1043.

(44) It was confirmed that the product yield determined from an increase in absorbance due to acetophenone agreed with that determined by GC.

(45) Hayashi, Y.; Takeda, M.; Miyamoto, Y.; Shoji, M. *Chem. Lett.* **2002**, 414.

(46) Correa, P. E.; Hardy, G.; Riley, D. P. *J. Org. Chem.* **1988**, *53*, 1695.

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