ARTICLES

Photocatalytic Oxygenation of Pivalic Acid with Molecular Oxygen via Photoinduced Electron Transfer using 10-Methylacridinium Ions

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Photoirradiation of the absorption band of the 10-methylacridinium ion ($AcrH^+$) with visible light in deaerated CH_3CN/H_2O (1:1 v/v) containing pivalic acid (Bu^tCOOH) and less than 1 equiv of NaOH results in the selective formation of 9-*tert*-butyl-9,10-dihydro-10-methylacridine ($AcrHBu^t$). The same product is obtained in O_2-saturated CH_3CN/H_2O under visible light irradiation. Photoirradiation of the absorption band of $AcrHBu^t$ with UV light in deaerated CH_3CN/H_2O (1:1 v/v) results in the formation of *tert*-butyl hydroperoxide (Bu^tOOH), accompanied by regeneration of $AcrH^+$. This cycle can be repeated several times. When $AcrH^+$ is replaced by the 9-phenyl derivative ($AcrPh^+$), $AcrPh^+$ acts as an effective photocatalyst for the one-pot photooxygenation of Bu^tCOOH in the presence of less than 1 equiv of NaOH relative to Bu^tCOOH with O_2 to yield Bu^tOOH and Bu^tOH. The photocatalytic oxygenation mechanism is discussed based on the detection of radical intermediates by laser flash photolysis and ESR measurements as well as quantum yield determination.

Introduction

Alkyl hydroperoxides are important organic oxidants in organic and biochemical oxidation reactions, playing a key role in the biochemical oxidation of lipids during oxidative stress.[1,2] The weak O−O bond of alkyl hydroperoxides can easily be cleaved by transition metal complexes, leading to the oxygenation of a variety of substrates.[3−6] Alkyl hydroperoxides have so far been produced by the autoxidation of hydrocarbons with oxygen via free radical chain reactions,[7−10] because the direct oxygenation of singlet hydrocarbons with triplet oxygen to produce singlet oxygenated products is spin-forbidden. However, the autoxidation of hydrocarbons involving free radicals usually affords complex product mixtures, precluding the selective oxygenation to yield alkyl hydroperoxides.[7−10] Alkyl hydroperoxides are also obtained by the reactions of metal alkyls with oxygen via metal−carbon cleavage to produce alkyl radicals which can react directly with oxygen.[11,12] Alkyl radicals can also be generated by the anodic oxidation of carboxylate ions (RCO_2^-), that is, the Kolbe reaction (eq 1),[13] in which carbon-centered radicals are formed via decarboxylation of carboxyl radicals ($RCOO^\bullet$). It is known that

$$RCO_2^- \xrightarrow{-e^-} RCO_2^\bullet \xrightarrow{-CO_2} R^\bullet \tag{1}$$

the photoinduced electron-transfer oxidation of carboxylic acids also gives carbon-centered radicals via decarboxylation,[14,15] because the redox process can be significantly enhanced by the photoexcitation.[16] While several synthetically useful reactions have been reported using the photosensitized decarboxylation in the presence of hydrogen donors,[17−21] the photocatalytic oxygenation of alkyl groups of RCO_2^- via decarboxylation with oxygen has yet to be explored.

We report herein that pivalic acid (Bu^tCOOH) is oxygenated with O_2 to produce Bu^tOOH by the repeated cycles of the photoreduction of the 10-methylacridiniun ion ($AcrH^+$) by Bu^tCOO^- to produce the Bu^t adduct, 9-*tert*-butyl-9,10-dihydro-10-methylacridine ($AcrHBu^t$), and the photooxidation of $AcrHBu^t$ with O_2 in the presence of perchloric acid ($HClO_4$) to yield *tert*-butyl hydroperoxide (Bu^tOOH), accompanied by the regeneration of $AcrH^+$.[22] We have also examined the photoreduction of $AcrH^+$ by a series of fatty acid anions ($RCOO^-$) to afford AcrHR in detail. When 9-phenyl-10-methylacridinium ion ($AcrPh^+$) is employed instead of $AcrH^+$, $AcrPh^+$ acts as an effective photocatalyst for the oxygenation of Bu^tCOOH to yield Bu^tOOH and Bu^tOH. The mechanisms of the photoreduction of $AcrH^+$ by $RCOO^-$, the photooxidation of $AcrHBu^t$ with O_2, and the photocatalytic oxygenation of Bu^tCOOH with O_2 are reported based on the quantum yield analysis and the detection of the radical intermediates by laser flash photolysis and ESR measurements.

Experimental Section

Materials. Pivalic acid was purchased from Tokyo Kasei Kogyo Co., Ltd. Acetonitrile (CH_3CN) and sodium hydroxide were purchased from Nacalai Tesque, Inc. Perchloric acid ($HClO_4$ aq 70%) was purchased from Wako Pure Chemical Ind., Ltd. Anhydrous *t*-butyl alcohol was obtained commercially from Aldrich. 10-Methylacridinium iodide ($AcrH^+I^-$) was prepared by the reaction of acridine with methyl iodide in acetone and

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was converted to the perchlorate salt ($AcrH^+ClO_4^-$) by the addition of magnesium perchlorate to the iodide salt ($AcrH^+I^-$) and purified by recrystallization from methanol.[23] 9-Phenyl-10-methylacridinium perchlorate ($AcrPh^+ClO_4^-$) was prepared by the reaction of 10-methylacridone with phenylmagnesium bromide in dichloromethane, then the addition of sodium hydroxide for the hydrolysis and perchloric acid for the neutralization, and purified by recrystallization from ethanol−diethyl ether.[24] 9-*tert*-Butyl-10-methyl-9,10-dihydroacridine ($AcrHBu^t$) was synthesized by the literature method.[25] Potassium ferrioxalate used as an actinometer was prepared according to the literature and purified by recrystallization from hot water.[26] Deuterated [$^2H_3$]acetonitrile (CD_3CN, 99.8%) and deuterated [^2H]chloroform ($CDCl_3$, 99.8%) were purchased from EURI SOTOP, CEA, France and used as received. An amount of 40% deuterated [^2H]sodium hydroxide/deuterium oxide ($NaOD/D_2O$) was purchased from Cambridge Isotope Laboratories and used as received.

Reaction Procedure. A CH_3CN/H_2O (1:1, v/v) solution (50 cm^3) containing $AcrH^+$ (6.8×10^{-3} M), pivalic acid (2.0×10^{-1} M), NaOH (6.8×10^{-2} M), and a magnetic stirrer in a pear-shaped flask was deaerated by vacuum degassing three times. The solution was then irradiated with a xenon lamp through a filter cutting off the light of $\lambda < 360$ nm at room temperature. The product ($AcrHBu^t$) was isolated by filtration after evaporating CH_3CN. In the case of $AcrPh^+$-catalyzed photooxygenation of Bu^tCOOH with a CD_3CN/D_2O (1:1, v/v) solution (0.6 cm^3) containing $AcrPh^+$ (2.0×10^{-2} M), pivalic acid (5.0×10^{-2} M) and NaOD (3.0×10^{-2} M) in an NMR tube sealed with a rubber septum were saturated with O_2 by bubbling with O_2 through a stainless steel needle for 5 min.

The solution was then irradiated with a mercury lamp through the filter cutting off the light of $\lambda < 300$ nm at room temperature. The irradiated solution was analyzed periodically by ^1H NMR spectroscopy. The ^1H NMR measurements were performed using a JEOL JMN-AL300 (300 MHz) NMR spectrometer. ^1H NMR (300 MHz, CD_3CN/D_2O, 1:1, v/v): pivalic acid δ 1.11 (s, 9H); *tert*-butyl hydroperoxide: δ 1.21 (s, 9H); *tert*-butyl alcohol: δ 1.21 (s, 9H). ^1H NMR (300 MHz, CD_3CN): 9-*tert*-butyl-9,10-dihydro-10-methylacridine: δ 0.72 (s, 9H), 3.33 (s, 3H), 3.59 (s, 1H), 6.8−7.3 (m, 8H); *tert*-butyl hydroperoxide: δ 1.16 (s, 9H); *tert*-butyl alcohol: δ 1.19 (s, 9H). The amount of hydroperoxide was determined by titration with iodide ion.[27] The aliquots of the product mixture in CH_3CN were treated with excess NaI, and the amount of I_3^- formed was determined by the UV−vis absorption spectrum ($\lambda_{max} = 361$ nm, $\epsilon_{max} = 2.5 \times 10^4$ M^{-1} cm^{-1})[27] using a Hewlett-Packard 8453 diode array spectrophotometer with a quartz cuvette (path length = 10 mm) at 298 K.

Quantum Yield Determination. A standard actinometer (potassium ferrioxalate)[26] was used for the quantum yield determination of photoreduction of $AcrH^+$ by Bu^tCOO^- and the formation of Bu^tOOH by the $AcrPh^+$-photosensitized oxygenation of Bu^tCOOH with oxygen. Typically, a square quartz cuvette (10 mm i.d.) which contained a CH_3CN/H_2O (1:1, v/v) solution (3.0 cm^3) of $AcrH^+$ (5.7×10^{-4} M), pivalic acid (4.0×10^{-1} M), and NaOH (1.0×10^{-2} to 1.0×10^{-1} M) was irradiated with monochromatized light of $\lambda = 358$ nm from a Shimadzu RF-5300PC fluorescence spectrophotometer. Under the conditions of actinometry experiments, all of the actinometers, $AcrH^+$ and $AcrPh^+$ absorbed essentially all the incident light. The light intensity of monochromatized light of $\lambda = 358$ nm was determined as 1.96×10^{-8} einstein s^{-1} and that of $\lambda = 288$ nm was 3.93×10^{-9} einstein s^{-1} with the slit width of 20 nm, respectively. The photochemical reaction was monitored using a Shimadzu UV-3100PC spectrophotometer. The quantum yields of the photochemical reactions were determined from an increase in $AcrHBu^t$ ($\lambda_{max} = 288$ nm, $\epsilon_{max} = 15\,000$ M^{-1} cm^{-1}),[25] $AcrH^+$ ($\lambda_{max} = 358$ nm, $\epsilon_{max} = 18\,000$ M^{-1} cm^{-1}),[23] or Bu^tOOH (titration with iodide ion). To avoid the contribution of light absorption of the products, only the initial rates were determined for the determination of the quantum yields.

Fluorescence Quenching. Quenching experiments of the fluorescence of $AcrH^+$ by $RCOO^-$ were performed using a Shimadzu RF-5300PC fluorescence spectrophotometer with the excitation wavelength (358 nm in CH_3CN/H_2O, 1:1 v/v). The monitoring wavelength was that corresponding to the maximum of the emission band (498 nm in CH_3CN/H_2O, 1:1, v/v). The solutions were deoxygenated by argon purging for 10 min prior to the measurements. Relative emission intensities were measured for solutions containing $AcrH^+$ (5.0×10^{-6} M), RCOOH (1.0×10^{-1} M), and NaOH ($(0-1.0) \times 10^{-2}$ M) in CH_3CN/H_2O (1:1, v/v). There was no change in the shape, but there was a change in the intensity of the fluorescence spectrum by the addition of NaOH. The Stern−Volmer relationship (eq 2)

$$I_0/I = 1 + K_{SV}[RCOO^-] \qquad (2)$$

was obtained for the ratio of the emission intensities in the absence and presence of an electron donor (I_0/I) and the concentrations of the quenchers [$RCOO^-$]. The fluorescence lifetime τ of $AcrH^+$ is 37 ns and that of $AcrPh^+$ is 1.5 ns.[24] The observed quenching rate constants k_q ($= K_{SV}\tau^{-1}$) were obtained from the Stern−Volmer constants K_{SV} and the fluorescence lifetimes τ.

ESR Measurements. An O_2-saturated CH_3CN/H_2O (1:1, v/v) solution of $AcrPh^+$ (5.0×10^{-2} M), pivalic acid (1.0 M), and NaOH (5.0×10^{-1} M) was irradiated at 243 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 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 were calibrated using an Mn^{2+} marker.

Laser Flash Photolysis. The measurements of transient absorption spectra in the $AcrPh^+$-photosensitized reactions of pivalic acid in the presence of O_2 were performed as follows. An O_2-saturated CH_3CN/H_2O (1:1, v/v) solution containing pivalic acid (1.0×10^{-1} M), NaOH (6.0×10^{-2} M), and $AcrH^+$ or $AcrPh^+$ (5.6×10^{-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/pulse. Transient absorption spectra were measured by using a continuous Xe lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as the probe light and detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz).

Results and Discussion

Photoreduction of 10-Methylacridinium Ion by Bu^tCOO^- under Visible Light Irradiation. Irradiation of the absorption band ($\lambda_{max} = 358$ nm) of $AcrH^+$ (1.0×10^{-4} M) in CH_3CN/H_2O (1:1, v/v) containing pivalic acid (Bu^tCOOH, 0.10 M) and NaOH (3.0×10^{-2} M) resulted in the increase in the absorbance at 288 nm, accompanied by the decrease in the absorbance due to $AcrH^+$ with a clean isosbestic point at 328 nm as shown in Figure 1.

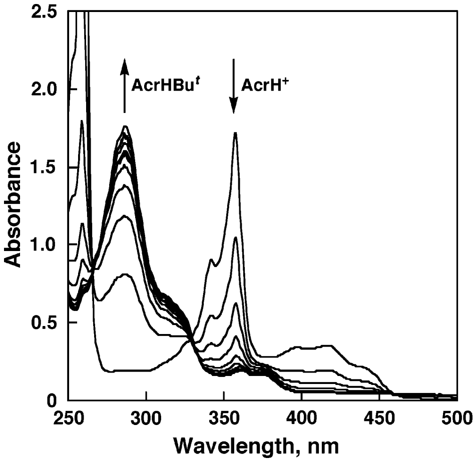


Figure 1. Absorption spectral change observed in the photoreduction of $AcrH^+$ (1.0×10^{-4} M) by pivalic acid (1.0×10^{-1} M) in the presence of NaOH (3.0×10^{-2} M) in deaerated CH_3CN/H_2O (1:1, v/v) under photoirradiation of monochromatized light of $\lambda = 358$ nm at 298 K. The irradiation time interval is 1 min.

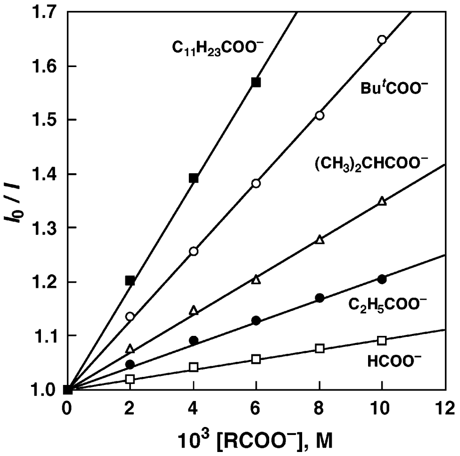


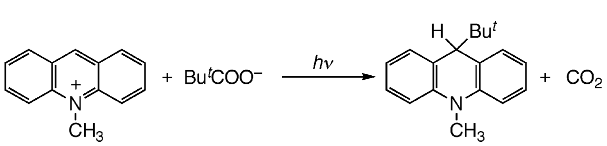
Figure 2. Stern–Volmer plots for the fluorescence quenching of $AcrH^+$ (5.0×10^{-6} M) by $RCOO^-$ in deaerated CH_3CN/H_2O (1:1, v/v) at 298 K.

The isolated product was identified as 9-*tert*-butyl-9,10-dihydro-10-methylacridine (AcrHBu^t) by the ^{1}H NMR spectrum and the elemental analysis (eq 3). After a 3 h photoirradiation with a xenon lamp through a filter cutting off the light of $\lambda < 360$ nm at room temperature, AcrHBu^t was afforded in 95% yield. The same product was obtained in O_2-saturated CH_3CN/H_2O. Thus, O_2 has no effect on the photoreduction of AcrHBu^t by Bu^{t}COO$^-$. The photoreduction of $AcrH^+$ by a series of fatty acid anions also proceeds to yield AcrHR. The yields of AcrHR are listed in Table 1.

TABLE 1: Yields of AcrHR, Rate Constants of Photoinduced Electron Transfer (k_q), Rate Constants of Formation of AcrHR (k_{obs}), and Limiting Quantum Yields (Φ_∞)

$RCOO^-$	yield of AcrHR, %[a]	k_q, $M^{-1}\,s^{-1}$ [b]	k_{obs}, $M^{-1}\,s^{-1}$ [a]	Φ_∞%[a]
R = H	84	2.9×10^8	2.8×10^8	3.3
C_2H_5	90	6.5×10^8	5.8×10^8	10
$CH(CH_3)_2$	90	1.1×10^9	1.1×10^9	22
$C(CH_3)_3$	92	2.0×10^9	2.1×10^9	32
$C_{11}H_{23}$	85	3.0×10^9	3.0×10^9	14
$C_{15}H_{31}$	87	3.8×10^9	3.6×10^9	16

[a] The experimental error is within 10%. [b] The experimental error is within 5%.



(3)

Irradiation of the absorption band of $AcrH^+$ result in fluorescence at 498 nm in CH_3CN/H_2O (1:1, v/v).[24,28] The fluorescence of the singlet excited state of $AcrH^+$ ($^1AcrH^{+*}$) is quenched efficiently by a variety of aromatic electron donors via electron transfer from aromatic electron donors to $^1AcrH^{+*}$.[24,28,29] The fluorescence of $^1AcrH^{+*}$ is also quenched efficiently by various fatty acid anions ($RCOO^-$) including Bu^{t}COO$^-$. The quenching rate constants k_q were determined from the slopes of the Stern–Volmer plot and the fluorescence lifetime of $^1AcrH^{+*}$ (Figure 2). The k_q values are listed in Table 1.

The quantum yields (Φ) of the photoreduction of $AcrH^+$ by $RCOO^-$ in CH_3CN/H_2O (1:1, v/v) were determined from the rate of formation of AcrHBu^t under irradiation of monochromatized light of $\lambda_{max} = 358$ nm (see the Experimental Section). The Φ values increase with an increase in concentration of $RCOO^-$ to reach a limiting value (Φ_∞) as shown in Figure 3a. Such dependence of Φ on the concentration of $RCOO^-$ is

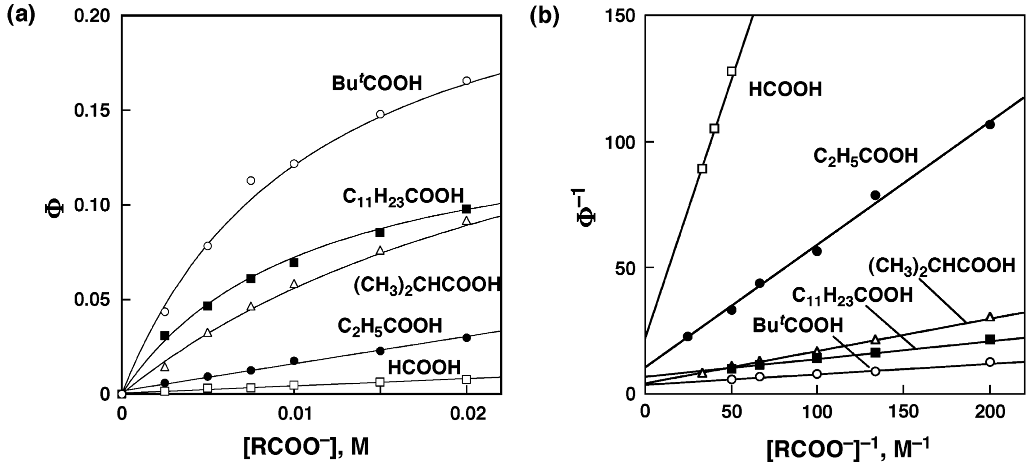


Figure 3. (a) Dependence of the quantum yield (Φ) on the [$RCOO^-$] concentration for the photoreduction of $AcrH^+$ by RCOOH (0.10 M) in the presence of NaOH in deaerated CH_3CN/H_2O (1:1, v/v). (b) Plots of Φ^{-1} vs [$RCOO^-$]$^{-1}$ for the photoreduction of $AcrH^+$ by $RCOO^-$ in deaerated CH_3CN/H_2O (1:1, v/v).

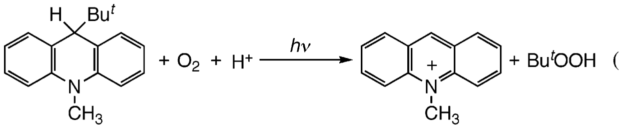
expressed as a linear correlation between Φ^{-1} and $[RCOO^-]^{-1}$ (eq 4). The linear plots of Φ^{-1} vs $[RCOO^-]^{-1}$ are shown

$$\Phi^{-1} = \Phi_\infty^{-1}[1 + (K_{obs}[RCOO^-])^{-1}] \qquad (4)$$

in Figure 3b. The rate constants ($k_{obs} = K_{obs}/\tau$) of the reactions of $^1AcrH^{+*}$ with $RCOO^-$ and the limiting quantum yields (Φ_∞) were determined from the slopes and the corresponding intercepts of the linear plots in Figure 3b. The k_{obs} and Φ_∞ values are listed in Table 1. The k_{obs} values obtained from the dependence of Φ on the $RCOO^-$ concentration agree well with the k_q values obtained independently by the fluorescence quenching of $^1AcrH^{+*}$ by Bu^tCOO^- (Table 1). Such agreement suggests that the photoreduction of $AcrH^+$ by $RCOO^-$ proceeds via the reaction of $^1AcrH^{+*}$ with $RCOO^-$.

Since alkyl radicals are generated by the electron-transfer oxidation of $RCOO^-$ (eq 1),[13] via decarboxylation of carboxyl radicals ($RCOO^•$), the photoreduction of $AcrH^+$ by $RCOO^-$ may proceed via electron transfer from $RCOO^-$ to $^1AcrH^{+*}$ to generate the geminate radical pair ($AcrH^•$ $RCOO^•$) in which $RCOO^•$ undergoes facile decarboxylation,[14,15] followed by the radical coupling in the geminate radical pair ($AcrH^•$ $R^•$) in the solvent cage to yield AcrHR selectively (Scheme 1). The radical coupling reaction may be fast enough to avoid the reaction of $R^•$ with O_2, because O_2 does not affect the photoreduction of $AcrH^+$ by $RCOO^-$ (vide supra). The electrostatic attraction between $RCOO^-$ and $AcrH^+$ certainly helps to promote formation of the tight ion pair and the subsequent reaction without incorporation of O_2.

Photooxidation of AcrHBu^t with O_2 under UV Irradiation. Photoirradiation of the absorption band (λ_{max} = 288 nm) of $AcrHBu^t$ (1.0×10^{-4} M) in O_2-saturated CH_3CN/H_2O (1:1, v/v) containing $HClO_4$ results in the regeneration of $AcrH^+$ as shown in Figure 4. The oxygenated products were identified as $AcrH^+$ and *tert*-butyl hydroperoxide (Bu^tOOH) as shown in eq 5; see the Experimental Section.



(5)

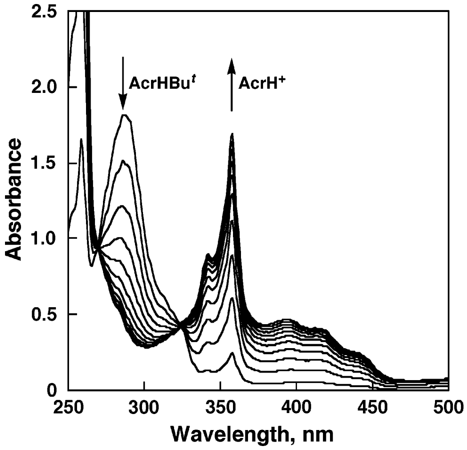


Figure 4. Absorption spectral change observed in the photooxidation of $AcrHBu^t$ (1.0×10^{-4} M) with O_2 in the presence of $HClO_4$ (1.2×10^{-1} M) in O_2-saturated CH_3CN/H_2O (1:1, v/v) under photoirradiation with monochromatized light of λ = 288 nm at 298 K. The irradiation time interval is 3 min.

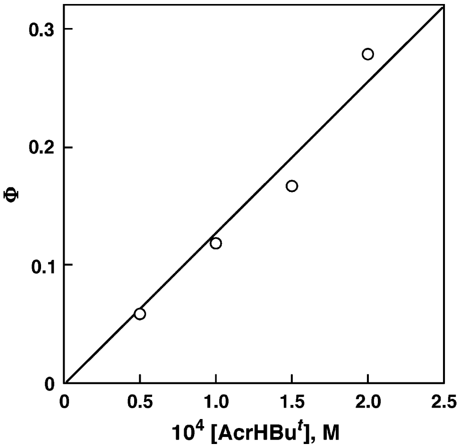


Figure 5. Dependence of the quantum yield (Φ) on the concentration of $AcrHBu^t$ for the photooxidation of $AcrHBu^t$ with O_2 in the presence of $HClO_4$ (1.2×10^{-1} M) in O_2-saturated CH_3CN/H_2O (1:1, v/v) at 298 K.

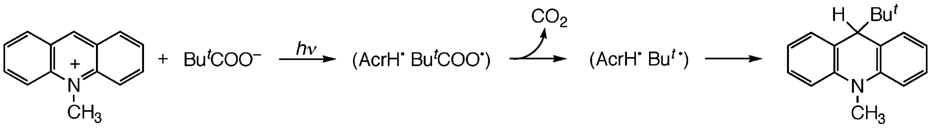
The quantum yield (Φ) of the formation of $AcrH^+$ increases linearly with increasing concentration of $AcrHBu^t$ as shown in Figure 5. On the other hand, the Φ value is constant at a fixed concentration of $AcrHBu^t$ irrespective of the change in $HClO_4$ concentration (Figure 6). The rate of photooxidation of $AcrHBu^t$ with O_2 remains the same when O_2-saturated CH_3CN/H_2O (1:1, v/v) is replaced by the air-saturated solvent (see Supporting Information S1).

The linear increase in the Φ value with increasing concentration of $AcrHBu^t$ and the invariant Φ value with the change in concentrations of $HClO_4$ and O_2 indicate that the photooxidation of $AcrHBu^t$ with O_2 proceeds via a radical chain process where the rate-determining chain propagation step is the reaction of $AcrHBu^t$ with $HO_2^•$ as shown in Scheme 2 (vide infra). The photoinduced electron transfer from $^1AcrHBu^{t*}$ to O_2 in the presence of H^+ results in the formation of $AcrHBu^{t•+}$ and $HO_2^•$, both of which combine in the cage to yield Bu^tOOH. The escaped $HO_2^•$ from the cage reacts with $AcrHBu^t$ to produce Bu^tOOH and $AcrH^•$. Electron transfer from $AcrH^•$ to O_2 in the presence of H^+ is known to occur efficiently to produce $AcrH^+$, accompanied by the regeneration of $HO_2^•$ in the radical chain process (Scheme 2). In such a case, the rate of formation of $AcrH^+$ is given by eq 6, where k_p is the rate constant of the

$$d[AcrH^+]/dt = k_p[HO_2^•][AcrHBu^t] \qquad (6)$$

reaction of $AcrHBu^t$ with $HO_2^•$. The rate of formation and decay of $HO_2^•$ is given by eq 7, where *In* is the light intensity absorbed by $AcrHBu^t$ and Φ_0 is the quantum yield of formation of $HO_2^•$ in the photoinduced electron transfer from $^1AcrHBu^{t*}$ to O_2.[30] Under steady-state conditions, the $HO_2^•$ concentration is given

SCHEME 1



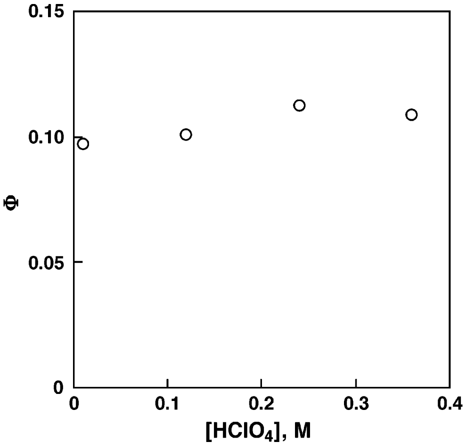
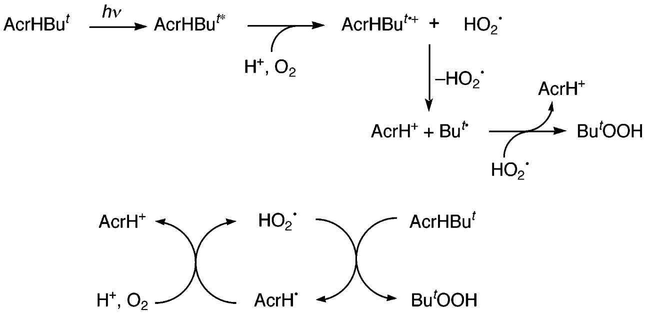


Figure 6. Dependence of the quantum yield (Φ) on the concentration of $HClO_4$ for the photooxidation of $AcrHBu^t$ (1.0×10^{-4} M) with O_2 in O_2-saturated CH_3CN/H_2O (1:1, v/v) at 298 K.

SCHEME 2



by eq 8. Then, the quantum yield of formation of $AcrH^+$ is derived from eqs 6 and 8 as given by eq 9.

$$d[HO_2^\bullet]/dt = \Phi_0 In - 2k_p[HO_2^\bullet]^2 \tag{7}$$

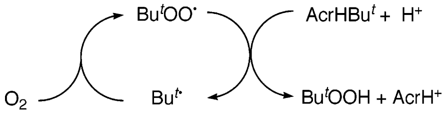
$$[HO_2^\bullet] = (\Phi_0 In/2k_p)^{1/2} \tag{8}$$

$$\Phi = k_p(\Phi_0/2k_t In)^{1/2}[AcrHBu^t] \tag{9}$$

According to eq 9, the Φ value is proportional to $[AcrHBu^t]$ and $In^{-1/2}$. The linear correlation between Φ and $[AcrHBu^t]$ is experimentally verified as shown in Figure 5. The linear correlation between Φ and $In^{-1/2}$ is also confirmed as shown in Figure 7.

Thus, it is confirmed that the photooxidation of $AcrHBu^t$ with O_2 proceeds via a radical chain process, initiated by photoinduced electron transfer from $AcrHBu^t$ to O_2 (Scheme 2). Another radical chain process via thermal electron transfer from $AcrHBu^t$ to $Bu^tOO^\bullet$, followed by the C−C bond cleavage to produce $Bu^{t\bullet}$ (Scheme 3) might also be operative in the photooxidation reaction. Although electron transfer from $AcrHBu^t$ to $Bu^tOO^\bullet$ is endergonic judging from the higher one-electron oxidation potential of $AcrHBu^t$ ($E_{ox} = 0.86$ V vs SCE (saturated calomel electrode))[25] than the one-electron reduction potential of $Bu^tOO^\bullet$ ($E_{red} = 0.50$ V vs SCE),[31] the presence of the proton may make it possible for the reaction to proceed.

SCHEME 3



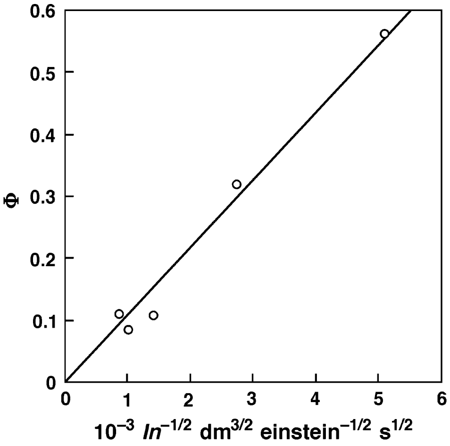


Figure 7. Plot of quantum yield vs $In^{-1/2}$ for the photooxidation of $AcrHBu^t$ (1.0×10^{-4} M) with oxygen in the presence of $HClO_4$ (1.2×10^{-1} M) in CH_3CN/H_2O (1:1, v/v).

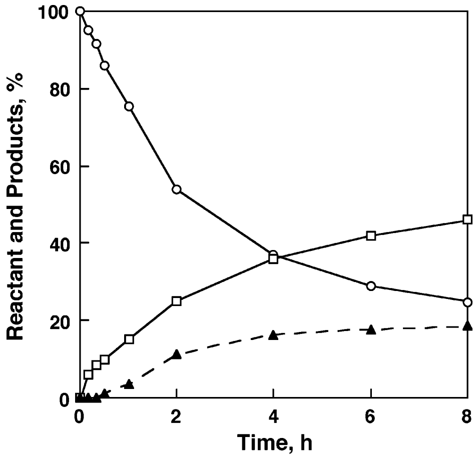
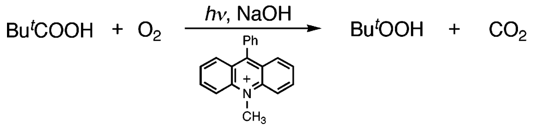


Figure 8. Time profiles of the disappearance of the reactant, pivalic acid (○), and formation of the products, Bu^tOOH (□) and Bu^tOH (▲), in the photocatalytic oxygenation of pivalic acid (1.0×10^{-1} M) in the presence of $AcrPh^+$ (2.0×10^{-2} M) and NaOH (3.0×10^{-2} M) in O_2-saturated CH_3CN/H_2O (1:1 v/v) under photoirradiation with a mercury lamp through the filter cutting off the light of $\lambda < 300$ nm at 298 K. The amounts of the reactant and products are given as percents in reference to the initial amount of pivalic acid.

Photocatalytic Oxygenation of Bu^tCOO^- with O_2. As described above, the photoreduction of $AcrH^+$ by Bu^tCOO^- under visible light irradiation affords $AcrHBu^t$ and the photooxidation of $AcrHBu^t$ with O_2 in the presence of $HClO_4$ under UV light irradiation yields Bu^tOOH, accompanied by the regeneration of $AcrH^+$. This cycle can be repeated to oxygenate Bu^tCOO^- with O_2, yielding Bu^tOOH and CO_2. However, the facile radical coupling between $Bu^{t\bullet}$ and $AcrH^\bullet$ has precluded the oxygenation of $Bu^{t\bullet}$ with O_2 (Scheme 1). When $AcrH^+$ is replaced by 9-phenyl-10-methylacridinium ion ($AcrPh^+$), the bulky phenyl group can prevent the radical coupling between $Bu^{t\bullet}$ and $AcrPh^\bullet$. In such a case, photoirradiation of the absorption band of $AcrPh^+$ (2.0×10^{-2} M) in an O_2-saturated CH_3CN/H_2O (1:1, v/v) solution containing pivalic acid (5.0×10^{-2} M) and NaOH (3.0×10^{-2} M) gave Bu^tOOH as a major product in addition to *tert*-butyl alcohol (Bu^tOH), as shown in eq 10.[32] Figure 8 shows the time course of the photocatalytic



$$Bu^tCOOH + O_2 \xrightarrow{h\nu,\ NaOH} Bu^tOOH + CO_2 \tag{10}$$

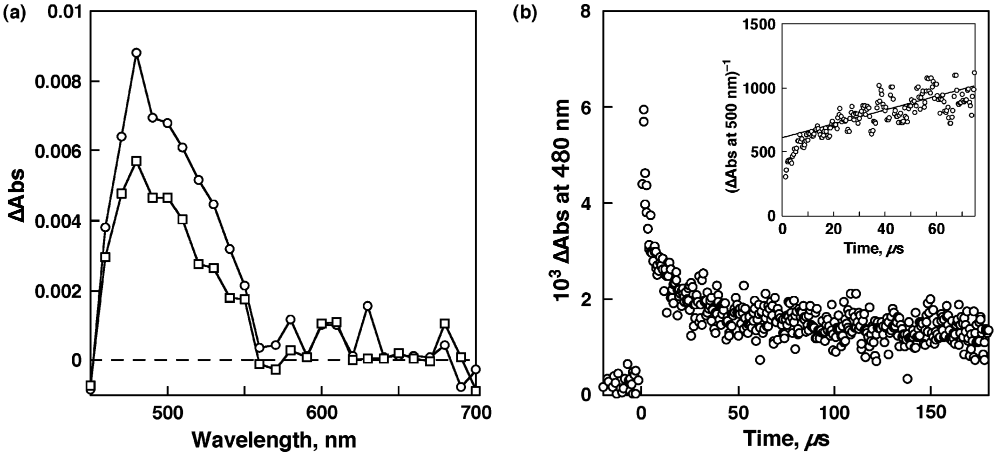


Figure 9. (a) Transient absorption spectra observed by photoexcitation of an O_2-saturated CH_3CN/H_2O (1:1, v/v) solution of $AcrPh^+$ (5.0×10^{-5} M), Bu^tCOOH (5.0×10^{-1} M), and NaOH (3.0×10^{-1} M) at 400 ns after laser excitation at 298 K. (b) Decay time profile of absorbance at 480 nm. The inset shows the second-order plot.

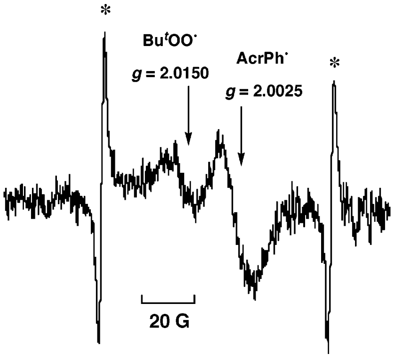


Figure 10. ESR spectrum observed under photoirradiation of an O_2-saturated CH_3CN/H_2O (1:1, v/v) solution of $AcrPh^+$ (5.0×10^{-2} M) containing pivalic acid (1.0 M) and NaOH (5.0×10^{-1} M) at 243 K. The arrows denote the center of each signal due to $Bu^tOO^\bullet$ and $AcrPh^\bullet$. The asterisk denotes an Mn^{2+} marker.

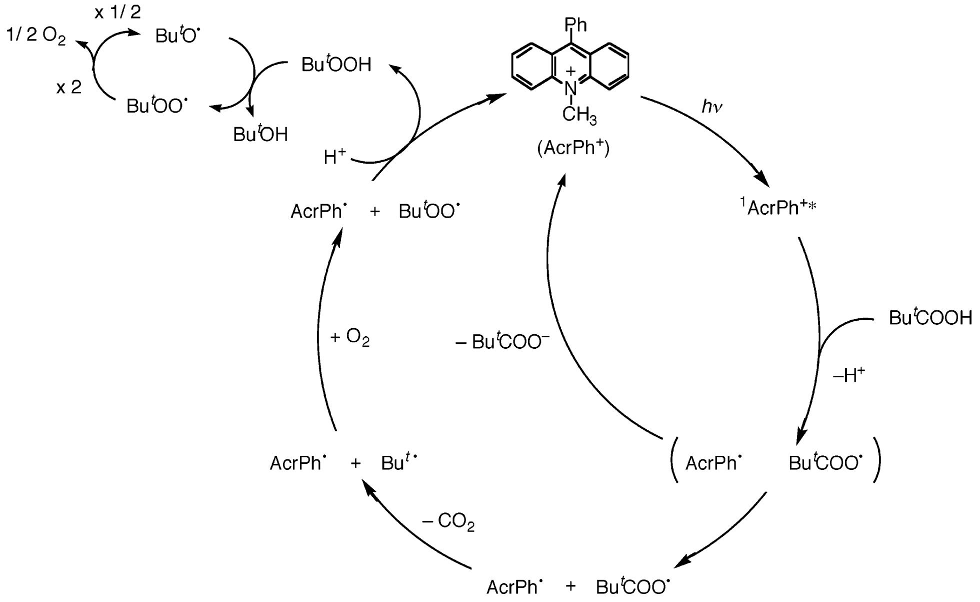
reaction. After the photochemical reaction for 8 h, the yield of Bu^tOOH was 46%. Thus, $AcrPh^+$ acts as a photocatalyst for the photoinduced oxygenation of pivalic acid with oxygen, although the concentration of $AcrPh^+$ decreases at prolonged photoirradiation.[33]

Photoexcitation of the absorption band of $AcrPh^+$ also results in fluorescence at 508 nm in CH_3CN/H_2O (1:1, v/v).[24,28] The fluorescence of the singlet excited state of $AcrPh^+$ ($^1AcrPh^{+*}$) is also known to be quenched efficiently by a variety of aromatic electron donors via electron transfer from aromatic electron donors to $^1AcrPh^{+*}$.[24,28] The fluorescence of $^1AcrPh^{+*}$ is also quenched by Bu^tCOO^-. The quenching rate constants k_q were determined as 1.4×10^9 M^{-1} s^{-1}, from the slopes of the Stern–Volmer plots and the lifetime of the singlet excited state, $^1AcrPh^{+*}$ (see Supporting Information, S2).

The occurrence of photoinduced electron transfer from Bu^tCOO^- to $^1AcrPh^{+*}$ is confirmed by laser flash photolysis experiments. Laser flash excitation (355 nm from an Nd:YAG laser) of $AcrPh^+$ (5.0×10^{-5} M) in O_2-saturated CH_3CN/H_2O (1:1 v/v) solution containing Bu^tCOOH (5.0×10^{-1} M) and NaOH (3.0×10^{-1} M) affords transient absorption bands at $\lambda_{max} = 480$ nm due to $AcrPh^\bullet$,[24,34] as shown in Figure 9a.

The decay rate constant of $AcrPh^\bullet$ in the reaction system was determined from the second-order plot as 1.9×10^{10} M^{-1} s^{-1}, which is close to the diffusion-limited rate constant.[35,36] $Bu^tCOO^\bullet$ or $Bu^{t\bullet}$ has not been detected in the wavelength region in Figure 9. The second-order decay rate constant of $AcrPh^\bullet$, which agrees with the diffusion-limited rate constant, indicates

SCHEME 4



that the geminate radical ion pair after the decarboxylation ($AcrPh^{\bullet}$ $Bu^{t\bullet}$) is separated into free radical ions in the solution. Then, molecular oxygen is added to $Bu^{t\bullet}$ out of the solvent cage.

The addition of O_2 to $Bu^{t\bullet}$ gives the peroxyl radical, $Bu^tOO^{\bullet}$, which was detected successfully by ESR. An O_2-saturated CH_3CN/H_2O (1:1, v/v) solution of pivalic acid (1.0 M) and NaOH (5.0×10^{-1} M) with $AcrPh^+$ (5.0×10^{-2} M) was irradiated by a high-pressure mercury lamp at 243 K. The resulting ESR spectrum consists of two isotropic signals at $g = 2.0150$ and at $g = 2.0025$ (Figure 10). The former signal is assigned to $Bu^tOO^{\bullet}$, because the g value is diagnostic of peroxyl radicals.[37] The g value of the latter signal agrees with that of $AcrPh^{\bullet}$.[28c]

On the basis of the above results, the reaction mechanism for the $AcrPh^+$-photosensitized oxygenation of pivalic acid is summarized as shown in Scheme 4. Photoinduced electron transfer from Bu^tCOO^- to $^1AcrPh^{+*}$ occurs to produce the radical pair ($AcrPh^{\bullet}$ $Bu^tCOO^{\bullet}$) as the case of $AcrH^+$ (Scheme 1). $Bu^tCOO^{\bullet}$ undergoes facile decarboxylation to produce $Bu^{t\bullet}$ in competition with the back electron transfer from $AcrPh^{\bullet}$. $Bu^{t\bullet}$ reacts with oxygen to produce the corresponding peroxyl radical, which is detected by ESR together with $AcrPh^{\bullet}$ in Figure 10. Since bimolecular electron transfer from $AcrPh^{\bullet}$ to $Bu^tOO^{\bullet}$ is exergonic,[38] the electron transfer may occur at the diffusion-limited rate to produce Bu^tOOH after protonation, accompanied by the regeneration of $AcrPh^+$ (Scheme 3). This is confirmed by the second-order plot of the decay of the absorbance at 480 nm due to $AcrPh^{\bullet}$ in Figure 9b, which affords the diffusion-limited value (1.9×10^{10} M^{-1} s^{-1}).

The alcohol (Bu^tOH) is also formed together with Bu^tOOH via the following radical chain decomposition of the hydroperoxide.[38] The bimolecular reaction of $Bu^tOO^{\bullet}$ gives 2 equiv of $Bu^tO^{\bullet}$, accompanied by the evolution of O_2. $Bu^tO^{\bullet}$ abstracts hydrogen from Bu^tOOH to produce Bu^tOH, accompanied by the regeneration of $Bu^tOO^{\bullet}$ (Scheme 4).

Summary

The photoreduction of $AcrH^+$ by $RCOO^-$ under visible light irradiation affords AcrHR via photoinduced electron transfer from $RCOO^-$ to $^1AcrH^{+*}$, followed by the decarboxylation of $RCOO^{\bullet}$ and the radical coupling with $AcrH^{\bullet}$. In the case of $R = Bu^t$, the photooxidation of $AcrHBu^t$ with O_2 in the presence of $HClO_4$ under UV light irradiation yields Bu^tOOH, accompanied by the regeneration of $AcrH^+$ via a radical chain process. The cycle of the photoreduction of $AcrH^+$ by Bu^tCOO^- and the photooxidation of $AcrHBu^t$ with O_2 can be repeated to oxygenate Bu^tCOO^- with O_2, yielding Bu^tOOH and CO_2. When $AcrH^+$ is replaced by $AcrPh^+$, $AcrPh^+$ can act as a photocatalyst for the one-pot photooxygenation of Bu^tCOO^- with O_2 to yield Bu^tOOH and Bu^tOH.

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Supporting Information Available: The rates of photocatalytic oxidation of $AcrHBu^t$ with O_2 in O_2-saturated and air-saturated CH_3CN/H_2O (1:1, v/v) (S1) and Stern−Volmer plots for the fluorescence quenching of $AcrPh^+$ by Bu^tCOO^- (S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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