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Photocatalytic oxygenation of olefins with oxygen Isolation of 1,2-dioxetane and the photocatalytic O–O bond cleavage

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Abstract

Formation of 1,2-dioxetane of tetraphenylethylene (TPE) occurs via formation of the electron transfer state of 9-mesityl-10-methylacridinium ion (Acr^+-Mes) under visible light irradiation, followed by electron transfer from TPE to the $Mes^{\bullet+}$ moiety together with electron transfer from the $Acr^\bullet$ moiety to O_2, and the subsequent radical coupling between $TPE^{\bullet+}$ and $O_2^{\bullet-}$ to yield the corresponding 1,2-dioxetane. The dioxetane thus formed was isolated using column chromatography. Photooxygenation of stilbene derivatives is also efficiently catalyzed by Acr^+-Mes, accompanied by efficient *cis–trans* isomerization, to afford the corresponding benzaldehydes via electron transfer from $Acr^\bullet$-$Mes^{\bullet+}$ to stilbene derivatives and oxygen.

Keywords: Dioxetane; Electron transfer; Oxygenation; Radical coupling; Olefin

1. Introduction

Molecular oxygen is an ideal reagent for economical and environmental benign oxygenation reactions because of its abundant availability and non-toxicity [1,2]. Since direct concerted reactions between singlet molecules and triplet oxygen ($^3O_2 : {}^3\Sigma_g^-$) are spin-forbidden, activation of oxygen by transition metal catalysts [3], photoexcitation to produce singlet oxygen ($^1O_2$) [4,5], or generation of radical species, which can react with $^3O_2$ directly (spin-allowed) [6], is required to use molecular oxygen as a terminal oxidant. Although radical coupling reactions between radical cations and radical anions ($O_2^{\bullet-}$) have profound fundamental and synthetic interest for the selective oxygenation of substrates, the difficulty of generating such highly reactive species together had precluded the exploitation of such reactions [7]. Radical cations and radical anions can be formed using an electron donor–acceptor linked molecule, since the photoexcitation results in formation of radical cation and anion pair which can oxidize and reduce substrates to generate radical cations and radical anions, respectively [8–12]. However, the lifetimes of charge-separated states of most donor–acceptor linked molecules reported so far were too short to be coupled with the redox reactions of substrates [8–12]. 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 ($Acr^\bullet$-$Mes^{\bullet+}$), which has an extremely long lifetime (e.g., 2 h at 203 K) and a high energy (2.37 eV) [13]. Acr^+-Mes acts as an efficient electron-transfer photocatalyst for highly selective oxygenation of anthracenes with O_2 via selective [4 + 2] radical coupling of anthracene radical cations and $O_2^{\bullet-}$ to produce epidioxyanthracenes under visible light irradiation [14].

1,2-Dioxetanes have attracted considerable interest because of the key roles in chemiluminescence and bioluminescence [15,16], which have a broad range of biological, chemical, and medical applications [17,18]. The most common preparation of 1,2-dioxetanes is through the formal [2 + 2] cycloaddition of singlet oxygen ($^1O_2$) to electron-rich alkenes [19,20]. Diastereoselective formation of dioxetanes has also been achieved by a chiral-auxially-induced [2 + 2] cycloaddition of $^1O_2$ with a chiral allylic alcohol and enecarbamates [21–23]. Nelsen and coworkers have reported the isolation and electron-transfer oxidation properties of 1,2-dioxetane such as

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adamantylidene adamantane [24]. However, there has been no report of the aromatic 1,2-dioxetane. Recently, we have succeeded in the selective oxygenation of anthracene derivatives with O_2 via [4 + 2] radical coupling using long-lived electron-transfer state of Acr^+-Mes as a photocatalyst [14].

We report herein the photooxygenation of olefins such as tetraphenylethylene (TPE) and stilbene derivatives with oxygen in the presecne of Acr^+-Mes, which acts as an efficient photocatalyst [25]. The photooxygenated intermediate, 1,2-dioxetane, has sucessfully been isolated in the photocatalytic oxygenation of TPE. The photocatalytic mechanism for the formation of the 1,2-dioxetane and the decompostion to the final product is clarified based on the reaction intermediates.

2. Experimental

2.1. Materials

Tetraphynylethylene (TPE), *trans*- and *cis*-stilbene, 4,4′-dimethyl-*trans*-stilbene, 4-methoxystilbene, *p*-(*N,N*-dimethylamino)stilbene, 4-aminostilbene, fullerene (C_{60}) and tetraphenylporphyrin were obtained commercially. Acetonitrile (MeCN) and chloroform ($CHCl_3$) were of spectral grade, obtained commercially and used without further purification. 9-Mesityl-10-methylacridinium perchlorate ($[Acr^+\text{-Mes}]ClO_4^-$) was prepared by the reaction of 10-methylacridone with mesityl magnesium bromide (MesMgBr) in tetrahydrofuran, followed by addition of sodium hydroxide (water) for the hydrolysis and perchloric acid for the neutralization [13,14]. The isolated compound was purified by recrystallization from methanol–diethyl ether. The yield was 87% based on acridone [26]. ^1H NMR (CD_3CN, 300 MHz) δ (ppm) 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). Anal. Calcd. for $C_{23}H_{22}ClNO_4$: C, 67.07; H, 5.38; N, 3.40. Found: C, 66.78; H, 5.33; N, 3.35.

2.2. Photooxygenation of TPE and isolation of TPE dioxetane

The photocatalytic oxygenation of TPE with O_2 was carried out by the following procedure. 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 $\lambda > 430$ nm at 278 K. After 5 h photoirradiation, the corresponding 1,2-dioxetane was isolated by silica gel column chromatography (hexane/chloroform v.v. 2/1) as pale yellow solid (27% yield). TPE dioxetane is moisture sensitive. TPE dioxetane: ^1H 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. *Caution*! *Dryness of dioxetane may result in explosion. All preparation should be manipulated with care and used only in small quantities*. Final oxygenated products, benzophenone and benzaldehydes were determined by ^1H NMR (300 MHz, $CDCl_3$). Benzophenone: δ 7.48–7.51 (m, 4H), 7.56–7.59 (m, 2H), 7.79–7.82 (m, 4H). Benzaldehyde: δ 7.49–7.53 (m, 3H), 7.86–7.92 (m, 2H), 10.03 (s, 1H). 4-Methylbenzaldehyde: δ 2.43 (s, 3H), 7.73 (d, 2H, $J = 8.1$ Hz), 7.78 (d, 2H, $J = 8.1$ Hz), 9.94 (s, 1H). 4-methoxybenzaldehyde: δ 3.86 (s, 3H), 6.98 (d, 2H, $J = 9.0$ Hz), 7.79 (d, 2H, $J = 8.8$ Hz), 9.86 (s, 1H). 4-aminobenzaldehyde: δ 975 (s, 1H) 4-(*N,N*-dimethylamino)-benzaldehyde: δ 3.09 (s, 6H), 6.81 (d, 2H, $J = 9.0$ Hz), 7.65 (d, 2H, $J = 9.0$ Hz), 9.74 (s, 1H).

2.3. Quantum yield determinations

A standard actinometer (potassium ferrioxalate) [27] was used for the quantum yield determination of the photocatalytic oxygenation of TPE with O_2 in the presence Acr^+-Mes. Typically, a square quartz cuvette (10 mm i.d.), which contained a deaerated MeCN or $CHCl_3$ solution (3.0 cm^3) of Acr^+-Mes (2.0×10^{-4} M) and TPE (2.0×10^{-4} M), was irradiated with monochromatized light of $\lambda = 430$ nm from a Shimadzu RF-5300PC fluorescence spectrophotometer. Under the conditions of actinometry experiments, the actinometer and Acr^+-Mes absorbed essentially all of incident light of $\lambda = 430$ nm. The light intensity of monochromatized light of $\lambda = 430$ nm was determined as 2.98×10^{-9} einstein s^{-1}. The photochemical reaction was monitored using a Hewlett Packard 8453 diode-array spectrophotometer. The quantum yields in the presence of oxygen were determined from decrease of olefins.

2.4. Electrochemical measurements

Second harmonic ac voltammetry (SHACV) [28] measurement of TPE dioxetane was carried out with ALS630B electrochemical analyzers in deaerated acetonitrile containing 0.10 M $Bu_4N^+ClO_4^-$ (TBAP) or in chloroform containing 0.2 M TBAP as a supporting electrolyte at 298 K. The gold working electrode (BAS, surface i.d. 1.6 mm) were polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/$AgNO_3$ (0.01 M) reference electrode. The E_{ox} and E_{red} values (versus Ag/$AgNO_3$) are converted into those versus SCE by addition of 0.29 V [29].

2.5. ESR measurements

ESR measurements were performed on a JEOL X-band ESR spectrometer (JES-ME-LX) at 233 K. A quartz ESR tube (internal diameter: 1.5 mm) containing an argon-saturated $CHCl_3$ solution of Acr^+-Mes (3.7×10^{-2} M) and TPE dioxetane (3.0×10^{-3} M) at 233 K was irradiated in the cavity of the ESR spectrometer with the focused light of a 1000-W high-pressure Hg lamp (Ushio-USH1005D) through an aqueous filter. The ESR spectra were measured under nonsaturating microwave power conditions. The amplitude of modulation was chosen to optimize the resolution and the signal-to-noise (*S/N*) ratio of the observed spectra.

2.6. Laser flash photolysis measurements.

Measurements of transient absorption spectra in the photochemical reaction of Acr$^+$-Mes with TPE were performed according to the following procedure. A deaerated MeCN solution containing Acr$^+$-Mes (6.0×10^{-5} M) and TPE (5.0×10^{-2} M) was excited by Nd:YAG laser (Continuum, SLII-10, 4–6 ns fwhm) at 430 nm. Time courses of the transient absorption spectra were measured by using a continuous Xe-lamp (150 W) and an In GaAs-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.

2.7. 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 [30] with the unrestricted Hatree-Fock (UHF) formalism for TPE dioxetane radical cation and the restricted Hatree-Fock (RHF) formalism for TPE dioxetane and as implemented in the Gaussian 03 program. Graphical output of the computational results were generated with the Cerius^2 software program developed by Molecular Simulations Inc.

3. Results and discussion

3.1. Photocatalytic oxygenation of olefins with oxygen

Fig. 1a–d show ^{1}H NMR spectral change under the visible light photoirradiation ($\lambda > 430$ nm) of the absorption band of Acr$^+$-Mes (5.0×10^{-3} M) in an O_2-saturated chloroform solution containing tetraphenylethylene (TPE: 1.5×10^{-2} M). Photooxygenation of TPE results in formation of the initial oxygenation product, i.e., 1,2-dioxetane after 30 min irradiation by a 500 W xenon lamp (Fig. 1b). The dioxetane is converted to benzophenone quantitatively (199% based on the consumption of TPE; note that two equivlanents of benzophenone is formed from TPE) at prolonged irradiation time. Benzophenone yields of the photocatalytic oxygenation of TPE with oxygen under various experimental conditions are listed in Table 1. No decomposition of Acr$^+$-Mes was observed under the present reaction conditions after the conversion all TPE to benzophenone (Fig. 1d). No oxygenation occurred in the absence of oxygen under otherwise the same experimental conditions. It is important to note that no oxygenation occurred in an O_2-saturated solution of TPE containing C_{60} or tetraphenylporphyrin as a singlet oxygen sensitizer instead of Acr$^+$-Mes. The photocatalytic oxygenation of TPE with O_2 in a preparative scale with Acr$^+$-Mes in chloroform was also performed to isolate the corresponding 1,2-dioxetane (27% yield) after 4 h photoirradiation at 278 K. The TPE dioxetane was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectra (see experimental section). The purity of TPE dioxetane was >99%, estimated by ^{1}H NMR as shown in Fig. 1e.

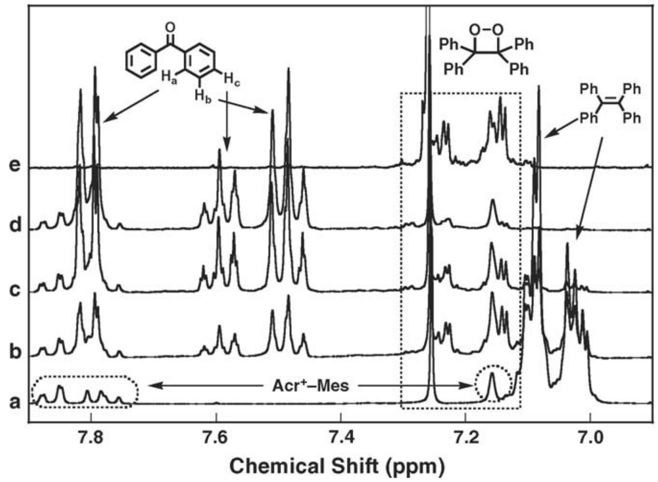


Fig. 1. Time course of ^{1}H NMR spectra observed under photoirradiation of an O_2-saturated $CDCl_3$ solution containing TPE (1.5×10^{-2} M) and Acr$^+$-Mes (5.0×10^{-3} M) at 298 K. Spectra measuered (a) before photoirradiation and after photoirradiation (b) at 30 min, (c) 60 min, and (d) 90 min. (e) ^{1}H NMR spectrum of TPE dioxetane after purification by column chromatography.

Table 1
Benzophenone yields in photooxygenation of TPE in the presence of various photocatalysts

Entry	Catalyst	Time (h)	Atmosphere	Solvent	Yield[a] (%)
1	Acr$^+$-Mes	1.5	O_2	$CDCl_3$	199
2	Acr$^+$-Mes	2.0	O_2	CD_3CN	156
3	Acr$^+$-Mes	2.0	Argon	$CDCl_3$	0
4	None	2.0	O_2	$CDCl_3$	0
5	C_{60}	2.0	O_2	$C_6D_5CD_3$	0
6	TPP	2.0	O_2	$CDCl_3$	0

[a] Determined by ^{1}H NMR based on the consumption of TPE.

Photooxygenation of TPE also occurred in MeCN, however, the rate is much slower than the case in $CHCl_3$. The product yield in MeCN determined as 156% after 2 h photoirradiation. The quantum yields (Φ) were determined from the formation rate of benzophenone in MeCN 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_∞) as 0.17 and 0.022 in $CHCl_3$ and MeCN, respectively.

Photooxygenation of olefins such as stilbene derivatives was also examined in MeCN and $CHCl_3$, respectively. In contrast with the case of TPE, the dioxetane intermediates were not detected under the same experimental conditions as employed for TPE. This indicates that the stilbene dioxetanes decompose to the corresponding benzaldehydes spontaneously under photoirradiation. The yields of the corresponding benzaldehyde derivatives are listed in Table 2. The one-electron oxidation potentials (E_{ox}) of stilbene derivatives determined by second harmonic AC voltammetry (SHACV) are also listed in Table 2. The yields of benzaldehyde derivatives obtained from *trans*-stilbene derivatives increase in order: R_1, $R_2 = H$, $H <$ Me, Me < OMe, H (entries 1–3 in Table 2), as the E_{ox} values of

Table 2
One-electron oxidation potentials (E_{ox}) and product yields of the Acr^+-Mes-catalyzed photooxygenation of stilbene derivatives in chloroform and acetonitrile

Entry	Stilbene	E_{ox} vs. SCE (V)		Product	Yield[a,b] (%)	
		$CHCl_3$	CH_3CN		$CDCl_3$	CD_3CN
1	*Trans*-stilbene	1.52	1.47	PhCHO	36	20
2	$(p\text{-Me})C_6H_4CH{=}CHC_6H_4(p\text{-Me})$[c]	1.28	1.28	$(p\text{-Me})C_6H_4CHO$	72	50
3	$(p\text{-MeO})C_6H_4CH{=}CHC_6H_5$[d]	1.14	1.16	PhCHO	92	36
				$(p\text{-MeO})C_6H_4CHO$	66	22
4	$(p\text{-Me}_2N)C_6H_4CH{=}CHC_6H_5$[d]	0.55	0.55	PhCHO	22	10
				$(p\text{-Me}_2N)C_6H_4CHO$	Trace	Trace
5	$(p\text{-H}_2N)C_6H_4CH{=}CHC_6H_5$[d]	0.72	0.57	PhCHO	26	16
				$(p\text{-H}_2N)C_6H_4CHO$	Trace	Trace
6	*Cis*-stilbene	1.54	1.58	PhCHO	32	18

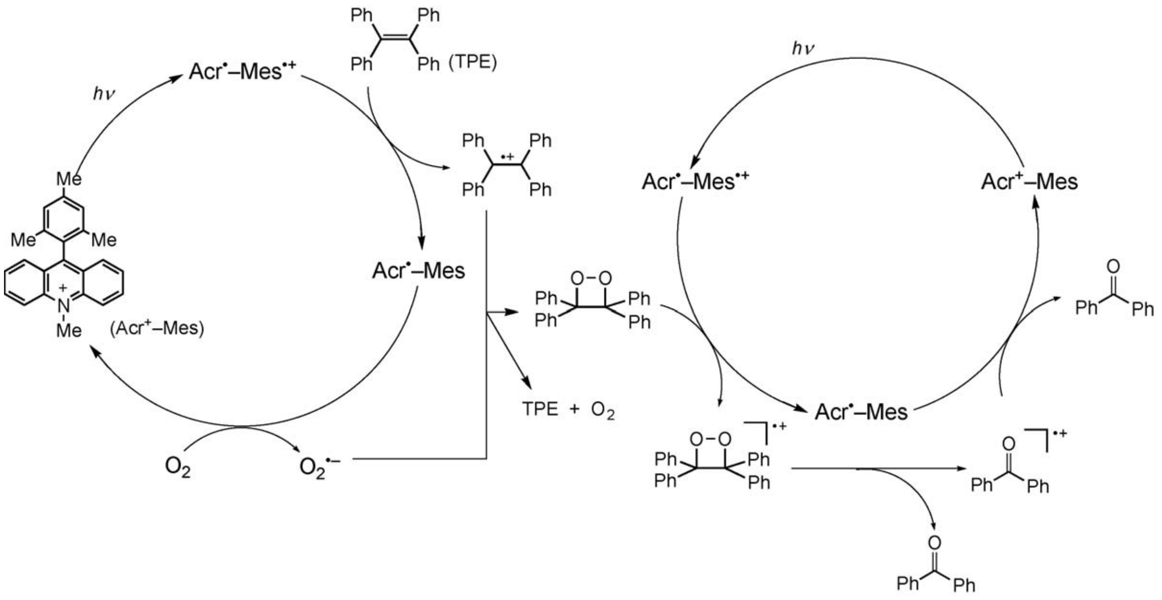
[a] Determined by ^1H NMR based on the consumption of TPE.
[b] Irradiation time with a xenon lamp is 3 h.
[c] *Trans* form.
[d] Mixture of *trans* and *cis* forms.

stilbene derivatives decrease. However, the yields from *trans*-stilbene derivatives with strong electron-donating substituents (R_1, R_2 = NMe_2, H and NH_2, H in entries 4 and 5, respectively) become much smaller than the case of stilbene. This may result from the oxidative decomposition of 4-(*N*,*N*-dimethylamino)-benzaldehyde and 4-aminobanzaldehyde under photoirradiation. Photooxygenation of *cis*-stilbene also affords benzaldehyde (entry 6).

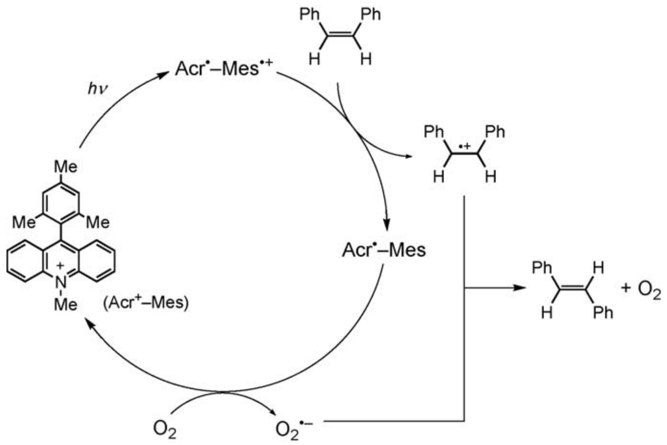
3.2. Photocatalytic mechanism of oxygenation of TPE

The photocatalytic mechanism of formation of TPE dioxetane catalyzed by Acr^+-Mes is shown in the left circle in Scheme 1. The electron transfer state of Acr^+-Mes ($Acr^\bullet$-$Mes^{\bullet+}$) is produced upon photoexcitation of Acr^+-Mes. The one-electron oxidation potential (E_{ox}) of TPE (1.56 V versus SCE) is less positive than the value of one-electron reduction potential (E_{red}) of $Mes^{\bullet+}$ (1.88 V versus SCE) [13,25]. Thus, electron transfer from TPE to the $Mes^{\bullet+}$ moiety of $Acr^\bullet$-$Mes^{\bullet+}$ is thermodynamically favorable, resulting in formation of $TPE^{\bullet+}$ and $Acr^\bullet$-Mes, which is confirmed by laser flash photolysis [25]. Then, the radical coupling of $TPE^{\bullet+}$ occurs with $O_2^{\bullet-}$, which is produced by electron transfer from the $Acr^\bullet$ moiety of $Acr^\bullet$-Mes to O_2, occurs to gives TPE dioxetane, accompanied by regeneration of Acr^+-Mes (Scheme 1).

The further photocatalytic conversion of TPE dioxetane is shown in the right circle in Scheme 1. Electron transfer from TPE dioxetane to the $Mes^{\bullet+}$ moiety of the electron-transfer state of Acr^+-Mes is energetically feasible, because the E_{ox} value of TPE dioxetane (1.56 V versus SCE) is less positive than the E_{red} value of $Mes^{\bullet+}$ moiety (1.88 V versus SCE) [13]. Thus, TPE dioxetane is oxidized by the electron-transfer state of Acr^+-Mes to produce TPE dioxetane radical cation, which undergoes the O–O bond homolysis to produce benzophenone and the radical cation of benzophenone. The benzophenone radical cation is readily reduced by the $Acr^\bullet$ moiety to produce another benzophenone molecule, accompanied by regeneration of Acr^+-Mes. Formation of TPE dioxetane radical cation was



Scheme 1.



Scheme 2.

confirmed by ESR (electron spin resonance) measurements under photoirradiation at low temperature [25]. The SOMO (singly occupied molecular orbital) of TPE dioxetane radical cation involves O–O π antibonding orbital [25], which is calculated by DFT method at B3LYP/6-31G* level. Thus, the O–O cleavage of TPE dioxetane is efficiently catalyzed by Acr$^+$-Mes via the electron-transfer oxidation of TPE dioxetane to form TPE dioxetane radical cation [31]. Photooxygenation also occurred in MeCN, however, the quantum yield is much lower than the case in CHCl$_3$, because of the much faster back electron transfer from superoxide anion to TPE radical cation in MeCN than the case in CHCl$_3$ (Scheme 1).

3.3. Photocatalytic mechanism of oxygenation of stilbene derivatives

The photooxygenation mechanism of *cis*-stilbene catalyzed by Acr$^+$-Mes is shown in Scheme 2, which is similar to that of TPE (Scheme 1). Electron transfer from stilbene derivatives to the Mes$^{\bullet+}$ moiety is energetically feasible, because the E_{ox} values of stilbene derivatives (0.55–1.58 V versus SCE) is less positive than the E_{red} value of the Mes$^{\bullet+}$ moiety. The electron transfer oxidation of *cis*-stilbene (E_{ox} = 1.58 V versus SCE in MeCN) by the Mes$^{\bullet+}$ moiety of electron transfer state of Acr$^+$-Mes result in the formation of *cis*-stilbene radical cation and Acr$^\bullet$-Mes.

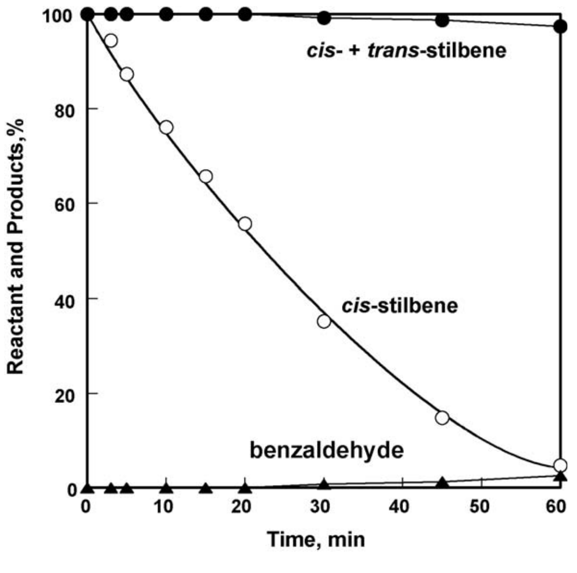


Fig. 2. Photoirradiation time profile of the photoisomerization of *cis*-stilbene (15 mM) in the presence of Acr$^+$-Mes (5 mM) in O$_2$-saturated CD$_3$CN monitored by ^{1}H NMR.

Isomerization of *cis*-stilbene to *trans*-stilbene observed in the photocatalytic oxygenation of *cis*-stilbene in the presence of Acr$^+$-Mes in an O$_2$-saturated MeCN as shown in Fig. 2, where concentrations of benzaldehyde, *cis*- and *trans*-stilbene were determined by the ^{1}H NMR spectra. The concentration of *cis*-stilbene decreases with a concomitant increase due to *trans*-stilbene, when the total concentration of *cis*- and *trans*-stilbene only slightly decreases together with an accompanied increase in the photooxygenation product, benzaldehyde. The observed yield of *trans*-stilbene was 96% after 60 min photoirradiation ($\lambda > 430$ nm), when the total consumption of *cis*- and *trans*-stilbene is still 4%. It is well-known that *cis–trans* isomerization occurs rapidly in the stilbene radical cation [32–34]. The steady-state *cis–trans* ratio of stilbene has been reproted to be 98.8: 1 [34]. It has been confimed that *trans*-stilbene has slightly been converted to *cis*-stilbene under the same experimental conditions as employed in Fig. 2 (3% yield of *trans*-stilbene). Thus, Acr$^+$-Mes acts as a photocatalyst for the *cis-trans* isomerization of stilbene via the radical cation (Scheme 2). Since stilbene radical cation has low reactivity toward O$_2$ [35–38], the photocatalytic oxygenation of stilbene with Acr$^+$-Mes takes place via the radical coupling between stilbene radical cation and $O_2^{\bullet-}$ rather than via the reaction of stilbene radical cation with O$_2$, accomapnied by the isomerization of the stilbene radical cation.

4. Conclusions

In conclusion, Acr$^+$-Mes acts as an efficient photocatalyst for the oxygenation of olefins with O$_2$, which proceeds via the radical coupling between the radical cation of olefin and $O_2^{\bullet-}$ to yield the 1,2-dioxetane. The final product (benzophenone or benzaldehyde) is obtained from the facile O–O bond cleavage of the 1,2-dioxetane radical cation by the electron-transfer oxidation.

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