Bull. Chem. Soc. Jpn., ***71***, *2211—2220 (1998)*

Photoreactivities of Contact Charge-Transfer Complexes between 1,1-Diarylethenes and Oxygen Molecules. Dimerization and Oxygenation Accelerated in Medium Polar Solvent

Masanobu Kojima,* Akito Ishida,† and Setsuo Takamuku†,#

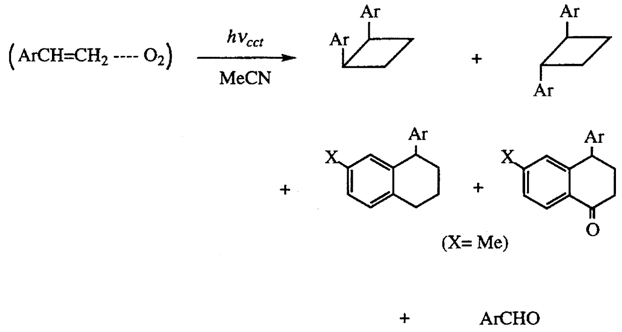
Department of Bioscience and Biotechnology, Faculty of Agriculture, Shinshu University, Matsumoto, Nagano 390-8621

†The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047

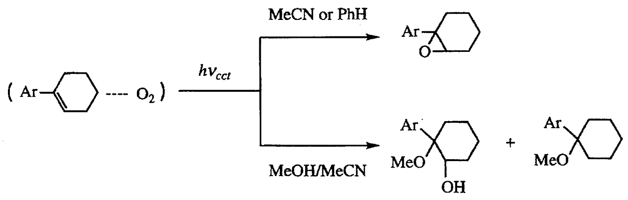
(Received March 27, 1998)

The selective excitation of contact charge-transfer (CCT) bands of 1,1-diarylethenes [Ar = 4-$MeOC_6H_4$ (**1a**); 4-MeC_6H_4 (**1b**); Ph (**1c**)] with molecular oxygen in CH_2Cl_2 and MeCN resulted in the formation of the corresponding 3,3,6,6-tetraaryl-1,2-dioxanes (**2**) as a primary product, together with diaryl ketones (**3**). The reaction mechanism and intermediates for the production of **2** and **3** were studied in terms of the effects of the solvent polarity, additives, substituents on the aromatic rings, and the excitation wavelength on the product distribution, as well as in terms of the result of the photolysis of **2**. On the basis of these results, it was shown that **2** was produced through dimer cation radicals of **1**, whereas **3** was formed through the photolysis of **2** and the autoxidation of **1** initiated by neutral radical species, which must have been generated by the reaction of monomer cation radicals of **1** ($\mathbf{1}^{\cdot+}$) with a superoxide anion radical. In particular, the formation of **2** depended to a large degree on the solvent polarity; namely, **2** was produced more efficiently in CH_2Cl_2 with moderate polarity rather than in MeCN with high polarity. Moreover, the reactivities of monomer and dimer cation radicals of **1** were investigated by γ-radiolyis and pulse radiolysis. For **1a** and **1b**, the transient-absorption spectra of their dimer cation radicals trapped by oxygen molecules were directly observed at 365 ns after pulse irradiation. The reactivities of $\mathbf{1}^{\cdot+}$ are also discussed based on the optimum structure, charge density, and spin density, obtained by semi-empirical molecular orbital calculations (PM3 method).

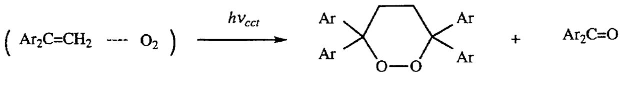
It is well-known that some organic substrates form contact charge-transfer (CCT) complexes with molecular oxygen.[1)] However, the photochemistry of the CCT complexes has attracted relatively little attention,[2)] in contrast to many investigations concerning singlet oxygen reaction[3)] and electron-transfer sensitized oxygenation.[4)] For the purpose of defining the reaction course of the CCT complexes, we have already investigated the photochemical reaction of CCT pairs comprising styrene derivatives and oxygen.[2b,2c,2e,2f)] The photoinduced electron transfer reactions of the CCT pairs result in the corresponding *cis*- and *trans*-1,2-diarylcyclobutane and tetralin-type dimers along with benzaldehydes, the products of oxidative cleavage (Eq. 1).[2b,2c)] Although it was explained, on the basis of the isomer ratio of the cyclic dimers, that the dimers are produced through dimer cation radicals of the olefins as intermediates, the mechanism for the formation of benzaldehydes has not been investigated. On the other hand, it was found that the excitation of CCT bands between 1-arylcyclohexenes and oxygen in MeCN yielded the corresponding epoxides as the main products (Eq. 2),[2f)] without producing dimeric products, by an autoxidation mechanism through the olefin cation radicals and superoxide anion radical ($O_2^{\cdot-}$).



(1)



(2)



1 **2** **3**

1a: Ar= 4-$MeOC_6H_4$; **1b**: Ar= 4-MeC_6H_4; **1c**: Ar= Ph

(3)

Present address: Department of Applied Physics and Engineering, Fukui University of Technology, 3-6-1 Gakuen, Fukui 910-8505.

In order to gain deeper insight into the photoreactivities of CCT complexes of aromatic olefins with oxygen, we investigated the photoinduced electron transfer reaction of the CCT complexes between 1,1-diarylethenes [**1** : Ar = 4-$MeOC_6H_4$ (**1a**), 4-MeC_6H_4 (**1b**), Ph (**1c**) and oxygen, which gives the corresponding 3,3,6,6-tetraaryl-1,2-dioxanes (**2**) as products trapped by oxygen on a reaction with open-chain 1,4-dimer cation radicals of the olefins, subsequently partially decomposing to benzophenones (**3**) upon further irradiation under oxygen (Eq. 3).$^{5)}$ We report here in detail on the solvent-polarity dependent photoreactivity of the above CCT complexes and the reactivities of intermediates generated in the reaction, studied by product analysis, time-resolved spectra, and molecular-orbital calculations.

Experimental

Materials. 1,1-Bis(4-methoxyphenyl)ethene (**1a**) and 1,1-bis(4-methylphenyl)ethene (**1b**) were prepared by a reaction of the corresponding 4,4′-substituted benzophenones with methylmagnesium bromide, followed by a treatment with *p*-toluenesulfonic acid in PhH.$^{6)}$ 1,1-Diphenylethene (**1c**) was purchased from Wako Pure Chem. Ind., Ltd. The olefins **1** were recrystallized or distilled before use. All of the solvents employed were guaranteed reagents (Nacalai Tesque, Inc. and Wako Pure Chem. Ind., Ltd.) and distilled over calcium hydride prior to use. Authentic samples for **2** were prepared according to Ref. 6.

Absorption Spectra of CCT Complexes. Diarylethenes **1** (0.05 M; 1 M = 1 mol dm^{-3}) in CH_2Cl_2, MeCN, and PhH were placed in a 10-cm path length sample cell. A stream of oxygen was passed for 30 min through the sample in the sample cell at room temperature for MeCN and PhH and at ice-bath temperature for CH_2Cl_2. The spectrum was measured, and immediately after this argon was again passed through the sample cell for 30 min at the above temperature and a second spectrum was recorded. The band observed under the oxygen atmosphere disappeared because of argon bubbling (Fig. 1).

Measurements of Oxidation Potentials. Oxidation potentials were measured by cyclic voltammetry using a potentiostat-galvanostat (Nikko Keisoku NPGS-501) and a function generator (Nikko Keisoku NFG-3). The measurements were carried out in MeCN using a three-electrode cyclic voltammetric cell. A platinum disk and a platinum wire were used as the working and counter electrodes, respectively, and the reference electrode was made of Ag/AgCl. Tetraethylammonium perchlorate (0.1 M) was used as a supporting electrolyte.

Irradiation of 1 under Oxygen. Diarylethenes **1** (0.04—0.05 M) were irradiated in oxygen-saturated CH_2Cl_2, MeCN, and PhH in a Pyrex glass tube ($\geq$290 nm bandpass; effective excitation wavelength, 313 nm) and a uranium glass tube ($\geq$340 nm bandpass for a 366-nm light) with a 400-W high-pressure mercury lamp (Riko UVL-400HA) or a quartz tube ($\geq$200 nm bandpass for a 254-nm light) with a 160-W high-pressure mercury lamp (Riko UVL-160LA) at 20 °C (Table 1). The conversion of **1** and the yields of **2** and **3** were determined with Shimadzu GC-8A and GC-14A gas chromatographs equipped with a flame ionization detector, as well as a JASCO 800 series high-performance liquid chromatograph.

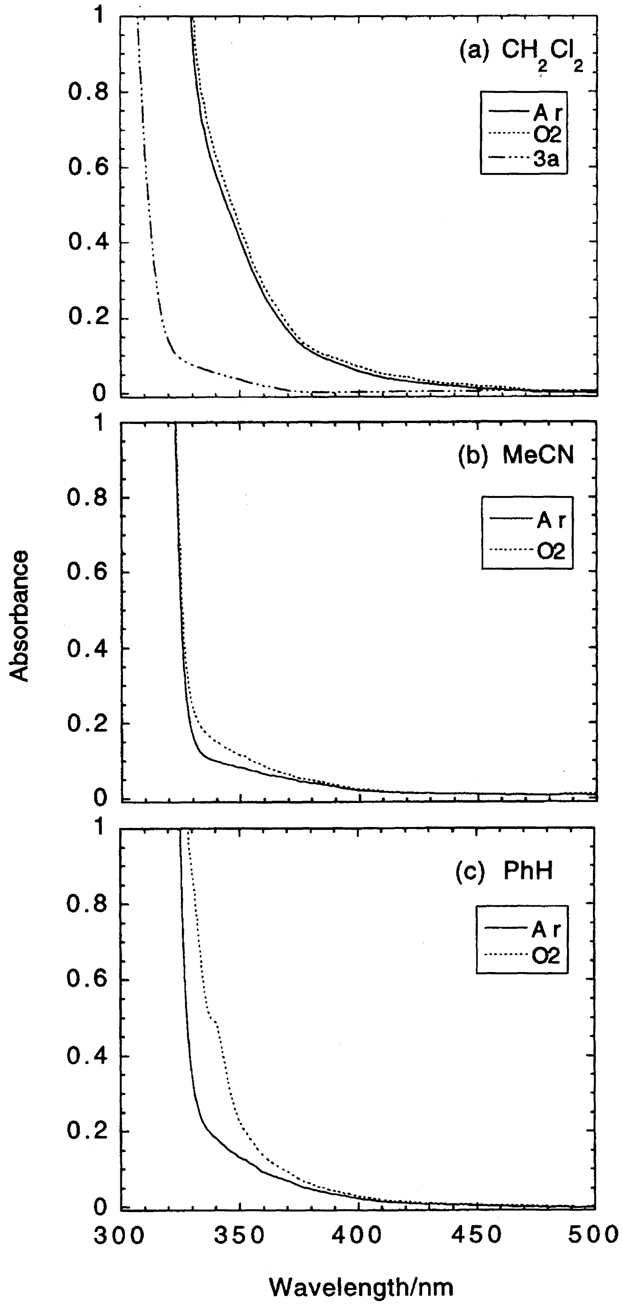


Fig. 1. UV absorption spectra of **1a** (0.05 M) under argon and oxygen, measured using a 10-cm path length cell: (a) in CH_2Cl_2, (b) in MeCN, and (c) in PhH. The absorption spectrum of **3** (10^{-4} M in CH_2Cl_2) measured using a 1-cm path length cell is also shown in (a).

Irradiation of 1 under Oxygen in the Presence of Electron Acceptor. Olefin **1** (0.04—0.05 M) was irradiated under oxygen in the presence of antimony (V) chloride ($SbCl_5$, 2—9$\times$10^{-4} M) in CH_2Cl_2 at −40 to −70°C through a Pyrex filter.$^{6)}$ In addition, 9,10-dicyanoanthracene-sensitized (DCA, 0.001 M) oxygenation of **1** was performed in MeCN at 20 °C in a uranium glass tube using a 400-W high-pressure mercury lamp.$^{7,8)}$ The reaction products were analyzed as explained above, and the results of a product analysis are given in Table 2.

Photolysis of 1,2-Dioxane 2. The photolysis of **2** (0.013—0.015 M) was carried out under oxygen and nitrogen in CH_2Cl_2 at 20 °C in a uranium glass tube with a 400-W high-pressure mercury lamp. Under oxygen, **3** was detected as the main product at 30—36% yield, together with a small amount of **1** (Table 3); however, under nitrogen, the formation of **3** was suppressed and several unknown

Table 1. Effect of Solvent Polarity and Excitation Wavelength on Product Distribution Resulting from Irradiation of the CCT Complex between **1** and Oxygen

1[a)] (E_{ox}/V)[b)]	Solvent	λ nm[c)]	Time[d)] h	Conv. %	Yields of products **2**/%	**3**/%	**2**/**3**
1a	CH_2Cl_2	366	2	3	46	6	7.7
	CH_2Cl_2	366	2	18[e)]	18[e)]	n.d.[f)]	—
	CH_2Cl_2	366	8	44	57	5	11.4
	CH_2Cl_2	366	10	70	28	9	3.1
	CH_2Cl_2	254	20	61	9	22	0.41
(1.35)	MeCN	366	2	3	—	56	—
	MeCN	366	10	52	28	16	1.75
	PhH	366	4	4	—	91	—
	PhH	366	10	40	—	66	—
1b	CH_2Cl_2	366	20	87	22	25	0.88
	CH_2Cl_2	254	20	44	9	25	0.36
(1.72)	MeCN	366	20	95	—	40	—
	PhH	366	20	36	—	59	—
1c	CH_2Cl_2	313	20	45	—	55	—
	CH_2Cl_2	254	20	18	—	49	—
(1.81)	MeCN	313	20	41	—	79	—

a) 0.04—0.05 M. b) Irreversible oxidation potentials of **1** vs. Ag/AgCl in MeCN [Ref. 8d: E_{ox}/V = 1.32 (**1a**), 1.66 (**1b**), 1.88 (**1c**) vs. SCE in MeCN]. c) Effective excitation wavelength. d) Irradiation time. e) In the presence of **3a** (0.01 M). f) Not determined.

Table 2. Photoinduced Electron-Transfer Oxygenation and Autoxidation of **1** with $SbCl_5$, DCA, and AIBN

1[a)]	Additive	Solvent	Temp[b)] °C	Time[c)] h	Conv. %	Yields of products **2**/%	**3**/%	**2**/**3**
1a	$SbCl_5$[d)]	CH_2Cl_2	<-40	3	100	93	3	31
	DCA[e)]	MeCN	20	4	100	19	23	ca. 1
	AIBN[f)]	MeCN	65	20	79	Trace	46	—
1b	$SbCl_5$	CH_2Cl_2	−70	3	100	79	6	13
	DCA	MeCN	20	2	56	Trace	13	—
	AIBN	MeCN	65	20	96	—	84	—
1c	$SbCl_5$	CH_2Cl_2	−70	4	94	86	2	43

a) 0.04—0.05 M. b) Reaction temperature. c) Reaction time. d) 2—9×10^{-4} M. e) 9,10-Dicyanoanthracene (0.001 M). f) 2,2′-Azobisisobutyronitrile (0.005 M).

Table 3. Photolysis of 1,2-Dioxane **2** in Dichloromethane under Oxygen[a)]

2[b)]	E_{ox}[c)] V	Time[d)] h	Conv. %	Yields of products **1**/%	**3**/%
2a	1.67	16	67	—	36
2b	2.11	16	98	3	30
2c	2.44	7	13	Trace	31

a) In a uranium glass tube with a 400-W high-pressure mercury lamp. b) 0.013—0.015 M. c) Irreversible oxidation potentials of **2** vs. Ag/AgCl in MeCN [Ref. 8d: E_{ox}/V = 1.66 (**2a**), >2 (**2b**), >2 (**2c**) vs. SCE in MeCN]. d) Irradiation time.

products were produced along with a trace amount of **1**.

γ-Radiolysis. The γ-radiolysis of a glassy rigid matrix of degassed 1-chlorobutane solutions was carried out in 1.5-mm-thick Suprasil cells cooled in liquid nitrogen at 77 K by a ^{60}Co γ source (dose, 4.5×10^6 Gy). The optical-absorption spectra of the 77 K matrix were measured with a multichannel photodetector (Otsuka Electronics, MCPD-100). An irradiated sample at 77 K was placed in a precooled (77 K) quartz Dewar vessel. After the liquied nitrogen was removed from the vessel, the absorption spectra were measured with the MCPD every 3 s as the temperature of the sample was allowed to warm up to room temperature.

Pulse Radiolysis. The L-band linear accelerator at Osaka University was used as the source of the electron pulse, with an energy value of 28 MeV, a pulse width of 8 ns, and a dose of 0.7 kGy per pulse. The diameter of the electron beam spot on the surface of the cell was ca. 3 mm. A 450-W xenon lamp (Osram, XBO-450) was used as the analyzing light source. The light passing through the sample solution was monitored first by using a monochromator (CVI-Laser, DIGIKROM-240) and then by a photomultiplier (Hamamatsu Photonics, R-1477). The light signal was amplified on a transient digitizer (Tektronix, 7912AD).

Molecular Orbital Calculation. The molecular-orbital calculations were carried out using MOPAC Ver. 6.0[9] and HyperChem Release 4.5 (Hypercube Inc.) installed in an NEC PC-9821Xn and an EPSON VT513R personal computer, respectively. A geometry optimization for neutral olefins **1** and their cation radicals $\mathbf{1}^{\cdot+}$ was performed using the PM3 method. The SCF convergence test was carried out on the total energy using the RHF/PM3 for **1** and the UHF/PM3 for $\mathbf{1}^{\cdot+}$. The convergence criterion was 1×10^{-5} to 1×10^{-7} and the RMS gradient was set at 0.01 kcal Å^{-1} mol^{-1} for the PM3 as the terminal condition for ending the calculation. RHF/PM3 method calculations also were performed to give the charge and spin density, dihedral angle (θ) between the aromatic rings and the ethylene bond for **1** and $\mathbf{1}^{\cdot+}$, the ionization potential (IP), the heat of formation (H), and the bond length (Table 4).

Results and Discussion

Formation of CCT Complexes of 1 with Oxygen. The CCT bands between **1** and oxygen were observed using a 10-cm path length cell in the region from 330 to 390 nm for **1a**, from 315 to 370 nm for **1b**, and from 310 to 350 nm for **1c** (Fig. 1). However, the absorbance of the observed bands was extremely weak (Abs. 0.02—0.03) when a 1-cm path length cell was used to measure their UV spectra.

Solvent effects on the oxygen-organic molecule charge-transfer absorption were examined in detail using 1-methylnaphthalene concerning the transition to a charge-transfer state.[1i] The results are consistent with a ground-state complex that does not have any substantial charge separation, and the absorption shift does not correlate with functions in which the static dielectric constant of the solvent is used. Therefore, it is most likely that a change in solvent influences the stabilization of the charge-transfer state, depending on the dielectric constant.

Irradiation of CCT Complexes of 1 with Oxygen. Effect of Solvent Polarity: Selective irradiation of the CCT bands of **1** with oxygen in CH_2Cl_2, MeCN, and PhH in a uranium glass tube (effective at 366 nm) for **1a** and **1b**, and a Pyrex glass tube (effective at 313 nm) for **1c** using a 400-W high-pressure mercury lamp gave **2** together with **3**, depending on the solvent polarity and substituents on the aromatic rings, as shown in Table 1 and Fig. 2. In contrast, similar irradiation of **1** under an argon atmosphere resulted in no consumption of **1**. It should be noted that during the 2 h irradiation, as shown in Fig. 2, the photoreactions of the CCT complex of **1a** with oxygen proceeded quite slowly regardless of the solvent polarity, where the consumption of **1a** was less than 3%. This is probably because the absorbance of the CCT bands is extremely weak, as pointed out above. However, the reactions accelerated after 2 h of irradiation, probably because some products sensitize the reactions, as discussed below. It is also worth noting that the distribution of **2a** and **3a** depended on the solvent polarity. In PhH (dielectric constant, $\varepsilon = 2.27$ at 25 °C), **3a** was the sole product, while **2a** (57% in 44% conversion) was the major product in CH_2Cl_2 ($\varepsilon = 8.93$), followed by a small amount of **3a** (5%). For MeCN ($\varepsilon = 35.9$), in the initial stage of the reaction (conversion, 3%), no formation of **2a** was observed and **3a** (56%) was the dominant product (Table 1). Interestingly, **2a** was obtained at a yield of 28% in 52% conversion, together with **3a** (16%). These results suggested that the production of **2a** is favored more by moderate polarity CH_2Cl_2 than by high-polarity MeCN, although it was completely suppressed in PhH with low polarity.

On the other hand, the oxidation potentials (E_{ox}) of **1** also affected the formation of **2** and **3**: $E_{ox} = 1.35$ V for **1a**, 1.72 V for **1b**, and 1.81 V for **1c** vs. Ag/AgCl. For **1c**, **3c** was the sole product regardless of the solvents used. For **1b**, however, **2b** was formed in CH_2Cl_2 at a yield of 22% together with **3b** (25%), while only **3b** (40%) was formed in MeCN.

Diaryl Ketone as a Sensitizer for the CCT Complexes: Because the conversion of **1a** and the yields of **2a** and **3a** increased significantly after the CCT complex of **1a** with oxygen was irradiated for 2 h, as shown in Fig. 2, we noted that some of the products could sensitize the reaction. The concentration of **3a** in the reaction mixture after irradiation for 2 h in CH_2Cl_2 was estimated to be approximately 10^{-4} M; therefore, **3a** would absorb a 366-nm light at the concentration shown in Fig. 1a. In fact, when the CCT complex of **1a** with oxygen was irradiated in CH_2Cl_2 in the presence of **3a** (0.01 M) for 2 h under these conditions, the consumption of **1a** increased from 3% to 18%, followed by an increased yield of **2a** (3.2% from 1.4% based on the initial amount of **1a**, Table 1).

Furthermore, the formation of **3b** was monitored at various times (0.5 to 6 h) upon the irradiation of **1b** under oxygen in MeCN and PhH in a uranium glass tube using a high-pressure mercury lamp. It was observed that **3b** was formed more efficiently in MeCN than in PhH. However, during the initial stage of the reaction up to 1.5 h, there was no significant

Table 4. Results of Molecular Orbital Calculation for **1** and $\mathbf{1}^{\cdot+}$ Using PM3 Method

1	$H(\mathbf{1})^{a)}$	$H(\mathbf{1}^{\cdot+})^{b)}$	$\Delta H^{c)}$	$I_p^{d)}$	$\theta_{1\text{-}2\text{-}3\text{-}4}^{e,f)}$	Bond length/Å$^{f)}$		Charge density$^{f)}$		Spin density$^{f,g)}$	
					$\mathbf{1}/\mathbf{1}^{\cdot+}$	C1–C2 $\mathbf{1}/\mathbf{1}^{\cdot+}$	C2–C3 $\mathbf{1}/\mathbf{1}^{\cdot+}$	C1 $\mathbf{1}/\mathbf{1}^{\cdot+}$	C2 $\mathbf{1}/\mathbf{1}^{\cdot+}$	C1	C2
1a	−10.92	179.18	190.10	8.71	48.9/24.0	1.34/1.41	1.47/1.43	−0.157/−0.037	−0.011/0.186	0.877	−0.184
1b	46.44	233.40	186.96	8.93	49.2/24.4	1.34/1.41	1.47/1.43	−0.151/−0.008	−0.021/0.191	0.845	−0.128
1c	65.66	256.81	191.15	9.14	50.8/24.7	1.34/1.41	1.47/1.44	−0.147/0.008	−0.026/0.198	0.830	−0.093

a) Heat of formation of **1** (kcal mol^{-1}). b) Heat of formation of $\mathbf{1}^{\cdot+}$ (kcal mol^{-1}). c) ΔH(kcal mol^{-1})$=H(\mathbf{1}^{\cdot+})-H(\mathbf{1})$. d) Ionization potential of **1** (eV). e) Dihedral angle of C1–C2–C3–C4. f) See Eq. 4 with regard to numbering. g) Spin density for $\mathbf{1}^{\cdot+}$.

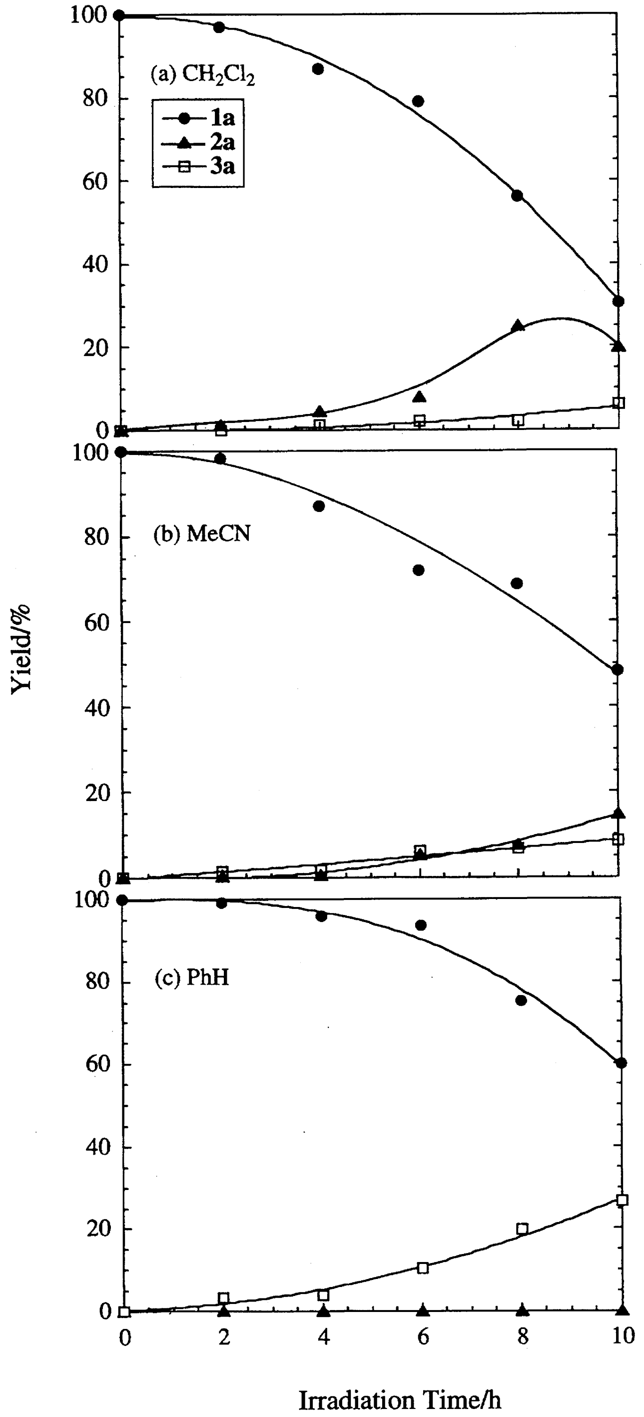


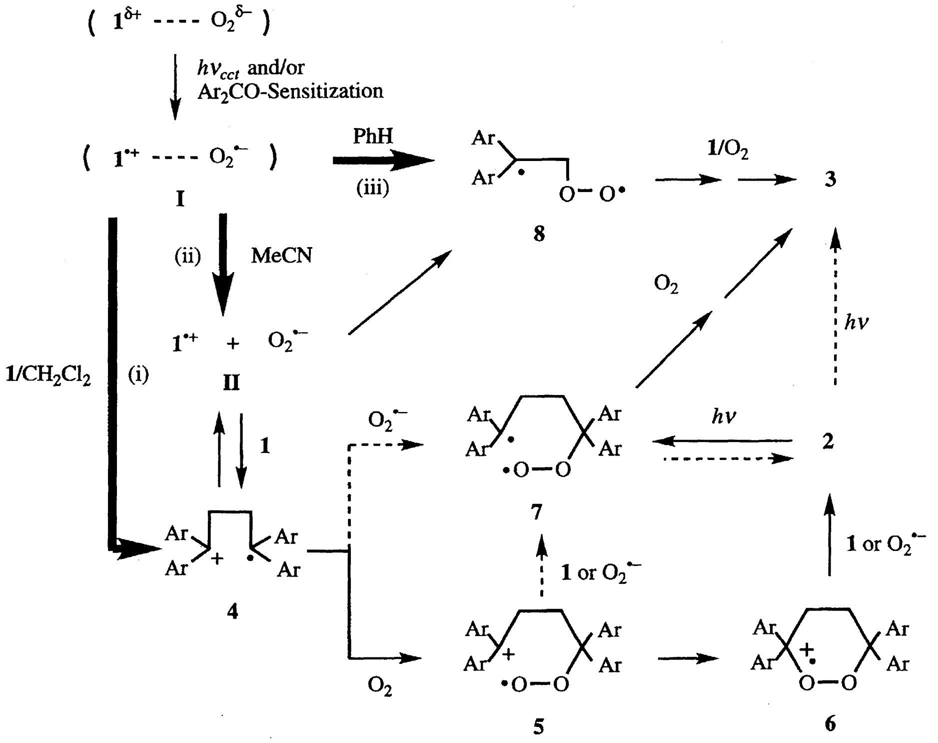
Fig. 2. Yields of 1,2-dioxane **2a** (▲) and bis(*p*-methoxyphenyl) ketone **3a** (□) produced by excitation of the CCT band between **1a** (●) and oxygen vs. irradiation time: (a) in CH_2Cl_2, (b) in MeCN, and (3) in PhH.

difference in the yield of **3b** in the two solvents. In addition, it seemed that there was an induction period for the formation of **3b** in either solvent, as can be observed for **1a** in Fig. 2. When **1b** was irradiated in the presence of a small, known amount of **3b** under the conditions mentioned above, the yield of **3b** increased approximately twofold. These results clearly indicate that diaryl ketones can play the role of sensitizers in the photochemical reaction of the CCT complexes of **1** with oxygen.

Effect of Excitation Wavelength: The distribution of **2** and **3** produced by the irradiation of **1** in CH_2Cl_2 under oxygen was considerably affected by the excitation wavelength (Table 1). When a solution in a quartz tube was irradiated using a 160-W low-pressure mercury lamp (effective excitation wavelength, 254 nm), the ratio of **2/3** was approximately 0.41 for **1a** and 0.36 for **1b**, respectively. However, the irradiation of a solution in a uranium glass tube with a 400-W high-pressure mercury lamp (effective at 366 nm) gave **2** at higher yield than the above reaction: **2**/**3** = 11.4 and 0.88 for **1a** and **1b**, respectively. For **1c**, however, there was no significant change in product formation due to the excitation wavelength; **3c** was the sole product upon the irradiation of **1c** by 254- and 313-nm lights under similar conditions to those used for **1a** and **1b**.

Effects of Lewis Acid, Electron Accepting Sensitizer, and Radical Initiator: It has been reported that the photooxygenation of 1,1-diarylethenes in the presence of a Lewis acid⁶⁾ ($SbCl_5$) and electron acceptors, such as DCA, tetracyanoanthracene, and acridinium ion,$^{7,8,10)}$ results in the formation of **2** at high yields due to electron-transfer reactions that generate cation radicals of the olefins as intermediates. As shown in Table 2, the irradiation of **1** in CH_2Cl_2 with $SbCl_5$ under oxygen at −40 to −70 °C yielded **2** (79—93%) with a high product selectivity, independent of E_{ox} of **1**. DCA-sensitized photooxygenation of **1a**,**b** at 20 °C in MeCN formed **2a**,**b** at lower yields (<20%) than those reported, as well as **3a**,**b** (13—23%),⁸⁾ which is probably because **2** is unstable under the reaction conditions we employed. On the other hand, the autoxidation of **1a**,**b** in MeCN at 65 °C under oxygen, with 2,2′-azobisisobutyronitrile (AIBN) as an initiator, gave **3a**,**b** at 46—86% yield and trace amounts of **2a**,**b**. These results clearly show that **2** is a characteristic product of the electron-transfer reaction of **1**, whereas **3** is produced mainly through the autoxidation of **1**, although another route through electron-transfer oxygenation cannot be ruled out.

Production of diaryl ketones 3 through Photolysis of 1,2-Dioxanes 2. When **2** (E_{ox} = 1.67 V for **2a**; 2.11 V for **2b**; 2.44 V for **2c** vs. Ag/AgCl) was irradiated in CH_2Cl_2 under oxygen in a uranium glass tube, **3** was yielded as a major product according to a GC analysis (31—36%), although not quantitatively, together with a small amount of olefin **1b** for **2b** (Table 3). A similar irradiation of **2** under nitrogen yielded a different product distribution than that obtained under oxygen. The detailed mechanism for the photolysis of **2** had not been investigated when we published a previous paper,⁵⁾ in which we suggested that it was unlikely that bond fission in the photolysis proceeded through a single reaction channel. Recently, Kamata et al. reported on the mechanism for the photolysis of **2a** under nitrogen.¹¹⁾ According to their results, the photolysis of **2a** under nitrogen gives 1,4,4-tris-(4-methoxyphenyl)-3-buten-1-one and 4-methoxyphenol as dominant products through a C–O bond cleaved 1,6-diradical intermediate **7** from the excited triplet **2a**, together with ca. 10% of **3a** from the excited singlet **2a** (See Scheme 1).



Scheme 1.

In our experiment, however, the above two products were not observed in photolysis under oxygen. Therefore, some proportion of **3** observed in the photoreaction of the CCT complexes can be explained as being a secondary product of the photolysis of **2**. However, the remaining quantity of **3** must be produced by another route, probably by an autoxidation mechanism initiated by neutral radical species, generated by a reaction between $\mathbf{1}^{\bullet+}$ and $O_2{}^{\bullet-}$.

Mechanism. As shown in Scheme 1, the selective excitation of the CCT bands between **1** and oxygen results in one electron transfer from the olefins to oxygen to generate a contact ion radical pair of the monomer cation radical $\mathbf{1}^{\bullet+}$ with $O_2{}^{\bullet-}$ in a solvent cage (Intermediate **I**). As can be seen in Table 1, the formation of **2** prefers CH_2Cl_2 to MeCN as a solvent. This suggests that medium polar solvents are more favorable for the production of a dimer cation radical of **1** than high polar solvents. This is probably because the return electron transfer rates in the contact ion radical pair **I** could be decreased in the medium polar solvent and the concentration of $\mathbf{1}^{\bullet+}$ could increase, similar to the efficient formation of a separated biphenyl cation radical in less polar solvents than MeCN using *N*-methylacridium salts as electron-accepting sensitizers.[12] It is also likely that for CH_2Cl_2 the ion radical pair **I** reacts with another **1** to directly generate an open chain 1,4-dimer cation radical **4** (Path i), which finally collapses to **2** through intermediates **5** and **6**, dimer cation radicals trapped by O_2. On the other hand, for MeCN the solvated $\mathbf{1}^{\bullet+}$ (Intermediate **II**) reacts with **1** and $O_2{}^{\bullet-}$ to form **4** and neutral radical species **8**, respectively (Path ii). The radical **8** could initiate autoxidation to finally produce **3**.[2f,13] In PhH, the CCT complex of **1** with O_2 is also formed and excitation of the CCT band may generate initially the contact ion radical pair **I**, similar to the cases of CH_2Cl_2 and MeCN. However, separation of the ion radical pair does not occur because of the low polarity of the solvent. Therefore, the combination between $\mathbf{1}^{\bullet+}$ and $O_2{}^{\bullet-}$ might occur to produce radical **8**, which probably causes autoxidation of **1** to finally give **3** (Path iii). Although 3,3-diaryl-1,2-dioxetane might be a plausible precursor to the production of **3**,[14] no evidence for the intervention of the dioxetane was obtained.

The direct excitation of **1a** and **1b** in CH_2Cl_2 under oxygen using a 254-nm light decreased the yield of **2a,b** to less than 10%, followed by the formation of **3a,b** at 20—25%; by contrast, the excitation wavelength had no significant effect on products for **1c** (Table 1). The low-pressure mercury lamp used for the irradiation can also give a 366-nm light with considerably lower intensity compared to the 254-nm light. Therefore, these results indicate that the photoinduced electron transfer is caused by excitation of the CCT band of **1** with O_2, and not by locally excited **1** and O_2. However, we cannot exclude the possibility that **2** photodecomposed by the 254-nm light to partially produce **3** under oxygen, as described above.

On the other hand, efficient electron-transfer oxygenation of olefins catalyzed by the Lewis acid at low temperature has been reported.[6,15] This is probably because the olefin cation radicals are stabilized by lowering the temperature, and have a longer lifetime than at room temperature. However, the irradiation of CCT complexes between **1** and O_2 in CH_2Cl_2 and MeCN at −40 to −70 °C gave no observable products. Thus, it is likely that there is a thermally activated process involved in the photoinduced electron-transfer reaction of the CCT complexes.

Finally, it is likely that excited triplet **3a** sensitizes **1a** to give excited triplet **1a**, which would react with another **1** to produce a 1,4-dimer biradical intermediate. The 1,4-biradical could further react with O_2 to form **7**, which would finally yield **3a** under oxygen. However, **2a** is a characteristic product through a dimer cation radical of **1**. Thus, energy transfer might also occur between the excited triplet **3a** and the CCT complex.

Observation of Monomer and Dimer Cation Radicals of 1. The transient absorption spectra recorded by γ-irradiation of 1-chlorobutane glass containing **1** (10 mM) at 77 K are shown in Fig. 3, where remarkable changes in the absorption spectra were observed along with an increase in the temperature. At low temperature, approximately 77 K, one expects to observe $\mathbf{1}^{\bullet+}$ initially in the glass matrix. Along with an increase in the temperature, dimer cation radicals of **1** should be produced by the reaction of $\mathbf{1}^{\bullet+}$ with **1** as the flexibility in the matrix increases. For **1a**, initial absorption bands around 330, 390, and 580 nm were attributable to its monomer cation radical ($\mathbf{1a}^{\bullet+}$), which decays with the simultaneous formation of new absorption bands at around 350 and 500 nm, probably attributable to the dimer cation radical of **1a** (Fig. 3a). Similar spectral changes were also observed for **1b**. In Fig. 3b, the absorption bands at 315, 385, and 560 nm were assigned to a monomer cation radical of **1b** ($\mathbf{1b}^{\bullet+}$), whereas the absorption bands at 340 and 460 nm were attributed to a dimer cation radical of **1b**. The assignment for monomer and dimer cation radicals of **1a** and **1b** described above is similar to that for styrenes.[16—18] As reported by Hayashi et al.,[19] the monomer cation radical of **1c** ($\mathbf{1c}^{\bullet+}$) has absorption bands similar to those of its dimer cation radical, particularly, in the wavelength region given in Fig. 3c. Therefore, no disappearance of the bands for $\mathbf{1c}^{\bullet+}$ was observed, in contrast to the cases of **1a** and **1b**. However, the figure also shows that the formation of the dimer cation radical of **1c** resulted in an increase in the absorption band at around 330, 390, 430, and 525 nm.

The transient-absorption spectra measured by pulse radiolysis of **1** (2 mM or 10 mM) in 1-chlorobutane under argon at room temperature are shown in Fig. 4.[20] Two main absorption bands were observed: $\lambda_{\text{max}} = 330$—350 nm and 390—490 nm. The absorption bands, centering around 330—350 nm, increased in intensity with time after pulse irradiation. However, other bands with λ_{max} around 390—490 nm exhibited different spectral changes. For **1a**, the 490-nm band increased in intensity with time after pulse irradiation similar to the 350-nm band (Fig. 4a). For **1b**, the intensity of the 400-nm band increased with time until 80 ns after irradiation and then decreased.[10] In the case of **1c**, the 390-nm band gradually decreased in intensity with time.

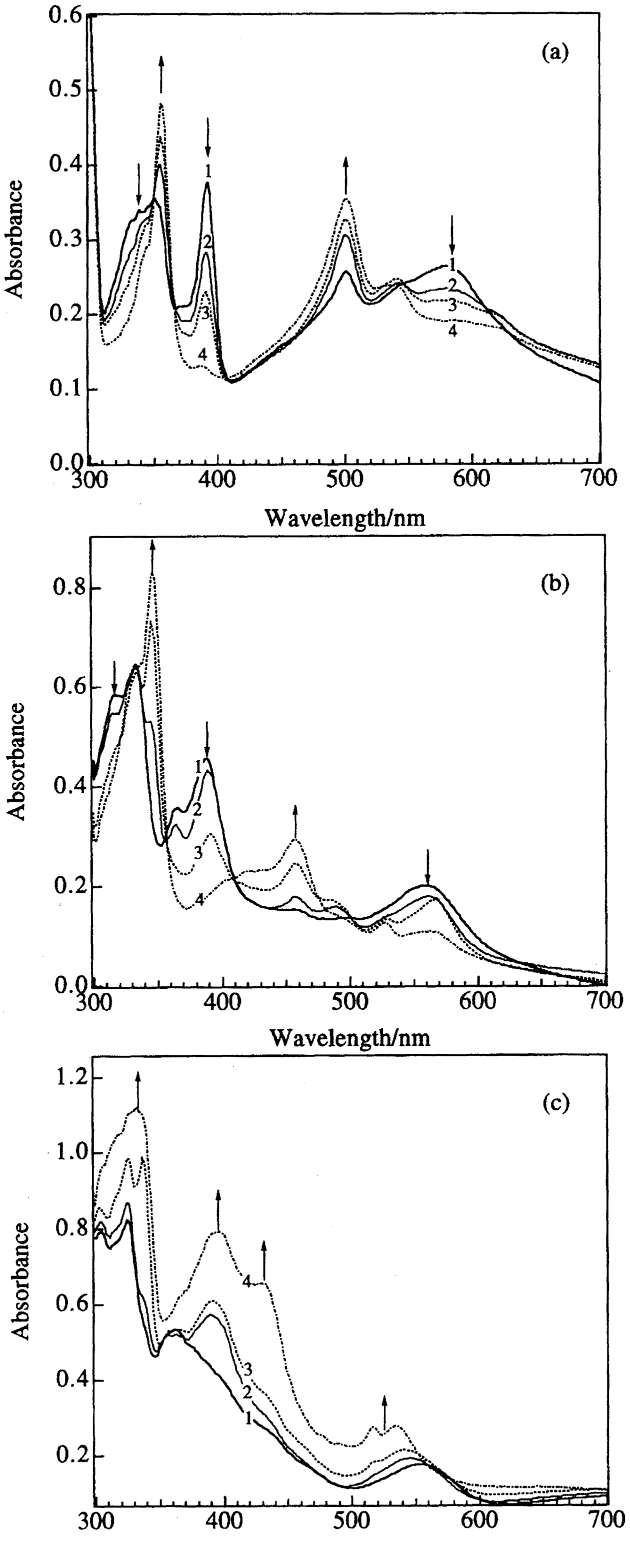


Fig. 3. Absorption spectra of γ-irradiated 1-chlorobutane glasses containing **1** (10 mM) at 77 K: (a) **1a**, (b) **1b**, and (c) **1c**; 1 at 77 K and 2—4 in warming.

Based on the spectra changes observed by the γ-irradiation of **1**, the absorption spectra obtained by pulse radiolysis of **1** in 1-chlorobutane under argon at room temperature can be attributed to dimer cation radicals of **1**. Moreover, we also noted that the transient absorption spectra shown in Fig. 4 are quite similar to those of 1,ω-bis(diarylvinyl)alkane cation radicals, the structure of which is considered to be almost identical with that of the dimer cation radical **4**.[21] However, we cannot rule out the possibility that 330—350 and 390—490 nm transients observed by the pulse radiolysis might be different species, because they show different decays. The

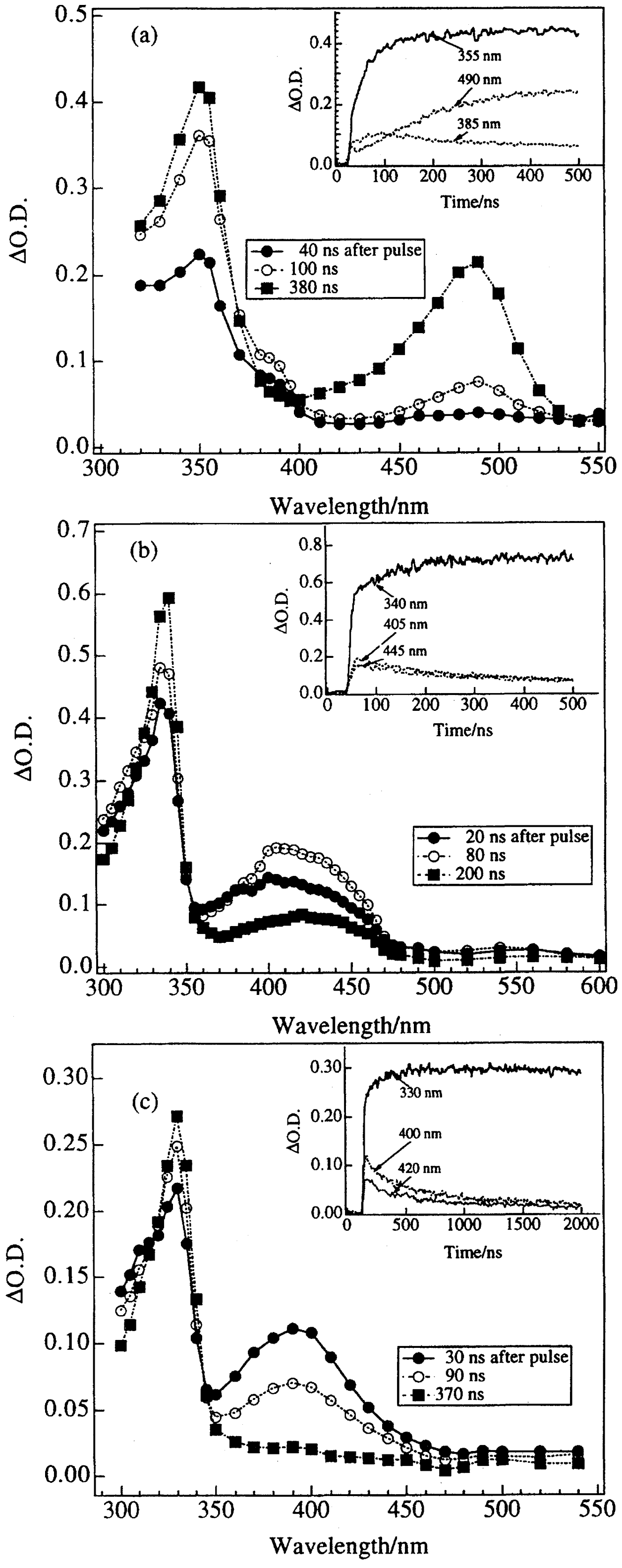


Fig. 4. Transient absorption spectra recorded at various times after an 8-ns pulse irradiation of 1-chlorobutane solutions of **1** under argon at room temperature: (a) 2 mM **1a**, (b) 10 mM **1b**, and (c) 10 mM **1c**.

increase in the intensity of 330—350 nm band transients may be explained by the formation of neutral benzyl-type radicals, through the addition of nucleophiles like chloride ion to $\mathbf{1}^{\bullet +}$.[22] In addition, the differences in the spectral changes in the 390—490 nm bands, shown in Fig. 4, probably indicate differences in the lifetime (namely, stability) of the dimer cation radicals of **1**.

Quenching of Transient Absorption Bands by Oxygen. Transient-absorption spectra were measured at various times after the pulse irradiation of 1-chlorobutane solutions of **1** (10 mM) under oxygen at room temperature, as shown in Fig. 5. For **1a**, the 350-nm band was quenched at a rate constant (k_r) of approximately 9×10^8 M^{-1} s^{-1}, whereas the 490-nm band shifted to around 500 nm with time after pulse irradiation, similar to the transient-absorption spectra observed in the laser flash photolysis of **1a** in aerated MeCN containing *N*-methylacridinium perchlorate.[10] The decay curves in Fig. 5a show the simultaneous formation of a new band with $\lambda_{\max}$ at around 505 nm along with a decrease in the 350 and 480-nm bands. For **1b**, as shown in Fig. 5b, the 340, 385, and 430-nm bands were quenched by oxygen (k_r = ca. 6×10^8 M^{-1} s^{-1} at 340 nm); in addition, similar to the case of **1a**, we observed a new absorption band around 465 nm. In contrast to the above cases, for **1c** the initial absorption bands found at around 330 and 390 nm were quenched by oxygen (k_r = ca. 3×10^8 M^{-1} s^{-1} at 330 nm), and no new absorption bands were observed after pulse irradiation.

Pulse Radiolysis of 1,2-Dioxane 2a. The pulse radiolysis of **2a** (5 mM) was also performed in 1-chlorobutane under argon at room temperature to give the transient absorption spectra shown in Fig. 6. It should be noted that the observed spectra closely resemble the spectrum generated at 365 ns after the pulse irradiation of **1a** under oxygen in Fig. 5a. However, the pulse radiolysis of **3a** (10 mM) under similar conditions produced a transient-absorption band with a $\lambda_{\max}$ of around 400 nm.

New Transient Absorption Band under Oxygen. Because all the olefins used showed the formation of dimer cation radicals, as can be seen in Figs. 3 and 4, at room temperature, quenching of their absorption bands by O_2 probably indicates reaction of the dimer cation radical **4** with O_2 to generate **5**, followed by 1,6-cyclization to give 1,2-dioxane cation radical **6** (See Scheme 1). The resultant **6** is reduced to **2** by **1** or $O_2^{\bullet -}$. However, the 1,6-cyclization of **5** to produce **6** must compete with the reduction process of **5** by **1** or $O_2^{\bullet -}$ to generate **7**, which may initiate autoxidation of **1** or decompose under oxygen to finally yield **3**. As described above, the absorption spectra obtained by the pulse radiolysis of **2a**, but not **3a**, are nearly identical to the spectrum generated at 365 ns after pulse irradiation of **1a** under oxygen; therefore, the new absorption bands observed by the pulse radiolysis of **1a** and **1b** under oxygen are probably attributable to **5** or **6**.

Difference in Reactivities of Monomer and Dimer Cation Radicals. As can be seen in Fig. 5, dimer cation radicals of **1** have remarkably different reactivities with O_2, depending on the substituents on the benzene rings. In order to explain these differences in the reactivities, semi-empir-

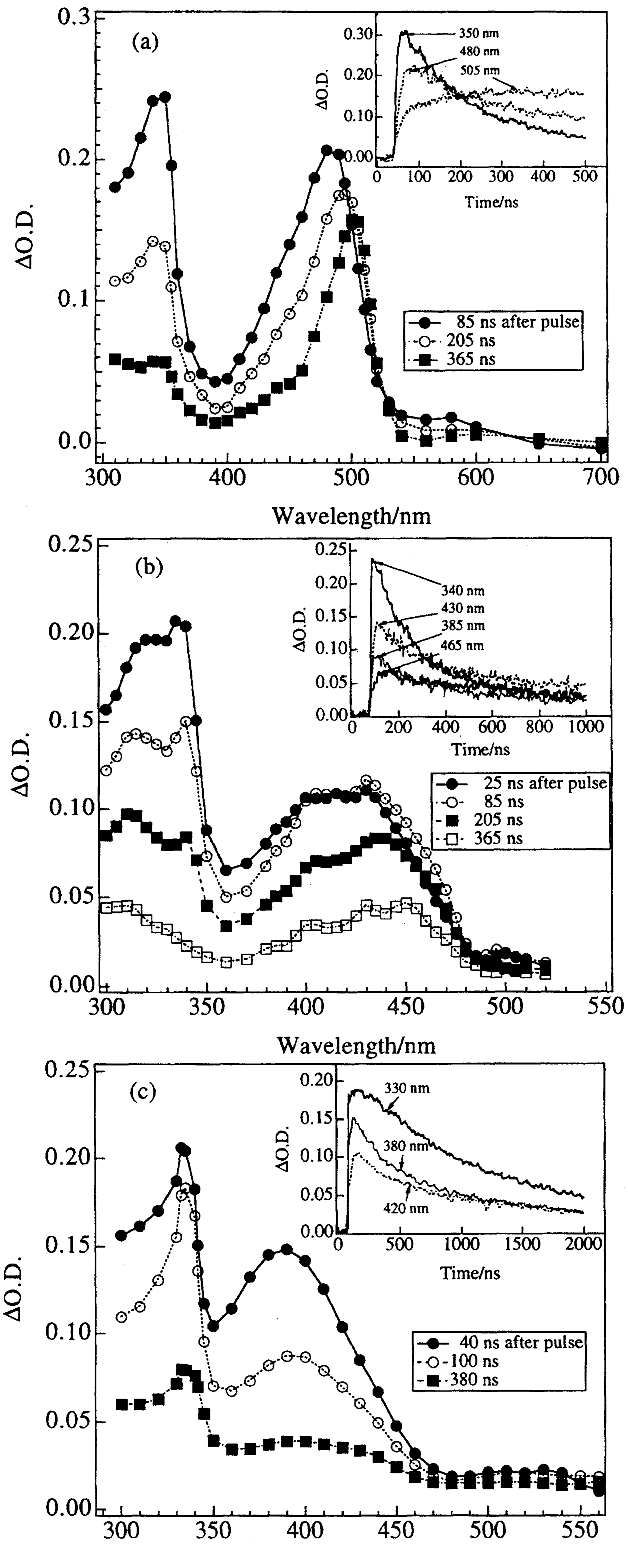


Fig. 5. Transient absorption spectra observed at various times after an 8-ns pulse irradiation of 1-chlorobutane solutions of **1** (10 mM) under oxygen at room temperature: (a) **1a**, (b) **1b**, and (c) **1c**.

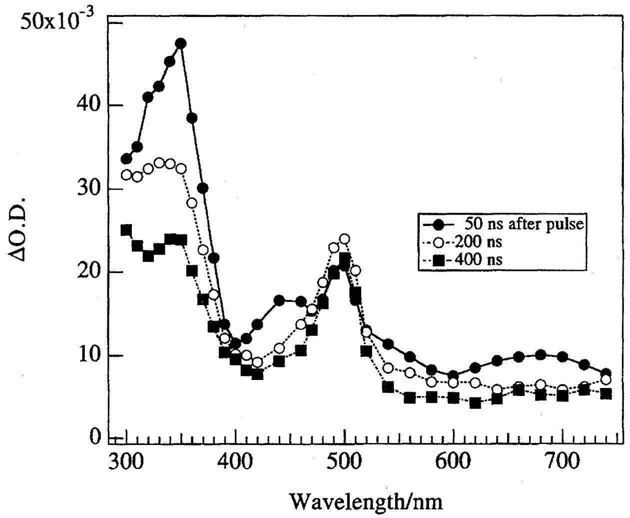
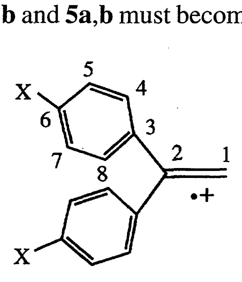


Fig. 6. Transient absorption spectra produced by pulse irradiation of **2a** (5 mM) in 1-chlorobutane under argon at room temperature.

ical molecular orbital calculation for **1** and $\mathbf{1}^{\bullet +}$ was carried out using the PM3 method (Table 4). On the basis of these results, it appears that the introduction of electron-donating groups (MeO and Me) on the benzene rings of $\mathbf{1c}^{\bullet +}$ affects the distribution of the charge and spin density. In particular, at the C1 and C2 positions of $\mathbf{1}^{\bullet +}$ (see Eq. 4), the charge density increases in the order $\mathbf{1a}^{\bullet +} < \mathbf{1b}^{\bullet +} < \mathbf{1c}^{\bullet +}$, whereas the spin density decreases in the order $\mathbf{1a}^{\bullet +} > \mathbf{1b}^{\bullet +} > \mathbf{1c}^{\bullet +}$. These changes are probably due to resonance between aromatic rings and an ethenyl group;[23] in fact, the dihedral angle of C1–C2–C3–C4 for $\mathbf{1}^{\bullet +}$ becomes smaller than that of **1** by ca. 25°, and also the bond length of C2–C3 for $\mathbf{1}^{\bullet +}$ becomes shorter than that of **1**, 1.43 and 1.47 Å, respectively. Therefore, it is likely that the change in the spin density of the diarylmethylcarbons of **4**, similar to the case of $\mathbf{1}^{\bullet +}$, occurs due to the introduction of substituents, which determines the reactivities of **4** with O_2. Furthermore, the substituents would affect the stabilities of **4** and **5** by resonance; namely, the lifetimes of **4a,b** and **5a,b** must become longer compared to **4c** and **5c**.



X= OMe, Me, H (4)

Conclusion

The selective excitation of the CCT complexes of some styrenes and 1,1-diarylethenes with O_2 gives dimeric products through an electron-transfer reaction from the olefins to O_2 to generate the olefin cation radicals and $O_2^{\bullet -}$, but not in the case of 1-arylcyclohexenes, as shown in Eq. 1 to Eq. 3. Based on our recent study of the ring-size dependent dimerization of 1-arylcycloalkene cation radicals,[24)] it can be concluded that the photoproducts of the CCT complexes are probably determined by the solvent polarity, the reactivities of the olefin cation radicals dependent on their structure,[24)] the charge and spin density,[21a,23)] the steric repulsion among aromatic rings,[7)] and the initial concentration of the olefins.[25)] This is also the case for aromatic olefin cation radicals generated by electron-transfer sensitized reactions.[4)]

References

1) a) H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960); b) M. Tamres and R. L. Strong, "Molecular Association," ed by R. Foster, Academic Press, London (1979), Vol. 2, p. 397; c) D. F. Evans, *J. Chem. Soc.*, **1953**, 345; d) V. I. Stenberg, R. D. Olson, C. T. Wang, and N. Kulevsky, *J. Org. Chem.*, **32**, 3227 (1967); e) K. S. Wei and A. H. Adelman, *Tetrahedron Lett.*, **1969**, 3297; f) J. C. W. Chien, *J. Phys. Chem.*, **69**, 4317 (1965); g) V. I. Sternberg, C. T. Wang, and N. Kulevsky, *J. Org. Chem.*, **35**, 1774 (1970); h) S. L. Logunov and M. A. J. Rodgers, *J. Phys. Chem.*, **97**, 5643 (1993); i) Y. Kuriyama, P. R. Ogilby, and K. V. Mikkelsen, *J. Phys. Chem.*, **98**, 11918 (1994).

2) a) K. Onodera, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **21**, 2831 (1980); b) M. Kojima, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **22**, 2889 (1981); c) M. Kojima, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **62**, 3863 (1989); d) H. Sakuragi, G. Furusawa, K. Ueno, and K. Tokumaru, *Chem. Lett.*, **1982**, 1213; e) K. Onodera, G. Furusawa, M. Kojima, M. Tsuchiya, S. Aihara, R. Akaba, H. Sakuragi, and K. Tokumaru, *Tetrahedron*, **41**, 2215 (1985); f) M. Kojima, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **60**, 3331 (1987).

3) "Singlet Oxygen," ed by H. H. Wasserman and R. W. Murray, Academic Press, New York (1979).

4) K. Mizumo and Y. Otsuji, "Topics in Current Chemistry," ed by J. Mattay, Springer-Verlag, Berlin (1994), Vol. 169, pp. 301—346.

5) M. Kojima, A. Ishida, and S. Takamuku, *Chem. Lett.*, **1993**, 979.

6) R. K. Haynes, M. K. S. Probert, and I. D. Wilmot, *Aust. J. Chem.*, **31**, 1737 (1978).

7) S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, **108**, 7356 (1986).

8) a) K. Gollnick and A. Schnatterer, *Tetrahedron Lett.*, **25**, 185 (1984); b) K. Gollnick and A. Schnatterer, *Tetrahedron Lett.*, **25**, 2735 (1984); c) K. Gollonick and S. Held, *J. Photochem. Photobiol. A: Chem.*, **59**, 55 (1991); d) K. Gollnick, A. Schnatterer, and G. Utschick, *J. Org. Chem.*, **58**, 6049 (1993).

9) J. J. P. Stewart, *QCPE Bull.*, **1989**, 9 and 10.

10) M. Fujita, A. Shindo, A. Ishida, T. Majima, S. Takamuku, and S. Fukuzumi, *Bull. Chem. Soc. Jpn.*, **69**, 743 (1996).

11) M. Kamata, T. Tanaka, and M. Kato, *Tetrahedron Lett.*, **37**, 8181 (1996).

12) W. P. Todd, J. P. Dinnocenzo, S. Farid, J. L. Goodman, and I. R. Gould, *J. Am. Chem. Soc.*, **113**, 3601 (1991).

13) K. Kanno, M. Hisaoka, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **54**, 2330 (1981).

14) a) W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and G. Ranney, *J. Am. Chem. Soc.*, **96**, 4045 (1974); b) W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and H. E. O'Neal, *J. Am. Chem. Soc.*, **96**, 7525 (1974).

15) a) S. F. Nelsen, *Acc. Chem. Res.*, **20**, 269 (1987); b) S. F. Nelsen, D. L. Kapp, and M. F. Teasley, *J. Org. Chem.*, **49**, 579 (1984).

16) a) S. Tojo, S. Toki, and S. Takamuku, *Radiat.Phys. Chem.*, **40**, 95 (1992); b) S. Tojo, S. Toki, and S. Takamuku, *J. Org. Chem.*, **56**, 6240 (1991).

17) a) S. Egusa, Y. Tabata, A. Kira, and M. Imamura, *J. Polym. Sci.*, **16**, 729 (1978); b) S. Egusa, S. Arai, A. Kira, M. Imamura, and Y. Tabata, *Radiat. Phys. Chem.*, **9**, 419 (1977).

18) M. Irie, H. Masuhara, K. Hayashi, and N. Mataga, *J. Phys. Chem.*, **78**, 341 (1974).

19) K. Hayashi, M. Irie, D. Lindenau, and W. Schnabel, *Radiat. Phys. Chem.*, **11**, 139 (1978).

20) The transient absorption spectra were affected by initial concentration of **1**. A weak absorption band at around 390 nm attributable to $\mathbf{1a}^{\cdot +}$ was observed for a 2 mM solution of **1a**, but not for a 10 mM solution.

21) a) K. Mizuno, T. Tamai, I. Hashida, Y. Otsuji, Y. Kuriyama, and K. Tokumaru, *J. Org. Chem.*, **59**, 7329 (1994); b) T. Tamai, K. Mizuno, I. Hashida, Y.Otsuji, A. Ishida, and S. Takamuku, *Chem. Lett.*, **1994**, 149.

22) J. Bartl, S. Steenken, H. Mayr, and R. A. McClelland, *J. Am. Chem. Soc.*, **112**, 6918 (1990).

23) a) D. R. Arnold, X. Du, and J. Chen, *Can. J. Chem.*, **73**, 307 (1995); b) D. R. Arnold, X. Du, and K. M. Henseleit, *Can. J. Chem.*, **69**, 839 (1991).

24) M. Kojima, A. Kakehi, A. Ishida, and S. Takamuku, *J. Am. Chem. Soc.*, **118**, 2612 (1996).

25) L. J. Johnston and N. J. Schepp, *J. Am. Chem. Soc.*, **115**, 6564 (1993).