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Mechanism of Photochemical Reaction of Contact Charge Transfer Pair between 1,1-Diarylethene and Oxygen

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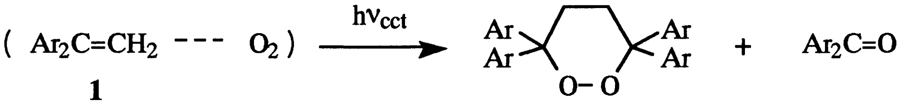
Selective excitation of the contact charge transfer band between 1,1-diarylethene and oxygen in dichloromethane and acetonitrile gave 3,3,6,6-tetraaryl-1,2-dioxane and benzophenone derivative through an electron transfer reaction. The proposed mechanism was confirmed by the direct observation of the dimer cation radical of the olefin trapped by a triplet oxygen in pulse radiolysis.

Electron-transfer photooxygenation[1] of aromatic olefins in the presence of electron acceptors such as cyanoaromatics,[2] Lewis acids,[3] and dyes[4] has been widely investigated until now. However, there are a few mechanistic studies on photochemical reaction of the contact charge transfer (CCT) pairs of aromatic olefins with oxygen.[5] Furthermore, it has not been clarified whether the cation radicals of aromatic olefins generated in the electron-transfer oxygenation react with a triplet oxygen (O_2) or a superoxide anion radical ($O_2^{-\bullet}$). Recently, cyanoaromatics-sensitized oxygenation of 1,1-diarylethene (**1**) was proposed to proceed through the reaction between the dimer cation radical of **1** and a triplet oxygen molecule based on the measurement of quantum yields, finally forming 3,3,6,6-tetraaryl-1,2-dioxane (**2**) as a predominant product together with a small amount of benzophenone derivatives (**3**).[2a,b] We now report here that the excitation of the CCT band of **1** with oxygen affords **2** and **3** through an electron transfer from **1** to oxygen and that the dimer cation radical of **1** trapped by a triplet oxygen is directly observed in time-resolved spectroscopy.



(1)

1 **2** **3**

1a: Ar= 4-$MeOC_6H_4$; **1b**: Ar= 4-MeC_6H_4; **1c**: Ar= C_6H_5

Selective irradiation of the CCT band (320-380 nm) of 1,1-diarylethenes (0.05 M; M= mol/dm^3, **1a**: Ar= 4-$MeOC_6H_4$; **1b**: Ar= 4-MeC_6H_4; **1c**: Ar= C_6H_5) with oxygen in CH_2Cl_2 through a uranium glass (effective at 366 nm) using a 400-W high pressure mercury lamp gave **2** and **3** as shown in Eq. 1 and Table 1. By contrast, similar irradiation of **1** under argon did not cause any consumption of **1** and gave no product. Distribution of products **2** and **3** depends on the polarity of solvent and on the oxidation potential (Eox) of **1**: in PhH **3** was a sole product regardless of the oxidation potentials. In CH_2Cl_2, however, **1a** and **1b** with electron

Table 1. Product Distribution Resulting from Excitation of the CCT Band between **1** and Oxygen

1$^{a)}$	Solvent	λ/nm$^{c)}$	Conv.	Yields of Products	
(Eox/V)$^{b)}$			/%	**2**/%	**3**/%
1a	CH_2Cl_2	366	93	67	13
(1.35)	CH_2Cl_2	254	61	9	22
	MeCN	366	100	34	30
	PhH	366	100	trace	87
1b	CH_2Cl_2	366	87	22	25
(1.72)	CH_2Cl_2	254	44	9	25
	MeCN	366	95	-	40
	PhH	366	36	-	59
1c	CH_2Cl_2	313	45	-	55
(1.81)	CH_2Cl_2	254	18	-	49
	MeCN	313	41	-	79

a) [**1**] = 0.04 - 0.05 M. b) Oxidation potential vs. Ag/AgCl in MeCN.
c) Effective excitation wavelength.

donating groups on their benzene rings gave **2a** (yield, 67%) and **2b** (22%), together with **3a** (13%) and **3b** (25%), respectively. In MeCN, production of **2a** decreased to 34% yield, followed by **3a** at similar yield, while **3b** was only observed in the case of **1b**. Olefin **1c** without the electron donating group afforded **3c** (55 - 79%), but did not yield **2c** in any solvent used.

The mechanism for production of **2** and **3** has now been elucidated as shown in Scheme 1. Excitation of the CCT band between **1** and oxygen results in one electron transfer from **1** to oxygen to generate the monomer cation radicals of **1** ($\mathbf{1}^{+\bullet}$) and $O_2^{-\bullet}$. The monomer cation radical reacts with another neutral **1** to give the open chain 1,4-dimer cation radical of **1** (**4**), which finally collapses to **2** through the intermediate **5** trapped by O_2. This scheme is supported by the results described below: first of all, selective excitation of **1a** and **1b** in CH_2Cl_2 under oxygen with a low pressure mercury lamp (effective at 254 nm) decreased the yields of **2** less than 10% (Table 1), followed by the formation of benzophenones **3** at 22 - 25% yield, in contrast to the case of **1c**. Secondly, it has been reported that photooxygenation of 1,1-diarylethenes in the presence of Lewis acid$^{3b)}$ and electron acceptors like 9,10-dicyanoanthracenes$^{2)}$ gave **2** at high yields through an electron transfer reaction to generate the cation radicals of the olefins as intermediates. In addition, autoxidation of **1** in MeCN with azobisisobutyronitrile as an initiator under oxygen gave **3** at 50 - 90% yield, accompanied by a trace amount of **2**. These results show that **2** is a characteristic product through an electron transfer reaction, suggesting that the significant electron transfer is caused by excitation of the CCT band of **1** with O_2. Thirdly, when 1,2-dioxanes (0.013 - 0.015 M: **2a**, Eox = 1.67 V; **2b**, 2.11 V vs. Ag/AgCl) were irradiated in CH_2Cl_2 under oxygen in a uranium glass tube with the high pressure mercury lamp, **3a** or **3b** (36% and 28%, respectively) was observed as a detectable major product on GLC analysis, together with a small amount of **1b** in the case of **2b**.6) However, there was no induction period for formation of **3b** in the photochemical reaction of the CCT pair of **1b** with oxygen both in MeCN and PhH. Therefore, autoxidation of **1** to produce 3 is considered to be involved in addition to a direct photolysis of **2** into **3**. As shown in Scheme 1, autoxidation of **1** would be initiated by some neutral radical species such as **6** and **7** generated from $\mathbf{1}^{+\bullet}$ and **4** with $O_2^{-\bullet}$, finally to give **3**, through chain processes similar to those reported already.7) Although 3,3-diaryl-1,2-dioxetane might be the other candidate to afford **3**, there is no evidence for intervention of the dioxetane in spite of careful analysis of the irradiated samples in terms of HPLC. Furthermore, the transient absorption spectra of the cation radical of **1** were measured at various delay times after an 8-ns electron pulse irradiation of **1** (2 mM) in butyl chloride (BuCl) at room temperature under argon.8,9) In the case of **1a**, a weak absorption band of $\mathbf{1a}^{+\bullet}$ was observed around

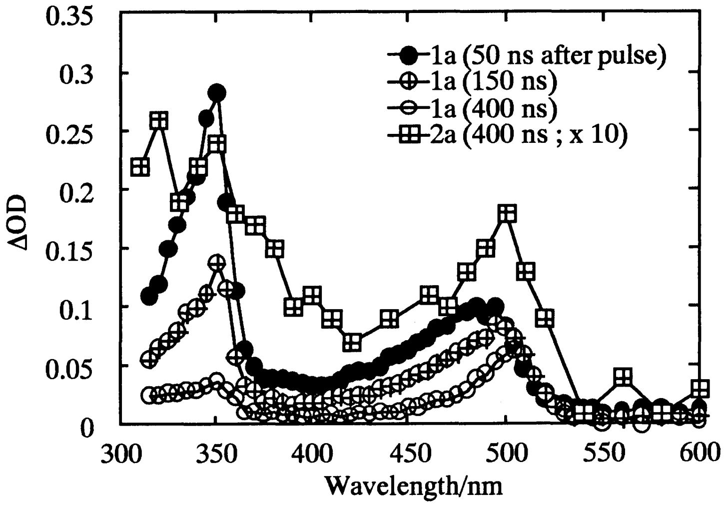
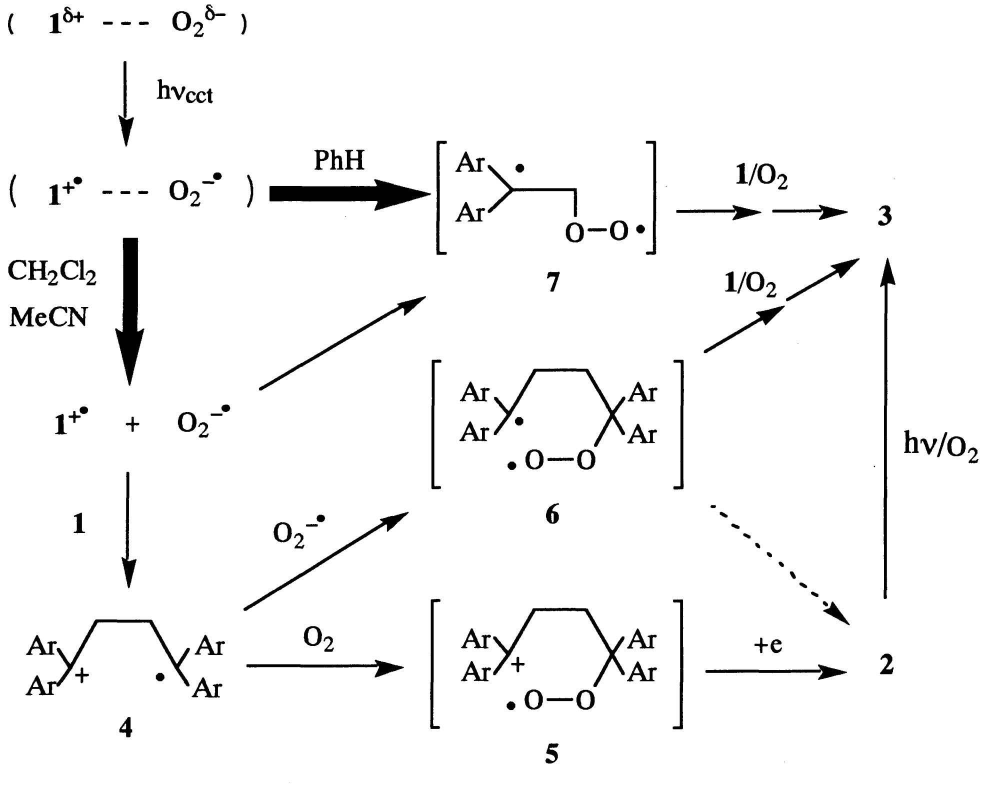


Fig. 1. Transient absorption spectra obtained by the pulse radiolysis of **1a** under oxygen and **2a** under argon in BuCl.



Scheme 1.

390 nm at 10 ns after the pulse, while a sharp absorption band with λmax at 350 nm, which would come from radical species or **4**, and a broad band with λmax at 480 nm, assigned to **4**, were obtained at 50 ns after the pulse with the collapse of $\mathbf{1a}^{+\bullet}$. The broad band was quenched by O_2 at the rate constant of 5.5×10^8 $M^{-1}s^{-1}$, forming a new absorption band with λmax at 500 nm, which agreed with the transient absorption spectra obtained by the pulse radiolysis of **2** (5 mM) in BuCl under argon (Fig. 1). These results indicate that the dimer cation radical **4** can react with O_2, although a super oxide anion would be still a possible active species in the photochemical reaction of the CCT pairs.

Further investigation on the reactivity of the monomer and dimer cation radicals of **1** with triplet oxygen is now in progress.

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6) Similar irradiation of **2** in CH_2Cl_2 under nitrogen showed the different products distribution from that under oxygen. The mechanism of the photolysis of **2** has not been studied in detail; however, production of **3** would not be a single channel of the photolysis.

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

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