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Generation of Polyphenylene Radical Cations and Their Cosensitization Ability in the 9,10-Dicyanoanthracene-Sensitized Photochemical Chain Reactions of 1,2-Bis(4-methoxyphenyl)cyclopropane

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Cosensitization effects of polyphenylene compounds (PP) such as biphenyl (BP), terphenyls (*o*-, *m*-, *p*-TP), and phenanthrene (Phen) in photoinduced electron-transfer reactions were examined. The 9,10-dicyanoanthracene (DCA)-sensitized cis−trans photoisomerization of 1,2-bis(4-methoxyphenyl)-cyclopropane (CP), which proceeds in a chain reaction via free radical cation of CP (CP$^{\bullet+}$) as a chain carrier, was accelerated by adding PP, particularly by TP. A similar accelerating effect was observed in the DCA-sensitized photooxygenation of CP as another example. BP and TP were more stable under the oxygenation condition than phenanthrene and naphthalene, which also accelerate the photooxygenation CP. CP$^{\bullet+}$ is generated by the direct electron transfer from CP to the excited singlet state of DCA (^{1}DCA*) and also by the secondary electron transfer from CP to PP$^{\bullet+}$, which is generated by the primary electron transfer from PP to ^{1}DCA*. The laser flash photolysis study revealed that the quantum yield for the formation of free CP$^{\bullet+}$ in the direct electron transfer from CP to ^{1}DCA* ($\Phi_{\text{CP}^{\bullet+}} \approx 0.1$) was smaller than that in the presence of PP. This is due to the high yield of free PP$^{\bullet+}$ generation by the primary electron transfer and the efficient secondary electron transfer from CP to PP$^{\bullet+}$. The secondary electron transfers were found to take place in nearly diffusion-controlled rates ($0.9-1.5 \times 10^{10}$ M^{-1} s^{-1}). The high yield of PP$^{\bullet+}$ as free radical ions does not seem to be the sole factor of the cosensitization of PP for the DCA-sensitized photoreactions of CP. The ratio of the quantum yields of the photoreactions to that of the initial CP$^{\bullet+}$ formation (turnover) also increased by the addition of PP from 3 (isomerization) and 15 (oxygenation) to 32−90 for both reactions. The second-order rate constant for the decay of CP$^{\bullet+}$ in aerated acetonitrile was decreased by a factor of 0.5−0.8 by the addition of PP. We concluded that the cosensitization effect in the photoreaction involves a π-complex formation between CP$^{\bullet+}$ and PP assisting the chain reaction as well as initial CP$^{\bullet+}$ formation.

Introduction

The photoinduced electron-transfer reaction has received considerable attention from synthetic and mechanistic viewpoints for these two decades.[1] In the primary process of the photoinduced electron-transfer reactions (Scheme 1), diffusion-controlled quenching of an excited state of an electron acceptor (A) by a donor (D) or vice versa gives a solvent-separated radical ion pair (SSRIP) (($A^{\bullet-}/D^{\bullet+})_S$), which undergoes further chemical processes mainly after dissociation into free ions or deactivation by back-electron transfer (BET). The BET process, which has attracted much interest from the theoretical and experimental chemists because its high exothermicity is favorable for the study of the "inverted region" in the Marcus theory,[2,3] often dominates resulting in the inefficient free ion formation. This deactivation process is undesirable for the purpose of photochemical energy conversion. A direct electron transfer from an electron-donating substrate molecule (S) to an excited state of an electron acceptor molecule (A*) often gives less amount of free S$^{\bullet+}$ because of a fast BET process suppressing the separation of SSRIP. It has been reported that several organic and inorganic additives induce the charge separation against the back-electron transfer within a radical ion pair.[4−10] Inorganic salts such as metal perchlorates enhance the separation of some SSRIP's through an

Scheme 1

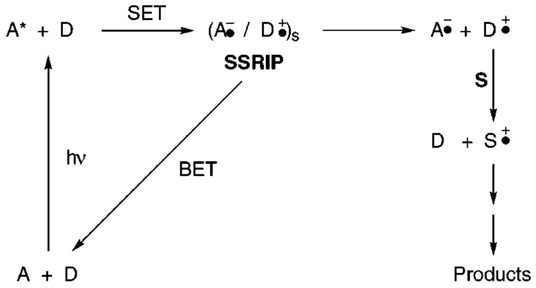

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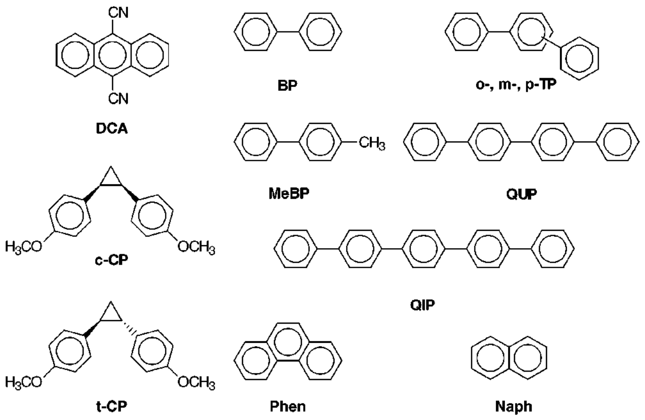
Chart 1



electrostatic interaction with radical ions.[4−6,9,10] On the other hand, aromatic hydrocarbons (ArH) such as pyrene or biphenyl (BP, Chart 1) form their free radical cations (ArH$^{\bullet+}$) through a photoexcitation with A, and ArH$^{\bullet+}$ undergoes a secondary electron transfer from S to give ArH and S$^{\bullet+}$.[7,8] When the free energy change of BET ($\Delta G_{-\mathrm{et}}$) for an SSRIP of A and ArH ((A$^{\bullet-}$/ArH$^{\bullet+}$)$_s$) is highly negative, separation of SSRIP takes place efficiently as a consequence of slow BET rate as demonstrated by Farid in 1990.[11] For example, the quantum yield of 0.72 has been reported for the formation of free radical cation of BP (BP$^{\bullet+}$) upon irradiation with 9,10-dicyanoanthracene (DCA) as an electron accepting sensitizer. A diffusive secondary electron transfer from S to BP$^{\bullet+}$, which is formed by competitive quenching of A*, gives free S$^{\bullet+}$ in a high quantum yield when BP is added to the S−A system and the oxidation potential of S is lower than that of BP by > 0.4 V. This cosensitizing effect often can meet the synthetic purposes. The redox cycle will reproduce ArH without consumption of ArH if chemical stability of ArH$^{\bullet+}$ is high enough. Since cosensitizers are generally used to accelerate the DCA-sensitized photoreactions in a high concentration of 0.01−0.2 M, their stability have not been studied deeply. Reactivity of ArH$^{\bullet+}$ toward oxygen would be one of the most important facors because preparative reactions are often conducted under aerated or imcompletely deoxygenated conditions. We reported an oxygenation of BP$^{\bullet+}$ upon photoirradiation in oxygen-saturated acetonitrile giving benzoic acid in a high yield in the presence of DCA as an electron acceptor.[6] It was a surprising experience for the authors to observe that the benzene ring had been completely decomposed under the mild condition. We have studied the DCA-sensitized photooxygenation of polyphenylenes (PP) (biphenyl, BP; *o*-, *m*-, and *p*-terphenyl, *o*-, *m*-, and *p*-TP; quaterphenyl, QUP; quinquephenyl, QIP) and some polyacenes such as phenanthrene (Phen) and their cosensitization ability in the DCA-sensitized *cis*−trans photoisomerization and photooxygenation of cis- and *trans*-1,2-bis(4-methoxyphenyl)cyclopropanes (*c*-CP and *t*-CP).[4,5] We discuss the chemical properties of PP$^{\bullet+}$ as a cosensitizing hole carrier and a role of the neutral PP in the cosensitization through the product analysis and laser flash photolysis studies.

Experimental Section

General. All the conventional analytical instruments are the same as reported previously.[4,5]

Materials. Acetonitrile was distilled three times over P_2O_5 and then once over anhydrous K_2CO_3 before use. Polyphenylenes (PP) (biphenyl, BP; *o*-, *m*-, and *p*-terphenyl, *o*-, *m*-, and *p*-TP; quaterphenyl, QUP) and other organic compounds were purified by recrystallization before use. *cis*- and *trans*-1,2-Bis(4-methoxyphenyl)cyclopropanes (*c*-CP and *t*-CP) were prepared and purified according to the previous papers.[4,5] Quinquephenyl (QIP) and inorganic chemicals were purchased and used without further purification.

DCA-Sensitized Photooxygenation of PP. A 16 mL portion of an acetonitrile solution containing *p*-TP (115 mg, 0.5 mmol), DCA (5 mg, 0.022 mmol), and $Mg(ClO_4)_2$ (56 mg, 0.25 mmol) was irradiated with a 500 W high-pressure mercury lamp (Eikosha) through an aqueous NH_3−$CuSO_4$ filter solution (>400 nm) under an oxygen stream for 5 h. The solvent was removed under reduced pressure. The residue was dissolved in benzene−ether (1:1) and extracted three times with a 20% NaOH aqueous solution. The aqueous layer was neutralized with a 20% H_2SO_4 solution and extracted with benzene−ether. The organic layer was dried over Na_2SO_4, and the solvent was removed to give a mixture benzoic acid (**1**, 36%; on the assumption that 1 M *p*-TP yields 2 molar equiv of **1**) and 4-phenylbenzoic acid (**2e**, 16%). The mixture was treated with diazomethane. The yields and product ratios were determined by GLC and ^{1}H NMR spectra of the mixture compared with those of authentic compounds. Photooxygenation of other PP was performed in a similar manner.

Measurement of Quantum Yields for the DCA-Sensitized Photoreactions of CP. Quantum yields were determined by the procedure of Murov, using a potassium ferrioxalate actinometer.[12] The light source was a 500 W high-pressure mercury lamp (Eikosha), and the 405 nm Hg line was isolated with an aqueous NH_3−$CuSO_4$ filter solution, a Toshiba UV-39 glass filter, and a KL-40 interference filter. The light intensity was measured twice before and after actual photoreactions. Photoreactions were carried out in a quartz cuvette (1 × 1 × 4 cm) up to 30−70% conversion of the starting materials. The reaction mixtures were analyzed by GLC to determine the conversion or yield of the reaction. The quantum yields were estimated from the slope of linear parts of plots in time course conversion.

A 4 mL portion of an aerated acetonitrile solution containing DCA (5×10^{-4} M) and *c*-CP (1×10^{-2} M) in a quartz cuvette was irradiated at 405 nm to determine the quantum yield for the *t*-CP formation. The progress of the isomerization was followed by GLC. The photochemical isomerization of *c*-CP

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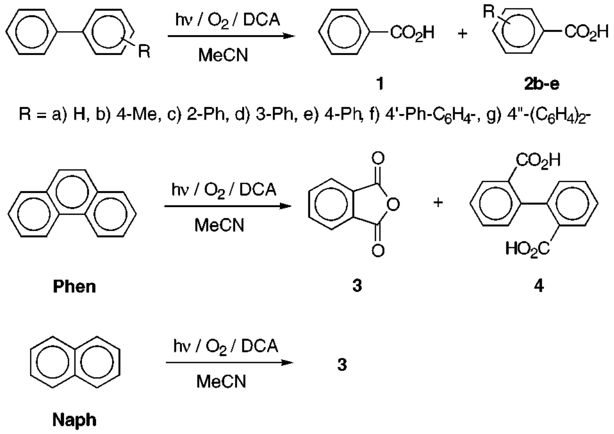
in the presence of PP was carried out by the irradiation of solutions (4 mL) in a Pyrex tube (i.d. 10 mm) at >400 nm with a high-pressure Hg lamp with an aqueous NH_3−$CuSO_4$ filter solution.[5] The concentration of PP was 5×10^{-3} M except for that of QUP (saturated, [QUP] < 4×10^{-4} M). Quantum yields of *t*-CP formation in the presence of PP were determined from the relative yield of *t*-CP to that in the absence of PP. In a similar manner, quantum yields of the photooxygenation of *t*-CP (2.5×10^{-2} M) in the absence and presence of PP (2.5×10^{-2} M) were determined. The progress of the photooxygenation was followed by the decrease of *t*-CP or the increase of the products using GLC.[4] The products of the photooxygenation of *cis*- and *trans*-3,5-bis(4-methoxyphenyl)dioxolane decomposed at the injection part of GLC (250 °C) upon the GLC analysis and gave the signals corresponding to the decomposition products, 4-methoxybenzaldehyde, 4-methoxyacetophenone, and 2-(4-methoxyphenyl)oxyrane in a ratio of 1:>0.9:<0.1. The yield of the dioxolane was quantified by GLC with the signal of 4-methoxybenzaldehyde. Since *t*-CP was converted to the dioxolane qantitatively and the dioxolane did not give its decomposition products during the photooxygenation until cyclopropane was consumed, the quantum yields obtained from the decrease of *t*-CP and from the increase of the dioxolane were identical each other within experimental error (5%).

Laser Flash Photolysis. Acetonitrile solutions of DCA (5×10^{-4} mol dm^{-3}) containing PP and CP were irradiated with a third harmonic pulse (355 nm, 6 ns, 15 mJ pulse^{-1}) from an Nd:YAG laser (Continuum Surelite I-10) or a pulse from an excimer laser (Lumonics EX-460) operated with an XeCl laser gas mixture (308 nm, 12 ns, 70 mJ pulse^{-1}). A focused Xe arc (300−800 nm, pulse width 2 ms) which was synchronized with the laser pulse by the use of a digital deley generator (Stanford Research Systems DG535) was passed through the sample as a monitor light for transient absorption measurement. The arc was monitored as a spectral or a temporal response signal of transient species with a gated-multichannel spectrometer (Hamamatsu PMA-50, gate time 5−100 ns) or with a monochromatic ns-transient measurement system (Otsuka NSP-1000G) equipped with a photomultiplier (Hamamatsu R-1894) and a digital oscilloscope (Tektronics TDS380P). The quantum yields of $CP^{\bullet+}$ in the presence of various cosensitizers and extinction coefficient of $CP^{\bullet+}$ were determined according to Farid et al.[11] from the transient absorption spectra at 100 ns after the laser excitation of aerated acetonitrile solutions containing PP, *t*-CP, and DCA. An aerated acetonitrile solution of BP (0.2 M) and DCA (5×10^{-4} M) was used as a standard actinometer.[11]

The rates for the secondary electron transfer from CP to $PP^{\bullet+}$ was determined by the laser flash photolysis of aerated acetonitrile solutions of 1,4-dicyanonaphthalene (DCN) ([DCN] = 1×10^{-4} M) containing PP (0.02−0.2 M) and CP (1×10^{-4} to 5×10^{-3} M) to monitor the decay curves of $PP^{\bullet+}$ around 650 nm and the rise time of the decay curves of $CP^{\bullet+}$ at 560 nm. The use of DCN instead of DCA was to avoid the disturbance by the strong fluorescence, ground-state absorption, and transient absorption of DCA in the wavelength of 400−650 nm. The rates were calculated from the slope of the plots of the first-order decay constant for $PP^{\bullet+}$ or rise time of $CP^{\bullet+}$ versus CP concentration and were almost identical within the error of 10%. The second-order rate constants for the decay of *t*-$CP^{\bullet+}$ by back-electron transfer from $O_2^{\bullet-}$ were determined by the decay curves of $CP^{\bullet+}$ at 560 nm in the absence and presence of PP (2.5×10^{-2} M). The rate constants were measured three times and averaged.

Chart 2



Results and Discussion

DCA-Sensitized Photooxygenation of PP. Irradiation of an acetonitrile solution (16 mL) containing *p*-TP (0.5 mmol), DCA (0.02 mmol), and $Mg(ClO_4)_2$ (0.25 mmol) with an oxygen bubbling for 5 h comsumed *p*-TP completely giving benzoic acid (**1**) and 4-phenylbenzoic acid (**2e**) in 72 (or 36% on the assumption that the 1 M *p*-TP yields 2 molar equiv of **1**, see below) and 16% yields, respectively (Chart 2). Without $Mg(ClO_4)_2$, the efficiency of the comsumption of *p*-TP was about half of that in the presence of $Mg(ClO_4)_2$, and a consumption of DCA giving anthraquinone was observed.[6b,13] In the case of *o*-TP, small amounts of phthalic anhydride (**3**) and diphenic acid (**4**) were obtained as well as **1** but not 2-phenylbenzoic acid (**2c**). Since biphenyl derivatives bearing an electron-withdrawing group are inert under the same conditions, a secondary oxygenation of **2c** to **3** and **4** seems unlikely. The formation of **3** and **4** from phenanthrene (see below) suggested that a cyclization of *o*-TP was involved during the oxygenation. However, no rearrangement products of *o*-TP such as triphenylene were observed upon the irradiation under nitrogen or in the presence of CP. These compounds would be formed as a primary product via a cyclization of an oxygenated intermediate to form a C−C bond between 2- and 2′-carbons of *o*-TP. Similar photooxygenation of *m*-TP afforded **1** and 3-phenylbenzoic acid (**2d**) in 76% and 38% molar equivalent yields, respectively. Since the sum of the yields exceed unity, the central ring must decompose into two carboxylic groups. Therefore, the yield of **1** was corrected to be 38%. This also will be the case for *o*- and *p*-TP. The photooxygenation of QUP and QIP was conducted in a mixed solvent of acetonitrile−benzene (8:2) because of their low solubility in acetonitrile. The irradiation of QUP afforded **1** and **2e** in low yields. In the case of QIP, consumption of QIP giving a complex mixture containing **1** was not completed owing to a rapid consumption of DCA. Alkyl-substituted derivatives such as 4-methylbiphenyl (MeBP) showed a high reactivity toward oxygenation affording α-carbonyl compunds 4-phenylbenzaldehyde (**5**) and **2e** via an oxidation of α-carbon as well as **1** and **2b** via the ring oxidation.[6b] The disappearance of Phen and Naph in their photooxygenation was much faster than that of PP and their photooxygenation gave **3** and **4** from Phen and **3** from Naph, respectively. PP derivatives were stable and recovered completely after the irradiation in nitrogen-saturated methanol in the presence of DCA.[14] The relatively low

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Table 1. DCA-Sensitized Photooxygenation of Polyphenylene Compounds[a]

compd	irradn time/h	product(s)/%			
		1	**2**	**3**	**4**
BP	5	76			
o-TP	5	35^{b}		12	3
m-TP	5	38^{b}	38 (**2d**)		
p-TP^{c}	5	36^{b}	16 (**2e**)		
QUP^{d}	8	20	31 (**2e**)		
MeBP^{e}	1	32	20 (**2b**), 5 (**2e**)		
Phen	1			8	8
Naph	1			86	

[a] [Polyphenylene compounds] = 3.1×10^{-2} M, [DCA] = 5×10^{-4} M, [$Mg(ClO_4)_2$] = 1.6×10^{-2} M in dry acetonitrile. Conversions of the reaction were >95%. [b] Yields on the assumption that 1 M TP yields 2 molar equiv of **1** (see text). [c] *p*-TP was suspended in acetonitrile because of its low solubility. [d] QUP was suspended in $CH_3CN-C_6H_6$ (8:2). [e] A small amount (2%) of 4-phenylbenzaldehyde (**5**) was also formed.

Table 2. Rate Constants for the Fluorescence Quenching of DCA, Oxidation Potentials and Ionization Potentials of Polyphenylene Compounds, and Calculated ΔG_{Et} Values for the One-Electron Transfer Process from Polyphenylene Compounds to ^{1}DCA* in Acetonitrile

compd	$k_q{}^a$/M^{-1} s^{-1}	$E^{ox}{}_{1/2}{}^b$/V	IP^c/eV	$\Delta G_{et}{}^d$/kJ mol^{-1}
BP	3.6×10^{9}	1.45	5.87	−16.4
o-TP	7.0×10^{9}	1.42		−30.9
m-TP	5.5×10^{9}	1.40		−18.3
p-TP	1.2×10^{10}	1.32	5.97	−26.1
QUP			5.90	
QIP			5.87	
MeBP	1.1×10^{10}	1.34		−27.0
Phen	1.4×10^{10}	1.17		−43.4
Naph	1.4×10^{10}	1.22		−38.6
t-CP	1.8×10^{10}	0.55		−103.2
c-CP	1.7×10^{10}	0.65		−93.6
DX^{e}	1.1×10^{10}	1.27		−33.8

[a] Rate constants for the fluorescence quenching of DCA in aerated acetonitrile: [DCA] = 4×10^{-4} M; τ(DCA, air) = 16.1 ns. [b] Oxidation potentials (V vs $Ag/AgClO_4$) were determined as half-peak potentials by cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate (0.1 M) in acetonitrile. [c] Solid-state ionization potentials taken from ref 16. [d] Calculated free energy changes for the one-electron-transfer process from polyphenylene compounds to ^{1}DCA* in acetonitrile. See ref 15. Reduction potential of DCA; −1.33 V vs $Ag/AgClO_4$ in acetonitrile. [e] Cis isomer, the values are taken from ref 4b.

Chart 3

$$\text{c-CP} \xrightleftharpoons[\text{MeCN} \atop \text{Additive}]{h\nu\ /\ \text{DCA}} \text{t-CP}$$

Table 3. Effect of Polyphenylene Compounds on the DCA-Sensitized Photoisomerization of *c*-CP to *t*-CP and the Turnover of $CP^{\bullet+}$

additive	(Φ_{sep})^a	concn/M	$\Phi_{c\to t}{}^b$	$\Phi_{CP^{\bullet+}}{}^c$	$\Phi_{c\to t}/\Phi_{CP^{\bullet+}}{}^d$
none	(0.12)		0.28^{g}	0.09	3
BP	(0.72)^{e}	5×10^{-3}	5.6	0.14	40
o-TP	(0.64)	5×10^{-3}	15.3	0.17	90
m-TP	(0.32)	5×10^{-3}	10.8	0.13	83
p-TP		5×10^{-3}	20.5	0.11^{h}	186
QUP		$<4 \times 10^{-4}$ ^{f}	0.48		
Me-BP		5×10^{-3}	7.2		
Phen	(0.62)^{e}	1×10^{-2}	13.0^{g}	0.31	42
Naph	(0.58)^{e}	1×10^{-2}	12.5^{g}	0.28	45

[a] Separation efficiency of SSRIP (counter radical anion: $DCA^{\bullet-}$) into free radical cation obtained by laser flash photolysis. [b] Quantum yields of the photoisomerization of *c*-CP to *t*-CP; [*c*-CP] = 0.01 M. [DCA] = 5×10^{-4} M in dry acetonitrile. [c] Quantum yields of free $CP^{\bullet+}$ generated by direct and indirect sensitization. The ^{1}DCA* quenching rates and concentrations of CP and PP were taken into account. [d] Turnover of $CP^{\bullet+}$ in the photoisomerization, see text. [e] The values were taken from ref 11. [f] Saturated solution. [g] The values were taken from ref 5. [h] Directly measured by laser flash photolysis.

reactivity of PP in the photooxygenation as well as nucleophilic addition has proved that PP is suitable for cosensitizer. The results are summarized in Table 1.

Formation of $PP^{\bullet+}$ via photoinduced electron transfer (PET) from PP to ^{1}DCA* must be involved in this photooxygenation as discussed in our previous papers.[6] Although the detailed pathway for the decomposition of the benzene ring of PP has not been completely clarified, $PP^{\bullet+}$ would be attacked by $^3O_2$ to give the oxygenated products. The free energy changes for one-electron transfer from PP to ^{1}DCA* (ΔG_{et}) estimated by the Rehm−Weller equation[15] are largely negative and the fluorescence of DCA was quenched by PP in nearly diffusion-controlled rates (Table 2). The generation of $PP^{\bullet+}$ was readily observed by laser flash photolysis. No oxygenated products were obtained by the irradiation of PP, Phen, and Naph in less polar solvents in the presence of DCA or by the irradiation in CH_2Cl_2 in the presence of methylene blue under oxygen to generate singlet oxygen ($^1O_2$). These results support the PET mechanism for the photooxygenation of PP. The efficiency of the photooxygenation of QUP and QIP was lower than that of *p*-TP. The oxidation potentials of QUP and QIP could not be measured in acetonitrile because of their low solubility but would be almost equal to or slightly smaller than that of *p*-TP on the comparison of their ionization potentials (Table 2).[16] The low reactivity of QUP and QIP would be attributed to a low reactivity of their radical cations $QUP^{\bullet+}$ and $QIP^{\bullet+}$ toward oxygen owing to the delocalization of their radical cites over the whole molecules.

Cosensitization of PP in the DCA-Sensitized Photoisomerization of Diarylcyclopropanes. As previously reported, irradiation of an aerated acetonitrile solution containing DCA (5×10^{-4} M) and *cis*- or *trans*-1,2-bis(4-methoxyphenyl)cyclopropanes (*c*-CP, *t*-CP, 1×10^{-2} M) at >400 nm (Chart 3) caused the cis−trans isomerization of the cyclopropanes, affording the photostationary state (*c*-CP:*t*-CP = 5:95).[5] The quantum yields for the isomerization from *c*-CP to *t*-CP were measured in the absence and presence of PP compounds such as BP, *o*-, *m*-, and *p*-TP, and also Phen. The results are summarized in Table 3. The addition of PP showed a remarkable enhancement in the quantum yields of the photoisomerization. The order of enhancement in the reaction efficiency was *p*-TP > *o*-TP > *m*-TP > MeBP > BP (> QUP). Undoubtedly the quantum yields exceeded unity indicating the reaction proceeds in a chain mechanism. The limiting quantum yield in the absence of PP also exceeded unity (1.8).[5] Addition of polyacene compounds, phenanthrene (Phen) and naphthalenes (Naph), also accelerated the photoisomerization. It was confirmed that all the PP compounds were not consumed even upon prolonged irradiation.

Cosensitization of PP in the DCA-Sensitized Photooxygenation of Diarylcyclopropanes. The

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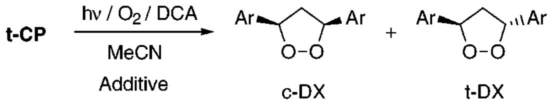
Table 4. Effect of Polyphenylene Compounds on the DCA-Sensitized Photooxygenation of *t*-CP and the Turnover of CP$^{•+}$

additive	(Φ_{sep})[a]	concn/M	Φ_{DX}[b]	$\Phi_{CP^{•+}}$[c]	$\Phi_{DX}/\Phi_{CP^{•+}}$[d]
none	(0.12)		1.6[f]	0.11	15
BP	(0.72)[e]	2.5×10^{-2}	1.9	0.16	12
o-TP	(0.64)	2.5×10^{-2}	11.6	0.21	55
m-TP	(0.32)	2.5×10^{-2}	9.3	0.13	71
Phen	(0.62)[e]	2.5×10^{-2}	10.9	0.34	32

[a] Separation efficiency of SSRIP (counter radical anion: DCA$^{•-}$) into free radical cation obtained by laser flash photolysis. [b] Quantum yields for the formation of DX by the photooxygenation of *t*-CP; [*t*-CP] = 2.5×10^{-2} M. [DCA] = 5×10^{-4} M in dry acetonitrile. [c] Quantum yields of free CP$^{•+}$ generated by direct and indirect sensitization. The ^{1}DCA* quenching rates and concentrations of CP and PP were taken into account. [d] Turnover of CP$^{•+}$ in the photooxygenation of CP, see text. [e] The values were taken from ref 11. [f] The values taken from ref 4a.

Chart 4



DCA-sensitized photooxygenation of *c*-CP or *t*-CP gave *cis*- and *trans*-3,5-bis(4-methoxyphenyl)-1,2-dioxolanes (cis/trans = 7/3) almost quantitatively.[5] The quantum yield of the dioxolane formation was 1.6, also indicating that the photoreaction involves a chain mechanism. As shown in Table 4, the addition of PP and also Phen to the reaction system increased the quantum yield efficiently (Chart 4). Neither any changes in the isomeric ratio of dioxolanes nor consumption of PP during the photooxygenation of CP was observed.

Determination of Radical Cation Yields by Laser Flash Photolysis. The mechanism of DCA-sensitized photoisomerization and photooxygenation of CP which involves photoinduced electron transfer and a chain process mediated by CP$^{•+}$ has been discussed in the previous reports.[4,5] The proposed mechanisms for the photoisomerization and photooxygenation are shown in Scheme 2. The PP radical cations also could be the key intermediate for the cosensitization in these reactions as well as the photooxygenation of PP. The fluorescence of DCA in acetonitrile was also quenched by CP at nearly diffusion-controlled rates. The values of ΔG_{et} for *c*- and *t*-CP were largely negative as given in Table 2, suggesting that radical cations of CP could be generated by one-electron transfer from these compounds to ^{1}DCA*. However, the turnover values in the chain isomerization and photooxygenation of CP are still unknown. Our questions are (1) how large are the quantum yields of free CP$^{•+}$ formation in the absence and presence of PP and (2) how the quantum yields for the reactions of CP reflect those of free CP$^{•+}$ formation.

Direct evidence for the generation of radical cation of PP upon the DCA-sensitized photoreaction was obtained from the nanosecond laser flash photolysis (LFP). The LFP of an acetonitrile solution of BP (0.2 M) containing DCA (5×10^{-4} M) under nitrogen was performed by a conventional nanosecond transient absorption measurement system using an Nd:YAG or XeCl excimer laser. The transient absorption was readily assigned to DCA$^{•-}$ and BP$^{•+}$ as reported by Farid et al.[11] The free BP$^{•+}$ yield of 0.72 and the molar extinction coefficient at 670 nm of 15 000 M^{-1} cm^{-1} were employed to determine the values of these parameters for CP$^{•+}$ and PP$^{•+}$. Though the transient absorption of DCA$^{•-}$ was quenched by the presence of oxygen, no fast quenching for the BP$^{•+}$ or no new transient species were observed within 1 μs by saturation of the solution with oxygen. The rate constant for the oxygen attack on BP$^{•+}$ was, therefore, smaller than 10^8 M^{-1} s^{-1}. This stability allowed us to assume that a secondary electron transfer from CP to BP$^{•+}$ will afford CP$^{•+}$ and BP in unit yield in the DCA−BP−*t*−CP system. The addition of *t*-CP (5×10^{-3} M) to the aerated acetonitrile solution ([BP] = 0.2 M and [DCA] = 5×10^{-4} M) gave a broad transient absorption at 450−580 nm and >650 nm after 400 ns from the laser pulse (Figure 1a). The transient was assigned to *t*-CP$^{•+}$ by comparison with those observed upon the low-temperatue γ-radiolysis and pulse radiolysis of *t*-CP.[17a] Assuming complete reduction of initially formed BP$^{•+}$ by *t*-CP giving the same amount of *t*-CP$^{•+}$ and a negligibly small contribution of *c*-CP$^{•+}$ in the transient absorption,[18a] the absorption coefficient of *t*-CP$^{•+}$ was determined to be 7500 M^{-1} cm^{-1} at 500 nm (Figure 1a). From this extinction coefficient, a qunantum yield of the formation of *t*-CP$^{•+}$ upon the photolysis of an aerated solution of *t*-CP (5×10^{-2} M) containing DCA (5×10^{-4} M) was determined to be 0.11, which was corrected to 0.12 for the incomplete quenching at the concentration of *t*-CP ($\Phi_f/\Phi_{f0} = 0.089$). This value corresponds to the quantum yield for the charge separation (separation efficiency, Φ_{sep}) if the SSRIP is formed in a unit quantum yield. Obviously the free *t*-CP$^{•+}$ yield was increased by the addition of BP as indicated by the transient absorption spectra of *t*-CP$^{•+}$ in Figure 2. On the other hand, although transient absorption of *c*-CP$^{•+}$ (Figure 1b) was obtained only by the photolysis of an aerated acetonitrile solution of *c*-CP (5×10^{-2} M) containing DCA in a similar manner, its extinction coefficient and yield could not be determined because of the too efficient isomerization to *t*-CP during the accumulation of the transient spectra in the presence of BP. The generation of *t*-CP$^{•+}$ and *c*-CP$^{•+}$ by the direct photolysis with DCA was not affected by the nitrogen purge suggesting that oxygen quenched the free DCA$^{•-}$ but not DCA$^{•-}$ in SSRIP.

The transient absorption measurement of *o*-TP− and *m*-TP−DCA solutions ([TP] = 0.02 M) indicated that *o*- and *m*-TP$^{•+}$ were stable within 1 μs in the presence of oxygen.[18b] When the concentration of TP was increased, the transient absorption of TP$^{•+}$ decreased considerably and was not observed at 0.2 M. This can be due to a quenching of a radical ion pair (DCA$^{•-}$/TP$^{•+}$) by TP. The rates for the secondary electron transfer from *t*-CP to TP$^{•+}$ were determined by the decay time of TP$^{•+}$ at 650 nm for *o*-TP or the rise time of *t*-CP$^{•+}$ at 560 nm for *o*-, *m*-, and *p*-TP upon the photolysis of TP−1,4-dicyanonaphthalene (DCN) solutions containing various concentration of *t*-CP. Typical decay and rise curves of the transient species are given in Figure 3a. All the rates showed nearly diffusion-controlled rates (*o*-TP, 1.4×10^{10}; *m*-TP, 9.7×10^9; *p*-TP, 1.3×10^{10} M^{-1} s^{-1}). Since TP$^{•+}$ was stable within the timeframe for secondary electron

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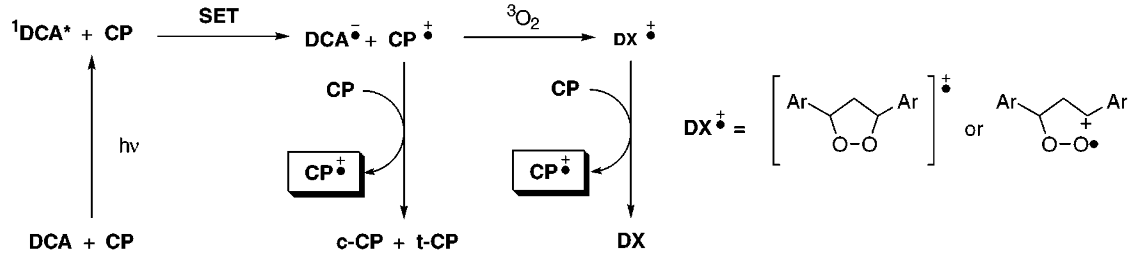
(18) (a) The quantitative charge transfer from CP to PP$^{•+}$ was confirmed by the observation of isosbestic points in the time-resolved absorption spectra of acetonitrile solutions containing DCN, PP, and *t*-CP in the period of 0−1 μs. (b) The transient species were readily assigned to TP$^{•+}$ by the comparison of the spectra with the reported ones of TP$^{•+}$. Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

Scheme 2



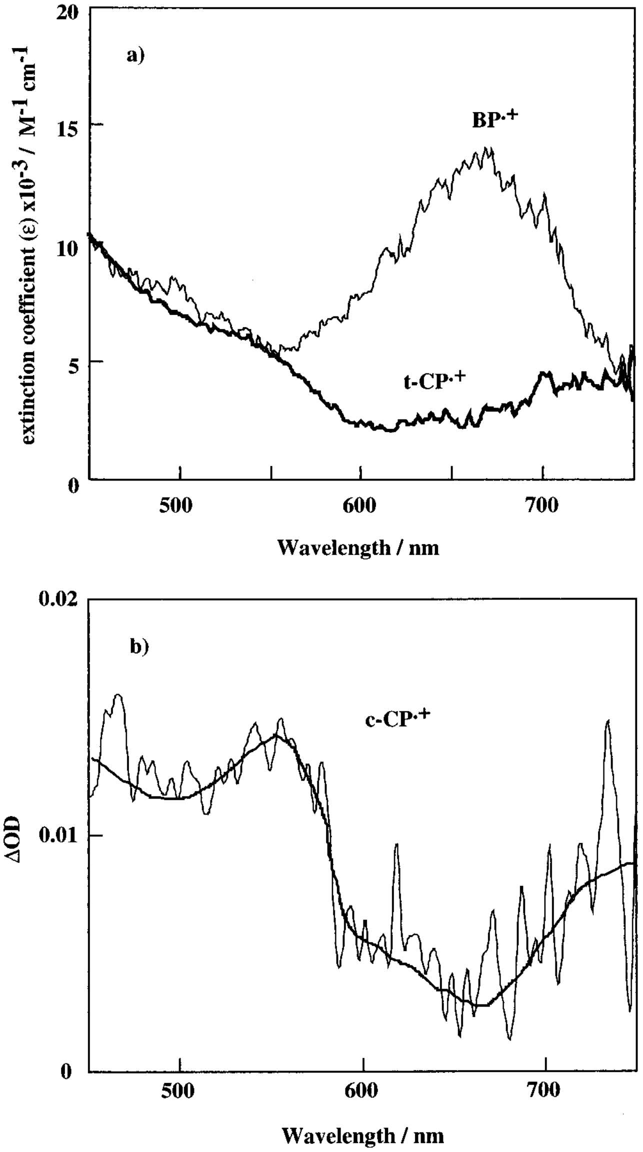


Figure 1. Transient absorption spectra of (a) BP$^{•+}$ and t-CP$^{•+}$ and (b) c-CP$^{•+}$ observed upon laser pulse excitation of an aerated acetonitrile solution containing (a) BP (0.2 M) and DCA (5×10^{-4} M) and BP (0.2 M), t-CP (5×10^{-3} M), and DCA (5×10^{-4} M) and (b) c-CP (5×10^{-2} M) and DCA (5×10^{-4} M). The spectra were taken at (a) 100 and 400 ns and (b) 100 ns after the laser pulse, respectively. Excitation wavelength: 308 nm. Laser intensity: 70 mJ pulse^{-1}. The extinction coefficient was determined according to ref 11.

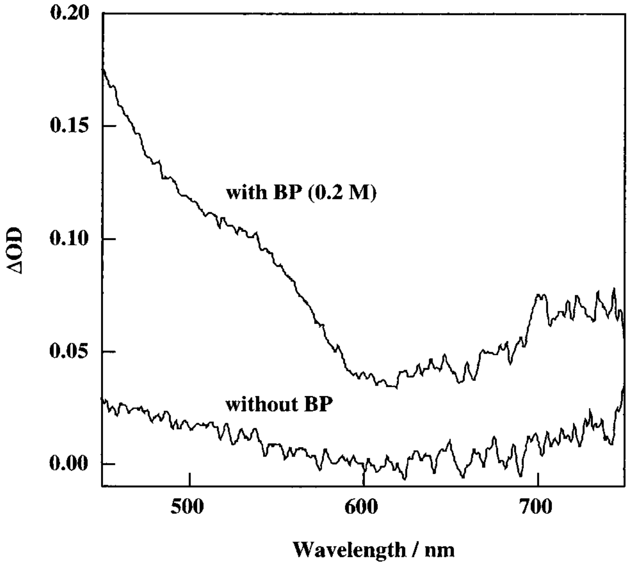


Figure 2. Transient absorption spectra of t-CP$^{•+}$ generated by the indirect (cosensitization) and direct sensitization upon laser pulse excitation of aerated acetonitrile solutions of t-CP (1×10^{-3} M) and DCA (5×10^{-4} M) in the presence and absence of BP (0.02 M). The spectra were taken at 400 ns after the laser pulse. Excitation wavelength: 355 nm. Laser intensity: 15 mJ pulse^{-1}.

transfer (400 ns) upon the photolysis of aerated soluions of TP containing t-CP (5×10^{-3} M) and DCA (5×10^{-4} M), the concentration of t-CP$^{•+}$ formed was expected to be equal to that of the initially formed TP$^{•+}$.[18a] By comparison of the values of the 500 nm transient absorbance at a time of 400 ns due to t-CP$^{•+}$ generated by the use of TP and BP, free TP$^{•+}$ yields were determined assuming direct formation of t-CP$^{•+}$ was small because of a low concentration of t-CP employed as compared to that of TP. The quantum yields of the formation of TP$^{•+}$ were 0.47 (o-TP) and 0.22 (m-TP), but that for p-TP could not be determined owing to its low solubility in acetonitrile. The values were also corrected for the imcomplete quenching to 0.64 (o-TP) and 0.32 (m-TP). Obviously, the free CP$^{•+}$ yield was increased also by the addition of TP.

Turnover of the Chain Reactions. The photochemical isomerization and photooxygenation of CP involve chain processes without doubt, because their quantum yields largely exceed unity. The triplet excited state of DCA (^{3}DCA*) was hardly observed throughout the photolysis study, ruling out the incorporation of triplet species for these reactions. From the values of the separation efficiencies (Φ_{sep}) and the fluorescence quenching rates for CP and PP, the initial quantum yields for CP$^{•+}$ generation ($\Phi_{CP^{•+}}$) both through the direct and indirect electron-transfer processes under the photoisomerization and photooxygenation conditions were calculated (Tables 3 and 4). The ratio of the quantum yield of the reactions (Φ_r) obtained by the stationary-state experiments to $\Phi_{CP^{•+}}$ ($\Phi_r/\Phi_{CP^{•+}}$) will be the turnover of the chain reactions of CP$^{•+}$. The results are also shown in Tables 3 and 4. Though the values of $\Phi_{CP^{•+}}$ vary from

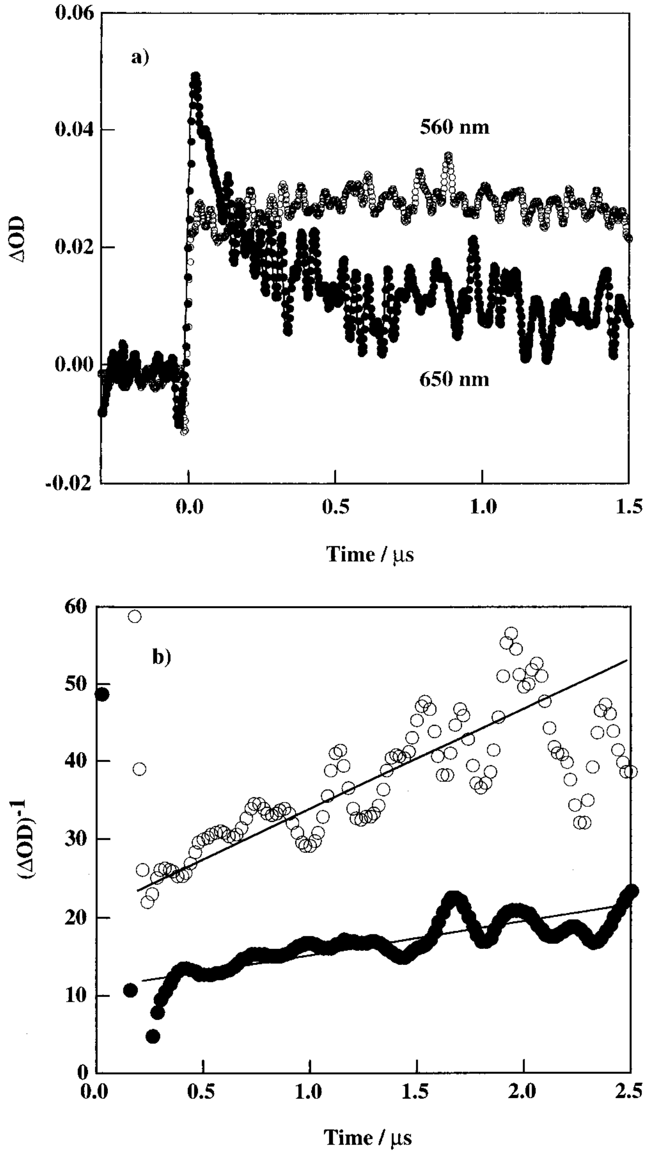
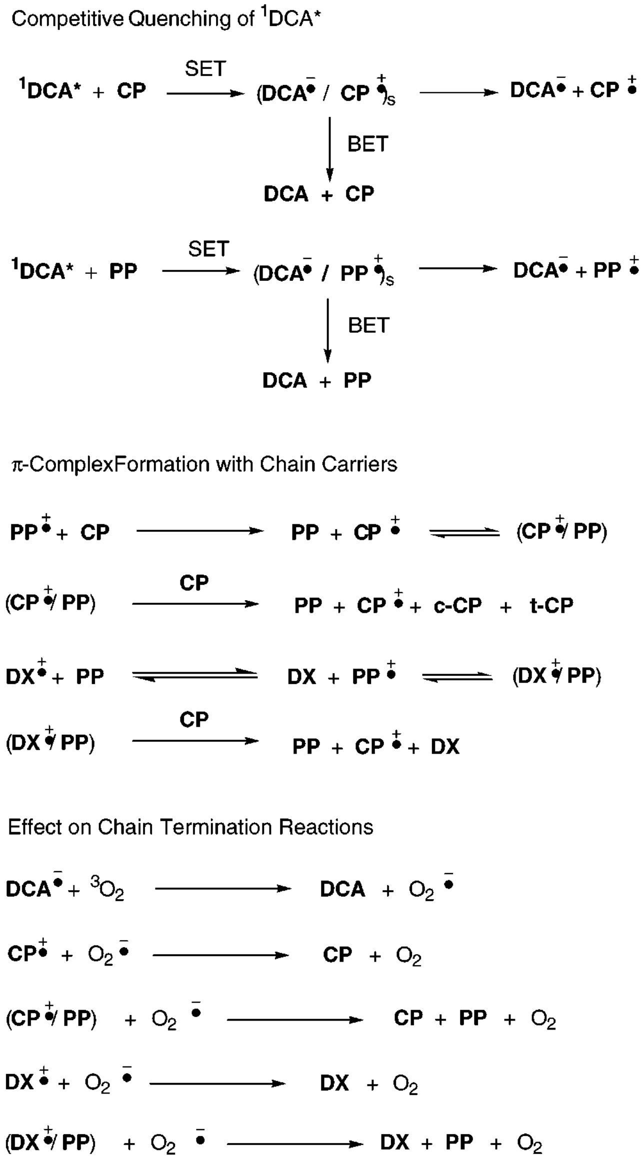


Figure 3. (a) Decay and rise curves of the transient absorption of *o*-TP$^{\bullet+}$ (650 nm, closed circle) and *t*-CP$^{\bullet+}$ (560 nm, open circle) observed upon laser pulse excitation of an acetonitrile solution of *o*-TP (0.025 M) in the presence of DCN (1×10^{-4} M) and *t*-CP (5×10^{-4} M) under nitrogen. An undershoot around 0 ns was due to the fluorescence of DCN. Excitation wavelength: 355 nm. Laser intensity: 15 mJ pulse^{-1}. (b) Plot of the reciprocal of transient absorption at 560 nm ((ΔOD)$^{-1}$) versus time obtained by the laser flash photolysis of an aerated acetonitrile solution of *t*-CP (0.025 M) containing DCN (1×10^{-4} M) in the absence (open circle) and presence (closed circle) of *o*-TP (0.025 M). Excitation wavelength: 308 nm. Laser intensity: 70 mJ pulse^{-1}.

Scheme 3



0.09 to 0.31 depending on the aromatic additive used, the quantum yields of photoisomerization range from 0.28 up to 20. The turnover in the photoisomerization was 3 in the absence of PP and greatly increased up to 40−190 in the presence of PP. Since the reciprocal plot of the quantum yield of the isomerization $\Phi_{c\rightarrow t}$ in the absence of PP and the concentration of *c*-CP ($(\Phi_{c\rightarrow t})^{-1}$ vs $[c\text{-CP}]^{-1}$) showed a linear relationship for a range of [*c*-CP] from 10^{-3} to 0.2 M, the turnover could be considered to be constant. We reported that the turnover of the isomerization of *c*-CP to *t*-CP induced by the ^{60}Co γ-ray irradiation in benzonitrile was ≈5 at a concentration of CP of 1×10^{-2} M.[17a] We also observed a high turnover of more than 50 when *c*-CP$^{\bullet+}$ was produced in the dry acetonitrile in dark by the use of cationic oxidants such as $Cu(BF_4)_2$, $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$, and $NO^+BF_4^-$.[17b] However, neutral oxidants such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave smaller turnover values of ≈5.[17b] These results strongly suggest that the turnover value depends on the charge of the electron donor for CP$^{\bullet+}$ in the back-electron-transfer processes, i.e., Cu$^+$, $(4\text{-}BrC_6H_4)_3N$, NO, (benzonitrile)$^{\bullet-}$, or DDQ$^{\bullet-}$.

The turnover in the photooxygenation was also increased by the addition of PP although the value in the absence of PP was higher than that of the isomerization. Interestingly the values of the turnover were strongly dependent on the additive used and the orders in the effects obtained for both reactions agreed with each other: BP < Phen, Naph < *o*-, *m*-TP. This strongly suggests that the high yield of CP$^{\bullet+}$ due to the high separation efficiency of solvent-separated radical ion pair (SSRIP) of DCA and PP (DCA$^{\bullet-}$/PP$^{\bullet+}$) into free ions is not the sole factor of the cosensitization of PP for the photoreactions of CP (Scheme 3).

A simple equilibrium between CP$^{\bullet+}$ and PP does not seem plausible because the oxidation potentials of PP are higher than that of CP by 0.6−0.9 V (redox equilibrium constants $\ll 10^{-9}$). The uphill electron transfer from allyltrialkylsilane and -stannane derivatives to PP$^{\bullet+}$ has been found to have a limit for the endothermicity of 0.4 V.[19] In fact, we observed that the secondary electron transfer took place in diffusion-controlled rates and a complete decay of PP$^{\bullet+}$ within 1 μs after the laser pulse. We did not observe PP$^{\bullet+}$ after >1 μs after the laser pulse. If there is a redox equilibrium with a constant of larger than 0.1, PP$^{\bullet+}$ should have been detected with our transient absorption measurement system. Though the irreversible chemical change in the substrate may assist the uphill electron transfer by shifting the equilibrium,[8a−c] this would not be the case.

The high turnover can be attributed to a specific interaction between CP$^{\bullet+}$ and PP like a π-complex formation of [CP$^{\bullet+}$/PP]. In the previous paper, we have reported that the inhibition of a photochemical $[4\pi + 2\sigma]$ cycloaddition of DCA and CP, which proceeds via their radical ion pair, by the addition of aromatic hydrocarbons such as Phen.[5] The inhibition of the reaction could be explained by the separation of a pair of DCA$^{\bullet-}$ and CP$^{\bullet+}$ through the complex formation as explained by Pac et al. for the endothermic sensitization reactions instead of the endothermic hole transfer.[5,7] Since radical cations of aromatic hydrocarbons tends to form dimer radical cations as a result of charge resonance stabilization whose transition band has been observed in the IR region of 1000−2000 nm,[20−22] the "hetero-type" π-complex formation would be acceptable.[22j] The charge resonance stabilization in the π-complex formation would be large when the SOMO level of CP$^{\bullet+}$ is close to the HOMO level of PP. Cross-type cycloaddition of alkenes may proceed via hetero-type dimer radical cations.[23] The reactivity of two alkenes is high owing to a high perturbation interaction between their SOMO and HOMO levels when their oxidation potentials are close each other. A weak perturbation between CP$^{\bullet+}$ and PP which does not lead to any reaction may raise the SOMO level of CP$^{\bullet+}$ reducing the reactivity but it would prevent CP$^{\bullet+}$ from its disappearance by a nucleophilic attack by impurities such as water. Increase of the lifetime of CP$^{\bullet+}$ by the π-complex formation could be fairly plausible.

For the photooxygenation of CP, the chain carrier must be a radical cation of the dioxolane (DX$^{\bullet+}$).[24] The oxidation potential of DX is higher than that of *t*-CP by 0.7 V and comparable to that of TP, Phen, and Naph. In this case, π-complex formation between DX$^{\bullet+}$ and PP [DX$^{\bullet+}$/PP] and also a redox equilibrium would be more likely than that between CP$^{\bullet+}$ and PP. However, the lifetime of DX$^{\bullet+}$ would be too short to form the π-complex or to reach the equilibrium in the presence of CP (see below). Therefore, the π-complex formation between PP and CP$^{\bullet+}$ rather than DX$^{\bullet+}$ would play an important role both in the photoisomerization and photooxygenation.

Since the material balance in the photoisomerization and photooxygenation was close to unity,[4,5] the termination of the chain would be the diffusive back-electron transfer from free $O_2^{\bullet-}$ to CP$^{\bullet+}$ or DX$^{\bullet+}$. The larger value of the turnover for the oxygenation than that of the isomerization in the absence of the additives could be explained by the competition between chain propagation and the termination by the back-electron transfer.[25] The hole transfer in the isomerization takes place from *t*-CP$^{\bullet+}$ to *c*-CP with a free energy change of −0.1 eV and its rate constant would be close to those of self-exchange reactions of 10^8−10^9 M^{-1} s^{-1}. On the other hand, the hole transfer from DX$^{\bullet+}$ to *t*-CP with an exothermicity of −0.7 eV in the oxygenation would take place in a diffusion-controlled rate ($\approx 10^{10}$ M^{-1} s^{-1}), although following attack of oxygen on CP$^{\bullet+}$ reproducing DX$^{\bullet+}$ is a slow process ($<10^8$ M^{-1} s^{-1}). Therefore, the lifetime of DX$^{\bullet+}$ would be much shorter ($<$10 ns) in the presence of 10^{-2} M CP as compared to that of CP$^{\bullet+}$ and the deactivation of the both reactions must be due to electron transfer from free $O_2^{\bullet-}$ to the long-lived CP$^{\bullet+}$.

We have measured the second-order rate constants for the decay of *t*-CP$^{\bullet+}$ in the absence and presence of PP upon the photolysis of an aerated acetonitrile solution of *t*-CP containing DCN. As shown in Figure 3b, the plots of the reciprocal of the transient absorbance at 560 nm (1/ΔOD) showed a linear relationship with time indicating the second-order kinetics. This can be attributed to the diffusive back-electron transfer from $O_2^{\bullet-}$ to CP$^{\bullet+}$ as shown in Scheme 3. The second-order rate constants for the decay of *t*-CP$^{\bullet+}$ were determined from the slope of the plots, the molar extinction coefficient at 560 nm (4800

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(24) The oxygenation of CP$^{\bullet+}$ giving DX must involve two DX$^{\bullet+}$ forms of an open-ring DX$^{\bullet+}$ and a closed-ring DX$^{\bullet+}$, although the structure of DX$^{\bullet+}$ as a chain carrier is not clear. The open-ring DX$^{\bullet+}$ seems to have a lifetime enough for an internal rotation giving a stable isomer of DX by ring closure. Ichinose, N.; Mizuno, K. Tamai, T.; Otsuji, Y. *J. Org. Chem.* **1990**, *55*, 4079.

(25) Since the quantum yield of the photoisomerization under nitrogen in the absence of additives is small ($<$0.01) and cis−trans ratio in the stationary state is the same as that in the presence of additives, the contribution of a 1,3-biradical[26] formed by the BET within the SSRIP of DCA and CP would be small.

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Table 5. Effects of Polyphenylene Compounds on the Second-Order Rate Constants for the Decay of *t*-CP$^{\bullet+}$ Generated by the Photoinduced Electron Transfer from *t*-CP to ^{1}DCN* in Aerated Acetonitrile

additive	concn/M	$10^{-9}k_{CP^{\bullet+}}$/M^{-1} s^{-1} [a]
none		14 ± 2
BP	2.5×10^{-2}	11 ± 1
o-TP	2.5×10^{-2}	7.3 ± 1
m-TP	2.5×10^{-2}	9.0 ± 1
p-TP	5.0×10^{-3}	9.5 ± 1.5
Naph	2.5×10^{-2}	8.0 ± 1

[a] Obtained by the laser flash photolysis of aerated acetonitrile solutions containing DCN as a sensitizer: [DCN] = 1×10^{-3}; [*t*-CP] = 2.5×10^{-2} M. Excitation wavelength: 355 nm. Laser intensity: 15 mJ pulse^{-1}. The rate constants were calculated from the slope of the plots of 1/Δ*OD* vs time (see text).

M^{-1} cm^{-1}) of *t*-CP$^{\bullet+}$, and a path length (0.6 cm). The results are listed in Table 5. Though the rate constant in the absence of PP showed a nearly diffusion-controlled rate of 1.4×10^{10} M^{-1} s^{-1}, the addition of PP decreased the rate constants by 0.5−0.7. The effects of TP on the decrease in the rate constants were larger than that of BP, being similar to those on the increase of turnover values for both reactions. This could be due to a stronger interaction of TP with CP$^{\bullet+}$ than that of BP possibly owing to the larger π-system of TP as compared with that of BP. The results could support the retardation of the chain termination and strongly suggest the formation of the π-complex formation between *t*-CP$^{\bullet+}$ and PP. The chain termination would be retarded for the π-complex formation for the reasons (i) the dispersion of the positive charge which reduces the Coulobmic interaction between CP$^{\bullet+}$ and O$_2^{\bullet-}$, and (ii) reduction of the diffusion constant by the increase of the molecular volume. The mechanism for the retardation of the diffusive back-electron transfer by the π-complex formation or hetero-dimer radical cation is currently being studied.

Conclusion

We have determined the turnover values for the photochemical chain reactions of 1,2-bis(4-methoxyphenyl)cyclopropane (CP) radical cation by a comparison between the quantum yields for the chemical reactions and the radical cation yield in the absence and presence of polyphenylene (PP) cosensitizers such as *o*- and *m*-terphenyls. The role of these compounds in the DCA−CP system is summarized in Scheme 3. These compounds effectively quench the fluorescence of DCA more than biphenyl giving their radical cation in fairly high yields and are more stable than phenanthrene or naphthalene which showed a similar cosensitization effect. The turnover depends on the cosensitizer used and not on the initial yield of CP$^{\bullet+}$. Though the mechanism involved has not been completely clarified, an interaction, possibly π-complex formation between CP$^{\bullet+}$ and cosensitizer, must play an important role in stabilizing CP$^{\bullet+}$ as a hole carrier.

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