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Chemical Behavior of Aromatic Radical Cations under Superoxide-Free Electron Transfer Photooxygenation Conditions

Shigeru FUTAMURA
Research Center for Advanced Science and Technology, The University of Tokyo,
4-6-1, Komaba, Meguro-ku, Tokyo 153

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The electron transfer photooxygenations of aromatic compounds were carried out with trityl salts. Under these superoxide-free reaction conditions, only anthracene and 1,1-diarylethylenes were photooxygenated, stilbenes isomerized, and quantitatively recovered were naphthalene, phenanthrene, alkylnaphthalenes, tetraphenylethylene and 1,1,4,4-tetraaryl-1,3-butadienes. The reactivities of their radical cations toward triplet oxygenation were discussed on the basis of the quantum yield measurements and product analyses.

Electron transfer photooxygenations of organic compounds have attracted much attention from synthetic and mechanistic viewpoints[1] since the pioneering work by Barton.[2] A variety of active oxygen species involved, however, makes the above reactions difficult to understand. This complexity cannot be avoided with arenecarbonitrile sensitizers such as 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene.

One of the current topics in this area could be the triplet oxygenation of organic radical cations generated under electron transfer photooxygenation conditions.[3] Akaba and co-workers have shown that no superoxide is generated in the 2,4,6-triphenylpyrylium cation-sensitized photooxygenation of adamantylideneadamantane although the fate of 2,4,6-triphenylpyranyl radical is not clear.[4]

The author's interest has been concentrated on the structure-reactivity relationship for the triplet oxygenation of organic radical cations. The triphenylcarbenium ion (Ph_3C^+) can be a useful probe in assessing the reactivities of the electron donor radical cations toward triplet oxygenation because of the good electron accepting ability of $^1Ph_3C^{+*}$ and the energetically unfavorable electron transfer from $Ph_3C\cdot$ to $^3O_2$.[5]

This paper presents the chemical behavior of the aromatic radical cations formed in one-electron transfer from unsubstituted arenes, alkylnaphthalenes, aromatic olefins and aromatic dienes to $^1Ph_3C^{+*}$.

Experimental

Instrumental. The HPLC analyses were carried out on a Shimadzu LC-3A with a column of μ-PORASIL (silica gel). The GC analyses were carried out on a Shimadzu GC-9A-FID apparatus with a stainless steel column of 5% OV 17 on Chromosorb W (DMCS). The MS and GC-MS analyses were carried out on a Shimadzu QP-1000 apparatus with a glass column of 1.5% OV 17 on Shimalite W (DMCS). The IR spectra were taken on a Shimadzu IR-420 Infrared Spectrophotometer. The NMR spectra were obtained on a JNM GX 400 FT NMR Spectrometer (400 MHz). The melting points were measured by means of a Yazawa hot plate and are uncorrected.

Materials. All the trityl salts were obtained from Aldrich and used as received.

Naphthalene, phenanthrene, and *trans*-stilbene were recrystallized from ethanol–$CHCl_3$. 1-Methyl- and 1-ethylnaphthalenes were column chromatographed (silica gel, hexane). Anthracene was purified by sublimation.

Di-1-naphthylmethane (DNM) was synthesized according to the method described in the literature.[6]

cis-Stilbene was synthesized in the $[Ru(bpy)_3]^{2+}$-sensitized isomerization of *trans*-stilbene in MeCN under nitrogen. The crude *cis*-stilbene (purity>97%) was purified by column chromatography (isolated yield=57%, purity>99%).

The three 1,1-diarylethylenes were synthesized as follows: A cyclohexane–ether (7 : 3) solution of methyltriphenylphosphonium bromide (0.1 mol) and phenyllithium (0.1 mol) was stirred under nitrogen at ambient temperature for 3 h, and then refluxed for 2—12 h after addition of an ethereal solution of a diaryl ketone. The salt was filtered out and the organic materials were column chromatographed (silica gel, hexane). The crude 1,1-diarylethylenes were recrystallized from ethanol–$CHCl_3$ twice.

1,1-Bis(4-chlorophenyl)ethylene (BCPE): Mp 79.4—80.2 °C; MS *m*/*z* 250 (50), 248 (76, M^+), 213 (44), 178 (100).

1,1-Bis(4-methylphenyl)ethylene (BYPE): Mp 56.1—56.8 °C; MS *m*/*z* 208 (100, M^+), 193 (91), 178 (55).

1,1-Bis(4-methoxyphenyl)ethylene (BTPE): Mp 131.7—132.3 °C; MS *m*/*z* 240 (100, M^+), 209 (26).

1,1,4,4-Tetraphenyl-1,3-butadiene (TPBD) and 1,1,4,4-tetrakis(4-methoxyphenyl)-1,3-butadiene (TMBD) were synthesized according to the method of Hüttel.[7]

TPBD: Mp 193.3—194.1 °C; MS *m*/*z* 358 (100, M^+), 167 (77).

TMBD: Mp 202.2—202.6 °C; MS *m*/*z* 478 (100, M^+), 227 (6.9).

Benzene was purified conventionally. MeCN (reagent special grade) was dried over P_2O_5 and distilled before use. CH_2Cl_2 and $CHCl_3$ were washed with water and dried over $MgSO_4$ and distilled.

Photooxygenation of Aromatic Compounds in the Presence of Trityl Salt. A solution of an aromatic compound (10^{-2} mol dm^{-3}) and a trityl salt (10^{-2} mol dm^{-3}) was irradiated with a 200-W superhigh-pressure mercury arc (Shimadzu–Bausch–Lomb SP-200) through a Toshiba glass filter L-39 ($\lambda \geqq 390$ nm) with O_2 bubbling at ambient temperature.

Product Analysis. The solvents were evaporated and the reaction mixtures were poured into water. The organic materials were extracted with $CHCl_3$. According to this procedure, the remaining Ph_3C^+ was recovered as triphenylmethanol. After isolation by column chromatography and TLC (hexane–ether), the products were identified by their spectral properties and by comparison with authentic samples.

1,1,4,4-Tetrakis(4-methoxyphenyl)butane (TMPB): ^{1}H NMR ($CDCl_3$) δ=1.68 (4H, d), 3.64 (12H, s), 4.67 (2H, t), 6.72 (8H, d), 7.03 (8H, d); IR 2847, 1178 cm^{-1}; MS (DI, 20 eV) *m/z* 482 (21, M$^+$), 227 (100), 165 (13); elemental analysis: Found: C, 79.48; H, 7.15%. Anal. Calcd. for $C_{32}H_{34}O_4$: C, 79.64; H, 7.10%.

The quantitative analyses were carried out by HPLC and GC.

Quantum Yields. Potassium tris(oxalato)ferrate(III) actinometry and the procedure described by Murov[8] were used. The light source was a 200-W superhigh-pressure mercury arc and the 405 nm line was isolated by a Shimadzu–Bausch–Lomb monochrometer. The light intensity was determined twice before the irradiation (1.08×10^{-9} E min^{-1}). No variation in light intensity was detected during the experiment. Irradiations of the substrate (10^{-2} mol dm^{-3}) and the trityl salt (10^{-2} mol dm^{-3}) in oxygen-saturated MeCN solutions in 3 ml cuvettes were carried out to ca. 3% conversion (2 h). The reactions were monitored by GC and HPLC. The photooxygenation of BCPE and $Ph_3C^+BF_4^-$ was used as an actinometer for the measurements of the quantum yields for the other photooxygenations, which were irradiated on a merry-go-round.

Results and Discussion

Mechanistic Aspects. Table 1 summarizes the oxidation potentials of the electron donors (ED) and the quantum yields for the loss of ED and Ph_3C^+ in their photooxygenations. Scheme 1 shows a set of the processes likely involved in the photooxygenation of Ph_3C^+ and ED.

Table 1. Oxidation Potentials of the Electron Donors (ED) and the Quantum Yields for the Loss of ED and Ph_3C^+ in Their Photooxygenations

Electron donor	$E^{Ox}_{1/2}(ED/ED^{+\cdot})$[a] (V vs. SCE)	ϕ_{-ED}	$\phi_{-Ph_3C^+}$
Naphthalene	1.79	≃0	0.5
Anthracene	1.12	0.7	0.9
DNM	1.79	≃0	0.4
trans-Stilbene	1.53	0.3	0.4
cis-Stilbene	1.67	0.3	0.4
Tetraphenylethylene	1.44	0.003	0.2
BCPE	1.87	0.7	0.6
BYPE	1.65	2.2	0.7
BTPE	1.38	5.9	0.5
TPBD	1.43	≃0	0.5
TMBD	1.08	≃0	0.7

DNM=Di-1-naphthylmethane, BCPE=1,1-bis(4-chlorophenyl)ethylene, BYPE=1,1-bis(4-methylphenyl)ethylene, BTPE=1,1-bis(4-methoxyphenyl)ethylene, TPBD=1,1,4,4-tetraphenyl-1,3-butadiene, TMBD=1,1,4,4-tetrakis(4-methoxyphenyl)-1,3-butadiene. a) Measured in MeCN, concentration of ED (10^{-3} mol dm^{-3}), tetrabutylammonium perchlorate (10^{-4} mol dm^{-3}) as supporting electrolyte, ferrocene (10^{-3} mol dm^{-3}) as internal standard.

One-electron transfer from ED to $^1Ph_3C^{+*}$ (Eq. 5) is exothermic according to the Rehm–Weller's equation ($\Delta G_{ET}=96.62[E^{Ox}_{1/2}(ED/ED^{+\cdot})-E^{Red}_{1/2}(Ph_3C^+/Ph_3C\cdot)-e^2/\varepsilon a-\Delta E_{0,0}(Ph_3C^+)]=-182\sim-111$ kJ mol^{-1}) since $E_S(Ph_3C^+)=2.66$ eV,[9] $e^2/\varepsilon a=0.06$ and $E^{Red}_{1/2}(Ph_3C^+/Ph_3C\cdot)=0.29$ V vs. SCE in MeCN.[10] The alternative process could be the electron transfer from ED to $^3Ph_3C^{+*}$ (Eq. 6), but the heavy atom effect on this reaction with $CHCl_3$ solvent or 1-iodopropane as additive in MeCN indicates that the electron acceptor is $^1Ph_3C^{+*}$ in this reaction system.

In the absence of ED, Ph_3C^+ was consumed more slowly ($\phi_{-Ph_3C^+}=0.1$), suggesting that BF_4^- is an ineffective electron donor to $^1Ph_3C^{+*}$. $Ph_3C\cdot$ and/or ED can be electron donors in the reduction of the ED-derived arylperoxyl radical cations such as $(ED\text{–}O_2)^{+\cdot}$ and $((ED)_2\text{–}O_2)^{+\cdot}$ (Eqs. 9 and 11).

The Schenck-type triplet oxygenation of $^3Ph_3C^{+*}$ (Eq. 4) is most unlikely from comparison of the product distribution with those in the precedent reports.[11,12]

Formation of superoxide is energetically unfavorable in the above photooxygenations because the electron transfer from $Ph_3C\cdot$ to $^3O_2$ is endothermic by 62.8 kJ mol^{-1}. Triphenylmethyl peroxide was exclusively afforded from Ph_3C^+ as primary product (Eq. 7). This

$$\mathrm{Ph_3C^+} \xrightarrow{h\upsilon} \mathrm{{}^1Ph_3C^{+*}} \tag{1}$$

$$\mathrm{{}^1Ph_3C^{+*}} \xrightarrow{isc} \mathrm{{}^3Ph_3C^{+*}} \tag{2}$$

$$\mathrm{{}^3Ph_3C^{+*} + {}^3O_2 \longrightarrow Ph_3C^+ + {}^1O_2} \tag{3}$$

$$\mathrm{{}^3Ph_3C^{+*} + {}^3O_2 \longrightarrow Ph_3C\text{-}O_2{}^+ \longrightarrow \longrightarrow Oxygenated\ products} \tag{4}$$

$$\mathrm{{}^1Ph_3C^{+*} + ED \rightleftharpoons Ph_3C\cdot + ED^{+\cdot}} \tag{5}$$

$$\mathrm{{}^3Ph_3C^{+*} + ED \rightleftharpoons Ph_3C\cdot + ED^{+\cdot}} \tag{6}$$

$$\mathrm{Ph_3C\cdot + {}^3O_2 \longrightarrow Ph_3C\text{-}O_2\cdot \xrightarrow{Ph_3C\cdot} Ph_3C\text{-}O\text{-}O\text{-}CPh_3} \tag{7}$$

$$\mathrm{ED + {}^1O_2 \longrightarrow Oxygenated\ products} \tag{8}$$

$$\mathrm{ED^{+\cdot} + {}^3O_2 \rightleftharpoons (ED\text{-}O_2)^{+\cdot} \xrightarrow{e^-} Oxygenated\ products} \tag{9}$$

$$\mathrm{ED^{+\cdot} + ED \longrightarrow (ED)_2{}^{+\cdot}} \tag{10}$$

$$\mathrm{(ED)_2{}^{+\cdot} + {}^3O_2 \rightleftharpoons ((ED)_2\text{-}O_2)^{+\cdot} \xrightarrow{e^-} Oxygenated\ products} \tag{11}$$

Scheme 1. Plausible reaction mechanism.

fact also supports that the triplet oxygenation of $Ph_3C\cdot$ predominates over the electron transfer from $Ph_3C\cdot$ to $^3O_2$.

$^1O_2$ is a possible active oxygen species because the energy transfer from $^3Ph_3C^{+*}$ to $^3O_2$ (Eq. 3) is exothermic ($E_T(Ph_3C^+)=2.48$ eV).[9] Singlet oxygenation of ED (Eq. 8), however, can be ruled out since the rates of ED and the product distributions are quite different from those in their singlet oxygenations.[13,14]

Thus, this reaction system is appropriate in discussing the chemical behavior of $ED^{+\cdot}$, which is relevant to its susceptibility to triplet oxygenation.

Unsubstituted Arenes. Documentation has been sparse on the triplet oxygenation of this compound class. In this research, naphthalene, phenanthrene and anthracene were chosen as representatives.

Anthracene was the most reactive, and anthraquinone was obtained in 35% yield at the anthracene conversion=77% (Fig. 1). Anthrone was not detected by GC.

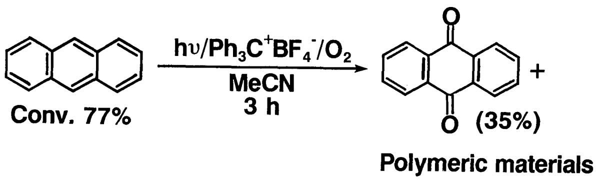


Fig. 1. Photooxygenation of anthracene in the presence of $Ph_3C^+BF_4^-$.

Intermediacy of anthracene radical cation can be supported by the facts that anthraquinone was not derived from singlet oxygenation or nonsensitized oxygenation of anthracene. The low selectivity of anthraquinone can be ascribed to the reversible triplet oxygenation of the anthracene radical cation (Eq. 9) and anthracene telomerization. Telomeric addition of anthracene radical cation to anthracene[15] is considered to predominate over its oxygenation even under oxygen.

On the other hand, naphthalene and phenanthrene were recovered in more than 95% yields, respectively, with no oxygenated products. These facts suggest that their radical cations are unreactive toward triplet oxygenation and electrophilic addition. They could be inert like those of methoxybenzenes.[16]

The contrast in the chemical behavior of these two compounds and anthracene would reflect the differences in the $^3O_2$ accepting abilities of their radical cations and in the stabilities of the arylperoxyl radical cations ($(ED-O_2)^{+\cdot}$ in Scheme 1).

The relative reactivities of the radical cations from anthracene and phenanthrene are interestingly the same as those in their anodic fluorination in $[N(CH_3)_4][H_2F_3]$.[17]

Alkylnaphthalenes. In the photooxygenation of DNM and $Ph_3C^+BF_4^-$, Ph_3C^+ was photooxygenated at almost the same rate as with naphthalene (Table 1), and DNM was also quantitatively recovered. This result contrasts with the DCA-sensitized photooxygenation of DNM, which rapidly affords 1-naphthaldehyde and 1,4-naphthoquinone as major products.[18]

No oxygenated products were obtained from 1-methylnaphthalene ($E_{1/2}^{ox}=1.35$ V vs. SCE) or 1-ethylnaphthalene although Ph_3C^+ was more rapidly photooxygenated compared with DNM addition. These facts suggest that the radical cations of alkylnaphthalenes are stable under the reaction conditions.[19]

No photooxygenation of the above alkylnaphthalenes proceeded with $Ph_3C^+PF_6^-$, $Ph_3C^+SnCl_5^-$ or $Ph_3C^+SbCl_6^-$ as trityl salt, indicating that the basicities of BF_4^-, PF_6^-, $SnCl_5^-$ and $SbCl_6^-$ are too low to deprotonate the radical cations of the alkylnaphthalenes (Fig. 2).

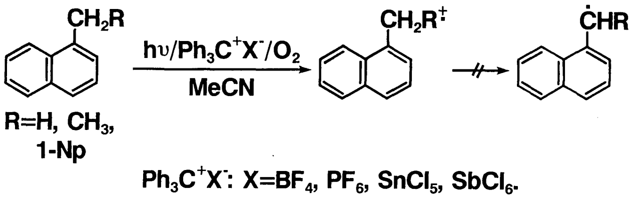


Fig. 2. Unlikely deprotonation from alkylnaphthalene radical cations in the presence of the trityl salt.

According to this work and the literature,[20] it can be said that electron transfer oxygenation of alkylarenes does not proceed in aprotic solvents such as MeCN and $CHCl_3$ in the absence of a good proton acceptor like superoxide.

Stilbenes. In the photooxygenations of $Ph_3C^+BF_4^-$ with *trans-* and *cis*-stilbenes for 3 h, the Ph_3C^+ conversions were only 37 and 33%, respectively. Comparison of the data in Table 1 suggests that the back electron transfer from $Ph_3C\cdot$ to the stilbene radical cations (Eq. 5) cannot be negligible.

No oxygenated products were obtained from *trans-* or *cis*-stilbene, and stilbene isomerized from trans to cis (8%) and from cis to trans (15%). These facts contrast with the Methylene Blue-sensitized photooxygenation of *trans*-stilbene reported by Foote.[21]

Energy transfer mechanism for the stilbene isomerization is unlikely because isomerization efficiency reverses the exothermicity in the triplet energy transfer from $^3Ph_3C^{+*}$ (E_T(*trans*-stilbene)=210 kJ mol^{-1} and E_T(*cis*-stilbene)=240 kJ mol^{-1}). The more effective isomerization from *cis-* to *trans*-stilbene is considered to reflect the different stabilities of the stilbene radical cations.

The low reactivities of the stilbene radical cations toward $^3O_2$ can be ascribed to the delocalization of the unpaired electron on its whole molecule.

Tetraphenylethylene. Both the quantum yields for the loss of tetraphenylethylene and Ph_3C^+ (Table 1) were unexpectedly low in spite of the strong electron donating ability of tetraphenylethylene. Even on 12 h irradiation, no benzophenone or tetraphenyloxirane was obtained from tetraphenylethylene. These observations do suggest the predominant back electron transfer from $Ph_3C\cdot$ to tetraphenylethylene radical cation in this system. Steric hindrance caused by nonplanar phenyl groups against the attack by $^3O_2$[16] could not be the unique explanation for the low reactivity of tetraphenylethylene.

1,1-Diarylethylenes. The chemical behavior of the 1,1-diarylethylene was greatly affected by the substituents on the aryl groups (Fig. 3).

The 3 h photooxygenations of BCPE and BYPE afforded the corresponding benzophenones in 53 and 89% yields without 1,2-dioxane formation, respectively. These benzophenones could be derived from the decomposition of the dioxetanes formed in Eq. 9.[16]

On the other hand, BTPE was completely consumed in 1 h to give TMPB and 3,3,6,6-tetrakis(4-methoxyphenyl)-1,2-dioxane in 68 and 19% yields, respectively. Only a trace amount of 4,4′-dimethoxybenzophenone was detected by GC-MS. The 1,2-dioxane yield is moderate, compared with the photooxygenations of BTPE with $SbCl_5$,[22] DCA,[23,24] or xanthene dyes.[25]

HPLC analysis showed that TMPB was a primary photoproduct. Thus, triplet oxygenation of the BTPE dimer radical cation is not necessarily a predominant process under the superoxide-free oxidation conditions.[1]

The above findings show that the reactivity of the 1,1-diarylethylene radical cation toward triplet oxygenation (Eq. 9) and formation of the dimer radical cation (Eq. 10) is greatly controlled by the substituents at the 4-positions of the phenyl groups under the conditions at [$^3O_2$]≈ 10^{-2} mol dm^{-3}≧[1,1-diarylethylene]. Formation of BTPE dimer radical cation could be promoted by the electron-rich nature of BTPE and the enhanced stability of the BTPE dimer radical cation, both of which are caused by the 4-methoxyphenyl groups.

The quantum yields for the loss of the olefins are lower than those in their DCA-sensitized photooxygenations.[16,26] These facts are reasonable because the quantum yields are expected to be smaller for the addition of $^3O_2$ to olefin radical cations, compared with superoxide addition.

Interestingly, the quantum yields for the loss of BCPE, BYPE and BTPE are 1.2- to 11.8-fold larger than that of Ph_3C^+. These facts show that a chain mechanism operates in the formation of the 1,1-diarylethylene radical cations.

No formation of epoxides is an interesting feature in the triplet oxygenation of the 1,1-diarylethylene radical cations. This can be explained in terms of the different reactivities of biradicals **A** and **B** in Scheme 2. Biradical **A**, which is formed in the coupling of the 1,1-diarylethylene radical cation and superoxide, has a relatively long lifetime because of delocalization of the unpaired electron on the carbon atom. Thus, tetroxide formation can compete with dioxetane formation (Eq. 12). Epoxides can be derived from the decomposition of the tetroxides (Eq. 13). On the other hand, such spin delocalization cannot be expected for biradical **B**, which is formed in the coupling with $^3O_2$. Thus, biradical **B** rapidly affords the dioxetanes and the benzophenones

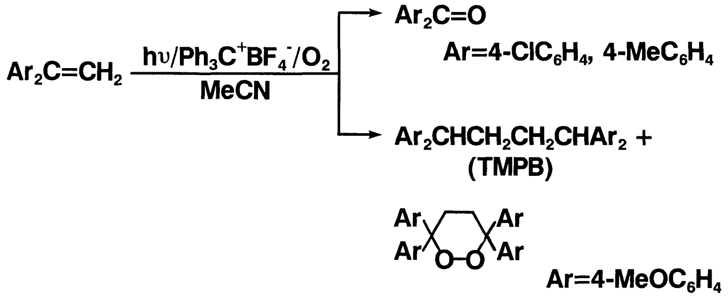
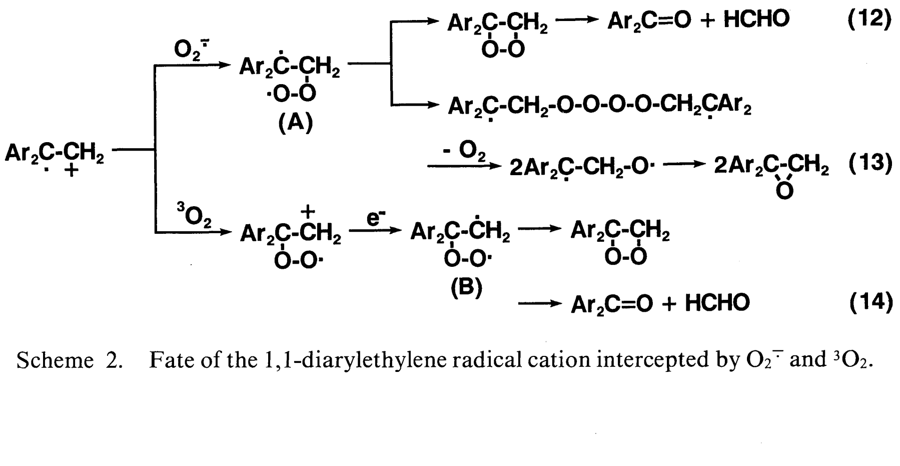


Fig. 3. Photooxygenation of 1,1-diarylethylenes in the presence of $Ph_3C^+BF_4^-$.



Scheme 2. Fate of the 1,1-diarylethylene radical cation intercepted by $O_2^{\cdot-}$ and $^3O_2$.

are exclusively derived from their decomposition.

The data in Table 1 have clearly shown that the olefin oxidation potential is not a pertinent measure to evaluate its reactivity in its electron transfer photooxygenation. The structure of the olefin radical cation can be the determining factor for its susceptibility to triplet oxygenation.

1,1,4,4-Tetraaryl-1,3-butadienes. When TPBD and TMBD were used as ED, the unexpectedly lower quantum yields were obtained for the loss of Ph_3C^+, compared with the 1,1-diarylethylenes (Table 1). These findings suggest that the back electron transfer cannot be neglected in the cases of TPBD and TMBD.

Either of TPBD and TMBD was quantitatively recovered after the 5 h reaction with Ph_3C^+. Therefore, their radical cations should be unreactive toward $^3O_2$.

Compared with the highly reactive natures of the 1,1-diarylethylenes, the almost no reactivities of the 1,1,4,4-tetraaryl-1,3-butadienes may be ascribed to the enhanced spin delocalization on their radical cations.

Conclusions

1) The reactivities of the aromatic compounds toward superoxide-free electron transfer photooxygenation highly depend on the structures of their radical cations ($ED^{+\cdot}$): photooxygenation of anthracene and 1,1-diarylethylenes, isomerization of stilbenes, and almost quantitative recovery of naphthalene, phenanthrene, alkylnaphthalenes, tetraphenylethylene, and 1,1,4,4-tetraaryl-1,3-butadienes.

2) The determining factor in the triplet oxygenation of $ED^{+\cdot}$ is its $^3O_2$ accepting ability, which may be controlled by the degree of spin delocalization on the $ED^{+\cdot}$ molelcule and the stabilities of the arylperoxyl radical cations such as $(ED-O_2)^{+\cdot}$ and $((ED)_2-O_2)^{+\cdot}$.

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