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Photoinduced Electron Transfer Oxygenation of Triphenylcarbenium Ion¹⁾

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Photooxidation of triphenylcarbenium ion in the presence of an electron donor affords bis(triphenylmethyl) peroxide via one electron transfer from the electron donor to the excited singlet state of triphenylcarbenium ion.

Trityl salts have been widely used as an effective catalyst in the Barton type oxidation reactions of dienes²⁾ and photooxidative cleavage of cyclobutanes,³⁾ but the chemical behavior of triphenylcarbenium ion toward photoinduced electron transfer reactions has been sparsely documented in the literature although triphenylcarbenium ion should be reduced to triphenylmethyl radical in these reactions.

We report here that the photooxidation of triphenylcarbenium ion in the presence of an aromatic compound as an electron donor affords bis(triphenylmethyl) peroxide.

An acetonitrile solution of triphenylcarbenium tetrafluoroborate (10^{-2} mol dm^{-3}) and naphthalene (10^{-2} mol dm^{-3}) was irradiated with a 200-W super high pressure mercury arc through a Toshiba glass filter L-39 ($\lambda \geqq 390$ nm) with O_2 bubbling at ambient temperature for 6 h. Column chromatographic separation (hexane-ether, silica gel) of the condensed reaction mixture afforded bis(triphenylmethyl) peroxide,⁴⁾ benzophenone, and phenyl triphenylmethyl ether,⁶⁾ in 11, 64, and 19% isolated yields, respectively (Scheme 1). This product distribution is quite different from those in the photooxidation of triphenylmethanol in H_2SO_4 and in H_2SO_4-CH_3COOH-H_2O, where fluoren-9-one⁷⁾ and diphenylmethylenedioxybenzene⁸⁾ have been obtained, respectively. The irradiation of the authentic sample of bis(triphenylmethyl) peroxide under the photooxidation conditions afforded benzophenone in 67% yield,⁹⁾ indicating that benzophenone can be a secondary product derived from the decomposition of bis(triphenylmethyl)

$$Ph_3C^+BF_4^- \xrightarrow[\substack{MeCN\\6\ h}]{h\nu/O_2,\ NpH} Ph_3C\text{-}O\text{-}O\text{-}CPh_3\ (11\%) + Ph\text{-}\overset{O}{\underset{}{C}}\text{-}Ph\ (64\%) + Ph_3C\text{-}OPh\ (19\%)$$

Scheme 1.

peroxide. Only benzophenone was detected with a trace amount of triphenylmethane by the direct GC analysis of the reaction mixture, which indicates that phenyl triphenylmethyl ether is derived from the decomposition of bis(triphenylmethyl) peroxide in the isolation process. This speculation was confirmed by the following experiments: the thermal decomposition of bis(triphenylmethyl) peroxide on the GC column afforded benzophenone almost quantitatively[9)] and bis(triphenylmethyl) peroxide decomposed on a silica gel column to give phenyl triphenylmethyl ether in 62% yield.

Triphenylcarbenium ion was not oxidized in the dark. In the absence of naphthalene, the conversion of triphenylcarbenium ion was as low as 24%.

In the 3 h photooxidation of triphenylcarbenium tetrafluoroborate in the presence of naphthalene, its conversion decreased from 60 to 10% on addition of 1-iodopropane (10^{-2} mol dm^{-3}). This external heavy atom effect suggests that the reaction proceeds via the excited singlet state of triphenylcarbenium ion ($^1Ph_3C^{+*}$).[3)]

Table 1 shows the additive effect of some aromatic compounds on the conversion of triphenylcarbenium ion. The aromatic compounds with lower oxidation potentials than that of naphthalene promote the photooxidation of triphenylcarbenium ion more effectively, but there seems to be a poor correlation between their oxidation potentials and the conversion of triphenylcarbenium ion, i.e. anthracene and 1,1,4,4-tetraphenyl-1,3-butadiene were less effective donors than expected. This can be ascribed to the different reactivities of the aromatic compounds under the reaction conditions. Naphthalene, di(1-naphthyl)methane, and phenanthrene were recovered almost quantitatively, while anthracene and 1,1,4,4-tetraphenyl-1,3-butadiene were completely consumed to afford anthraquinone and phenyl 1,3,3-triphenylprop-2-enyl ketone,[10)] respectively.

Singlet oxygen cannot be an active oxygen species in these reactions since the $Ru(bpy)_3{}^{2+}$-sensitized photooxidation of anthracene and 1,1,4,4-tetraphenyl-1,3-butadiene did not give any oxygenated products.

Table 1. Additive effect of aromatic compounds on the conversion of triphenylcarbenium ion

Additive	$E_{1/2}^{Oxd}$ /V vs. SCE[a)]	Ph_3C^+ conv./mol%[b)]
Naphthalene	1.79	60
Di(1-naphthyl)methane	1.79	61
Phenanthrene	1.38	79
Anthracene	1.12	77
1,1,4,4-Tetraphenyl-1,3-butadiene	1.43	68

a) The oxidation potentials of the additives (5.0×10^{-3} mol dm^{-3}) were measured in dry MeCN, using tetrabutylammonium perchlorate (10^{-2} mol dm^{-3}) as supporting electrolyte. b) The photooxidation reactions were carried out at room temperature for 3 h. The concentrations of triphenylcarbenium tetrafluoroborate and aromatic additives were 10^{-2} mol dm^{-3}.

Table 2. Solvent effect on the photooxidation of triphenylcarbenium tetrafluoroborate (TTFB) in the presence of naphthalene

Solvent	ε	Ph_3C^+ conv./mol%
CH_3CN	37.5	65
CH_3CN-PhH (2:8 v/v)		30
CH_2Cl_2	9.08	14
$CHCl_3$	4.81	9.8
PhH	2.28	a)

The photooxidation reactions were carried out at room temperature for 3 h. The concentrations of TTFB and naphthalene were 10^{-2} mol dm^{-3}.

a) TTFB was insoluble.

These results suggest that the aromatic compounds act as an electron donor, and that the cation radicals derived from anthracene and 1,1,4,4-tetraphenyl-1,3-butadiene are oxygenated, competing with triphenylcarbenium ion. High recovery of naphthalene, di(1-naphthyl)methane, and phenanthrene suggests that the regenerative one electron transfer from these compounds to the corresponding cation radicals predominates over the triplet oxygenation of these cation radicals. The lower reactivities of naphthalene and phenanthrene cation radicals toward triplet oxygen can be ascribed to their higher planarities, compared with anthracene cation radical. For di(1-naphthyl)methane cation radical, steric hindrance by a naphthyl group is also indicated.

Table 2 shows that the conversion of triphenylcarbenium ion decreases in less polar solvents even in the presence of naphthalene. This solvent effect indicates that a triplet oxygen molecule reacts with free triphenylmethyl radical and the free cation radical of the electron donor, both of which are derived from the dissociation of the exciplex, one of the possible intermediates.

All these findings support a reaction mechanism depicted in Scheme 2. An

$$Ph_3C^+BF_4^- \xrightarrow{h\nu} {}^1(Ph_3C^+BF_4^-)^* \qquad (1)$$

$${}^1(Ph_3C^+BF_4^-)^* + ED \longrightarrow {}^1[Ph_3C\cdot BF_4^- \cdots ED^{+\cdot}]^* \qquad (2)$$

$${}^1[Ph_3C\cdot BF_4^- \cdots ED^{+\cdot}]^* \longrightarrow Ph_3C\cdot + ED^{+\cdot} + BF_4^- \qquad (3)$$

$$Ph_3C\cdot + {}^3O_2 \longrightarrow Ph_3C\text{-}O\text{-}O\cdot \qquad (4)$$

$$Ph_3C\text{-}O\text{-}O\cdot + Ph_3C\cdot \longrightarrow Ph_3C\text{-}O\text{-}O\text{-}CPh_3 \qquad (5)$$

$$ED^{+\cdot} + {}^3O_2 \rightleftarrows ED\text{-}O\text{-}O^{\rceil +\cdot} \qquad (6)$$

$$ED\text{-}O\text{-}O^{\rceil +\cdot} \longrightarrow \text{Oxygenated products} \qquad (7)$$

ED=Electron donor

Scheme 2. Plausible reaction mechanism.

electron transfer from BF_4^- to the excited state of Ph_3C^+ cannot be excluded completely at this stage[11] since triphenylcarbenium ion was slowly photooxygenated in the absence of an electron donor.

References

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4) The IR data of bis(triphenylmethyl) peroxide were identical with those of the authentic sample prepared according to Tanaka's method.[5]

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10) Mass spectral data for phenyl 1,1,3-triphenylprop-2-enyl ketone: m/z 374 (5.9, M^+), 269 (100), 191 (76), 105 (29), 91 (27).

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