Triphenylpyrylium-salt-sensitized Electron Transfer Oxygenation of Adamantylideneadamantane. Product, Fluorescence Quenching, and Laser Flash Photolysis Studies

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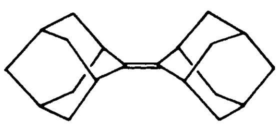
Triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$) has been found to sensitize oxygenation of adamantylideneadamantane to its dioxetane in good yield. Product studies, measurements of quantum yields for dioxetane formation, laser flash photolysis, and quenching experiments of TPP^+ fluorescence by various electron donors have been carried out to elucidate the mechanism for dioxetane formation. Cyclic voltammetry was also used to examine the reactivity of pyryl radicals ($TPP^•$) with molecular oxygen. The results are consistent with a mechanism involving electron transfer from the alkene to the excited states of TPP^+ to give radical pairs consisting of the alkene radical cations and $TPP^•$. The alkene radical cation reacts with molecular oxygen to afford the dioxetane. A singlet oxygen mechanism is not likely since the quenching rate of the excited triplet state of TPP^+ by the alkene is 400 times faster than by dissolved oxygen under the photooxygenation conditions.

Electron transfer oxygenation has been of great recent interest.[1] 9,10-Dicyanoanthracene (DCA) and 9-cyanoanthracene (CNA) have most frequently been employed as sensitizers,[2] and it has been proposed that the oxygenation sensitized by these cyanoaromatics proceeds through the initial electron transfer from a substrate to the excited singlet state of the sensitizer. The electron transfer generates the substrate radical cation and the sensitizer radical anion, which subsequently reduces molecular oxygen to afford a superoxide radical anion. The substrate cation radical reacts with the superoxide anion to give oxygenated products. DCA and CNA are also known to produce their excited triplet states through substrate- or oxygen-enhanced intersystem crossing of their excited singlet states, the triplet states thus formed giving singlet oxygen *via* energy transfer to molecular oxygen.[3] Since the same products or similar product distribution is observed in the reactions of the substrate radical cations with molecular oxygen or the superoxide anion, and in the reactions of the substrate with singlet oxygen, care must be taken to identify the real mechanism involved in the cyanoaromatic-sensitized oxygenation. In order to clarify the mechanisms involved in electron transfer oxygenation in general, it is highly desirable to employ a sensitizer which produces neither singlet oxygen nor the superoxide anion under photooxygenation conditions.

Our own interest in this field has been centred around possible reactions of alkene radical cations with molecular oxygen,[4–6] and we have recently reported our preliminary results on 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$)-sensitized oxygenation of adamantylideneadamantane (**1**) to its dioxetane (**2**), and suggested that the oxygenation proceeds through a reaction of the alkene radical cation with molecular oxygen, but not with the superoxide anion.[5] Although TPP^+ has been used as a sensitizer for a number of electron transfer reactions,[7] little attention has been directed towards TPP^+-sensitized oxygenation of organic compounds. In this paper, we report details of the TPP^+-sensitized electron transfer oxygenation of **1** as studied by measurements of quantum yields for dioxetane formation, quenching of TPP^+ fluorescence by electron donors, and laser flash photolysis. The results show that the TPP^+-sensitized oxygenation of **1** proceeds through electron transfer from **1** not only to the excited singlet state but to the excited triplet state of TPP^+ to generate the radical cation, $1^{+•}$, and $TPP^•$, and that the resulting $1^{+•}$ reacts with molecular oxygen to afford **2**. It was also revealed that the singlet oxygen mechanism is not important in the present oxygenation.



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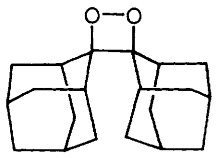

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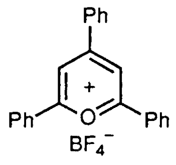
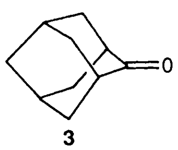


$\overset{+}{TPP}BF_4^-$

Results

TPP^+-Sensitized Oxygenation of **1**.—TPP^+ exhibits its intense absorption bands in the UV–VIS region. The absorption spectra of TPP^+ and **1** are shown in Fig. 1. Since **1** exhibits no absorption in the wavelength region above λ = 300 nm, TPP^+ can be selectively excited in the presence of **1** by a tungsten–halogen lamp through a Pyrex filter (λ > 300 nm).

When a dichloromethane solution of **1** (0.05 mol dm^{-3}) and TPP^+ (2.4×10^{-3} mol dm^{-3}) was irradiated for 10 min with light from a 650 W tungsten–halogen lamp, whilst oxygen at ambient temperature was bubbled through the solution, the dioxetane of **1** (**2**) was obtained in 90% isolated yield (based on amount of **1** consumed). Prolonged irradiation (30 min) of a similar solution



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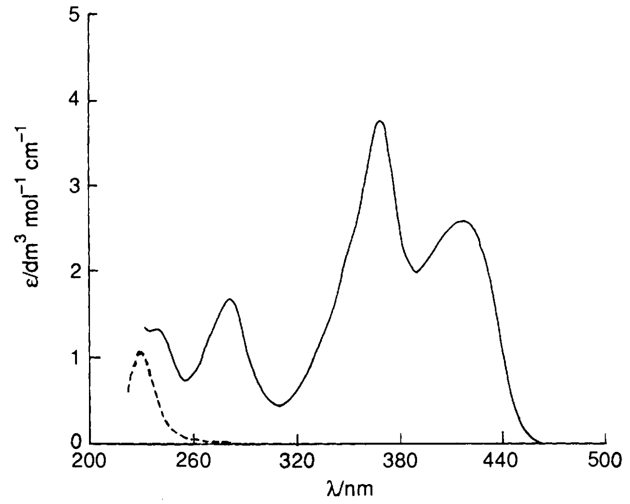


Fig. 1 Absorption spectra of TPP^+ (——) and adamantylideneadamantane **1** (– – –) in dichloromethane

Table 1 Product yield on TPP^+-sensitized oxygenation of adamantylideneadamantane in CH_2Cl_2[a]

Run	Irradiation wavelength λ/nm	Reaction time *t*/min	Yield isolated (%)		
			1	**2**	**3**
1	≥300	10	60	36	unobs.
2	≥300	30	unobs.	unobs.	75
3	≥300[b]	10	83	7	unobs.
4	≥350[c]	25	52	4	37

[a] Unobs.: products not observed. [b] With 1,4-dimethoxybenzene added. [c] A Toshiba L-39 filter was used.

Table 2 Quantum yields for dioxetane **2** formation on TPP^+ sensitization

Run	[**1**]/mol dm^{-3}	Quantum yield
1	0.05	0.08
2	0.03	0.06
3	0.015	0.08

under otherwise identical conditions gave adamantanone (**3**) in 75% isolated yield; **3** was formed by decomposition of **2** under the experimental conditions. Addition of 1,4-dimethoxybenzene (**4**), whose oxidation potential (1.34 V/SCE in CH_3CN)[1b] is lower than that of **1** (1.45 V in CH_3CN[8] and 1.55 V in CH_2Cl_2), retarded the oxygenation appreciably. Thus, irradiation of **1** in dichloromethane in the presence of **4** (6.5 × 10^{-3} mol dm^{-3}, 0.13 equiv.) for 10 min gave **2** in 41% yield (17% conversion). The results are summarized in Table 1.

Bleaching of the sensitizer during photooxygenation was also studied to estimate a catalytic nature of TPP^+ by measuring the absorbance of a λ = 417 nm band of TPP^+ in the reaction mixture. Irradiation of a dichloromethane solution of **1** (0.051 mol dm^{-3}) and TPP^+ (2.4 × 10^{-3} mol dm^{-3}) for 18 min under otherwise the same conditions exerted 26% bleaching of TPP^+ while 54% of **1** was consumed as determined by a weighed yield of recovered **1**. This finding shows that *ca.* 40 times less TPP^+ was consumed compared with **1** during the photooxygenation. Hence, TPP^+ acts as a catalyst in the oxygenation of **1**.

The quantum yield for formation of **2** was determined at several concentrations of **1** (0.015–0.05 mol dm^{-3}), as listed in Table 2. As shown in Table 2, the quantum yield was *ca.* 0.1 under the conditions employed, and does not depend significantly on the concentration of **1** used.

Table 3 Oxidation potentials of donors, Stern–Volmer constants and fluorescence quenching rate constants, and free energy changes associated with electron transfer from the donors to the excited singlet state of TPP^+

Substrate	$E_p^{ox\,a}$/ V(SCE)	$k_q^S\tau_s$/ mol dm^{-3}	k_q^S/dm^3 mol^{-1} s^{-1}	$\Delta G^{\circ\,b}$/ kJ mol^{-1}
1,4-Dimethoxybenzene	1.34[c]	96.3	3.6 × 10^{10}	−113.7
Tetraphenylethylene	1.33[d]	65.6	2.4 × 10^{10}	−114.5
Adamantylideneadamantane	1.45 1.55[e]	63.9	2.4 × 10^{10}	−103.2
trans-Stilbene	1.42[f]	92.3	3.4 × 10^{10}	−106.3
Triphenylethylene	1.53	74.9	2.8 × 10^{10}	−95.3
Biphenyl	1.80[c]	59.4	2.2 × 10^{10}	−69.4
Mesitylene	2.10[g]	53.1	2.0 × 10^{10}	−40.5
4-Chlorotoluene	2.36[g]	32.4	1.2 × 10^{10}	−15.5
Toluene	2.39[g]	29.6	1.1 × 10^{10}	−12.5
Chlorobenzene	2.76[g]	0.48	1.8 × 10^{8}	23.0
Benzene	2.83[g]	0.29	1.1 × 10^{8}	29.7

[a] Values in CH_3CN unless otherwise indicated. [b] A value of −0.28 V (SCE in CH_2Cl_2) was used for the reduction potential of TPP^+. [c] Ref. 1(*b*). [d] Ref. 15(*b*). [e] In CH_2Cl_2. [f] Ref. 4(*c*). [g] S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, 1981, **103**, 7240.

Fluorescence Quenching and Fluorescence Quantum Yield.—To get some insight into the photophysical behaviour of the excited singlet state of TPP^+, quenching of TPP^+ fluorescence by **1** and other electron donors such as aromatic alkenes and hydrocarbons was carried out. The fluorescence quantum yield was determined to be 0.58 in dichloromethane at room temperature (*ca.* 25 °C) under argon.

The bright blue fluorescence (λ_{max} = 467 nm in CH_2Cl_2) was efficiently quenched by **1**. The plot of fluorescence intensity *versus* concentration of **1** fits the Stern–Volmer equation, giving the Stern–Volmer constant ($K_{SV} = k_q^S\tau_S$) as 64 dm^3 mol^{-1}. The quenching rate constant k_q^S is calculated to be 2.4 × 10^{10} dm^3 mol^{-1} s^{-1} by using the singlet lifetime of TPP^+ τ_S = 2.7 ns.[9] Similar experiments were performed for other donors, and the values of K_{SV} and k_q^S are summarized in Table 3. The free energy changes associated with electron transfer from these substrates to the excited singlet state of TPP^+ were estimated according to the Rehm–Weller equation [eqn. (1)],[10] in which $E(D^+/D)$ and

$$\Delta G^\circ(\text{kJ mol}^{-1}) = 96.48[E(D^+/D) - E(A/A^-) - E_{0,0} + e_0^2/\varepsilon a] \quad (1)$$

$E(A/A^-)$ are the electrochemical oxidation potential of donor and reduction potential of acceptor, respectively, and $E_{0,0}$ is the singlet excitation energy of the sensitizer. The term $e_0^2/\varepsilon a$ represents the energy gained by bringing the radical or radical ion species into an encounter distance a in a solvent of relative permittivity ε. In the present calculation, we ignored the contribution of this term, since TPP^+ is positively charged, and hence there is no net change of charge upon electron transfer. The ΔG° values are also shown in Table 3, and a plot of log k_q^S *vs.* ΔG° is depicted in Fig. 2. The correlation in Fig. 2 clearly indicates that electron transfer takes place from the donors to the excited singlet state of TPP^+. It is evident that the quenching of the excited singlet TPP^+ by **1** is diffusion-controlled as calculated above.

Laser Flash Photolysis.—Laser flash photolysis (LFP) is one of the most powerful tools with which to elucidate the nature of the primary events involved in photoinduced electron transfer

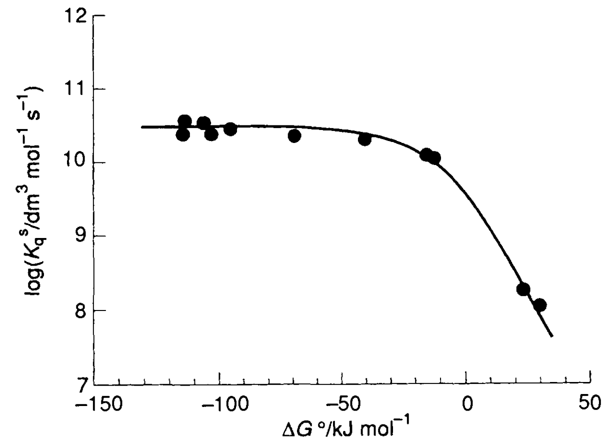


Fig. 2 Plot of log k_q^S as a function of the free energy changes (ΔG°) associated with electron transfer from the donors to the excited singlet state of TPP^+

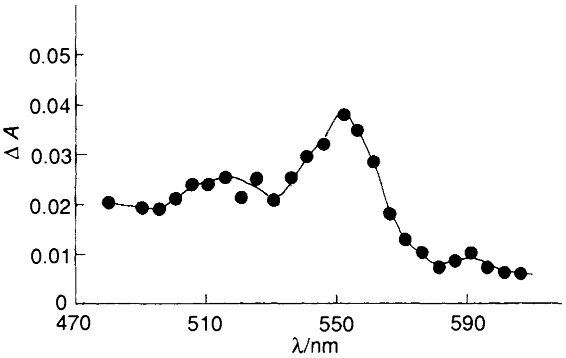


Fig. 3 Transient absorption spectrum derived from laser excitation of TPP^+ (1.6×10^{-4} mol dm^{-3}) in the presence of **1** (6.2×10^{-2} mol dm^{-3}) in dichloromethane under argon (0.8 μs after laser pulse)

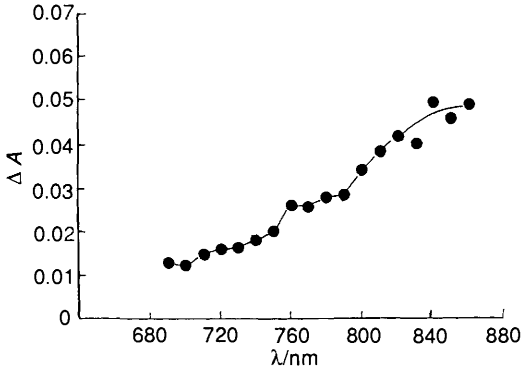


Fig. 4 Transient absorption spectrum derived from laser irradiation of TPP^+ (1.1×10^{-4} mol dm^{-3}) in dichloromethane under argon (1.1 μs after laser pulse)

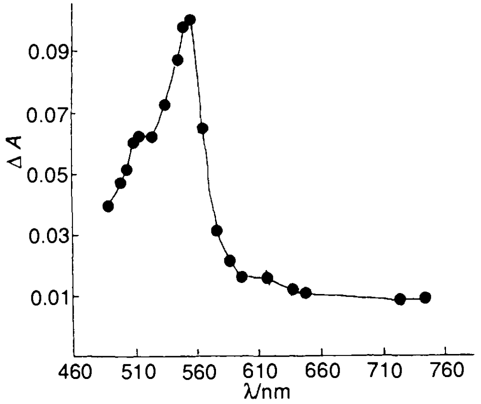


Fig. 5 Transient absorption spectra derived from laser irradiation (λ = 351 nm) of TPP^+ (9.5×10^{-5} mol dm^{-3}) in the presence of **1** (1.4×10^{-4} mol dm^{-3}) in dichloromethane under argon (2 μs after laser pulse)

reactions. In order to get deeper insight into the primary processes in the present oxygenation, we have carried out LFP of TPP^+ in the presence and absence of **1**.

LFP of TPP^+ (1.6×10^{-4} mol dm^{-3}) in the presence of **1** (0.062 mol dm^{-3}) by nitrogen laser pulses (λ = 337 nm) under argon in dichloromethane, where 80% of TPP^+ excited singlets are quenched by **1**, gave a transient absorption (Fig. 3) which can be assigned to pyryl radicals ($TPP^{\bullet}$) by comparison with the spectrum of authentic $TPP^{\bullet}$ generated electrochemically.[11] Laser excitation [excimer (XeCl) laser-pumped dye laser (DPS), λ = 408 nm] of a dichloromethane solution of **1** (0.062 mol dm^{-3}) and TPP^+ (6.0×10^{-5} mol dm^{-3}) under oxygen gave an identical spectrum attributable to $TPP^{\bullet}$. Kinetic traces of a λ = 550 nm band due to $TPP^{\bullet}$ in the presence and absence of oxygen seem to fit second-order kinetics. The second-order rate constants (k_2/ε) in the absence of oxygen was 7.6×10^5 cm s^{-1}, while that in its presence was 9.7×10^5 cm s^{-1}. Hence, there is essentially no difference in recombination rates of $\mathbf{1}^{+\bullet}$ and $TPP^{\bullet}$. The results show that the reaction of the pyryl radical with molecular oxygen, which would be observed as pseudo-first-order kinetics, is too slow to be detected under the time-scale of the laser experiments.

The absorption spectrum of $\mathbf{1}^{+\bullet}$ is reported to have the maximum at *ca.* λ = 540 nm,[12] and it overlaps with that of $TPP^{\bullet}$. We could not observe a distinct absorption band attributable to $\mathbf{1}^{+\bullet}$. Also, we were not able to detect any absorption spectrum which can be assigned to intermediates leading to **2** such as $^{+}\mathbf{1}\text{–}O_2^{\bullet}$ (*vide infra*).

Triplet Quenching.—Triplet energy of TPP^+ is reported to be 2.3 eV[13] and hence electron transfer from **1** to the excited triplet state of TPP^+ is also expected to occur efficiently in dichloromethane ($\Delta G^{\circ} = -45.1$ kJ mol^{-1}). This was found to be the case. LFP of TPP^+ (1.6×10^{-4} mol dm^{-3}) by nitrogen laser pulses under an inert atmosphere in the absence of any quencher gave a transient absorption spectrum which can be assigned to T–T absorption of TPP^+. The assignment was secured by its relatively long lifetime (*ca.* 10 μs) and by the fact that it is efficiently quenched by dissolved oxygen and electron donors (*vide infra*). The T–T absorption spectrum is very broad as shown in Fig. 4 and its absorption maximum would be at λ = *ca.* 850 nm.

Evidence for electron transfer in the excited triplet state of TPP^+ was obtained by LFP in the presence of low concentrations of **1**. Thus, LFP of TPP^+ (9.5×10^{-5} mol dm^{-3}) in the presence of **1** (1.4×10^{-4} mol dm^{-3}) by excimer laser (XeF, λ = 351 nm) under argon in dichloromethane, where quenching of the excited singlet state of TPP^+ by **1** is negligible, gave a transient absorption spectrum which can safely be assigned to pyryl radicals as shown in Fig. 5. The results clearly indicate that the excited triplet state of TPP^+ also undergoes efficient electron transfer to afford the pyryl radical and $\mathbf{1}^{+\bullet}$ though absorption attributable to the latter species was not observed as in the case of the singlet quenching.

The quenching rate constant k_q^T of the excited triplet state of TPP^+ by **1** was obtained by eqn. (2) by measuring pseudo-first-

$$k_d = k_0 + k_q^T[\mathbf{1}] \qquad (2)$$

order rate constants k_d (decay of the T–T absorption) as a

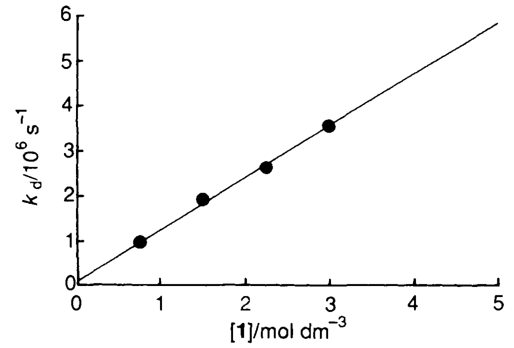


Fig. 6 Plot of the pseudo-first-order decay rate constant (k_d/s^{-1}) of the T–T absorption as a function of the concentration of **1** in dichloromethane under argon

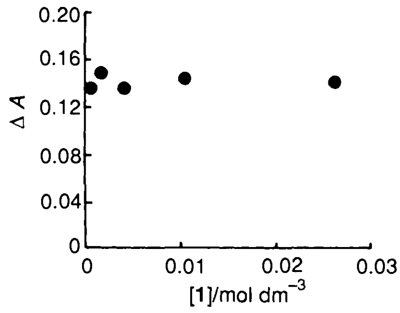


Fig. 7 Plot of ΔA at λ = 550 nm as a function of the concentration of **1**

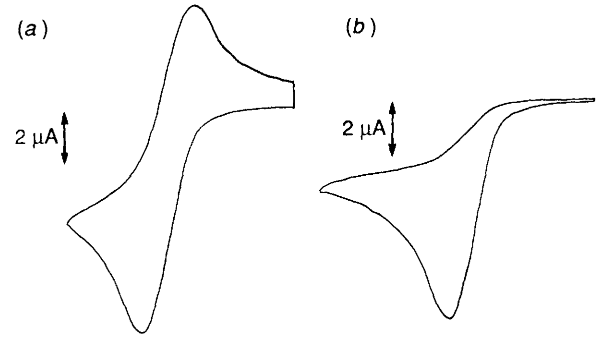


Fig. 8 Cyclic voltammograms of TPP$^+$ (1.5×10^{-3} mol dm^{-3}) in dichloromethane in the absence (a) and presence (b) of oxygen

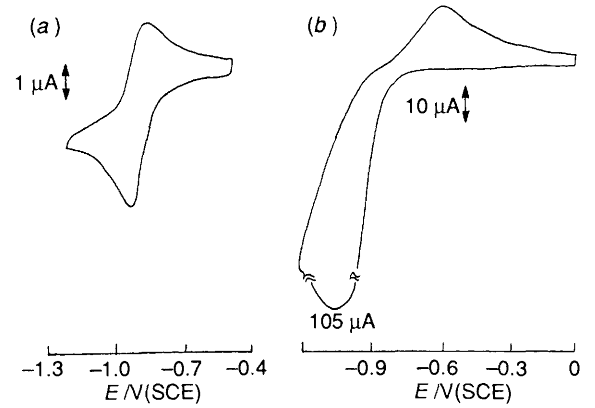


Fig. 9 Cyclic voltammograms of DCA (2.0×10^{-4} mol dm^{-3}) in acetonitrile in the absence (a) and presence (b) of oxygen

function of [**1**], where k_0 is the decay rate constant of the TPP$^+$ triplet ($= 1/\tau_T$).

LFP of TPP$^+$ (1.6×10^{-4} mol dm^{-3}) in the presence of **1** (0–3.0 $\times 10^{-4}$ mol dm^{-3}) by nitrogen laser pulses under argon gave a linear Stern–Volmer plot as shown in Fig. 6. The slope gave $k_q{}^T = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. Similar laser experiments under oxygen gave $k_q{}^O[O_2] = 1.3 \times 10^6$ s^{-1} for quenching of triplet TPP$^+$ by oxygen.

In order to understand further the role of electron transfer through the excited triplet state of TPP$^+$ in the present oxygenation, we have also studied by LFP the effect of the concentration of **1** on the absorbance A at λ = 550 nm, which reflects the yield of the radical pairs consisting of the radical cations of **1** and the pyryl radicals. The results are shown in Fig. 7 in which ΔA at λ = 550 nm is plotted *vs.* the concentration of **1**. As shown in Fig. 7, ΔA values at low concentrations of **1** (*ca.* 10^{-4} mol dm^{-3}) are nearly the same as those at high concentrations of **1** (*ca.* 10^{-2} mol dm^{-3}) indicating that the triplet-mediated electron transfer is very efficient in generating the free radical ions.

Cyclic Voltammetry Study of TPP$^+$.—One-electron reduced species of a sensitizer may play an important role in electron transfer-induced oxygenation since it may react with molecular oxygen or reduce it to afford the superoxide anion. Reactions of initially formed radical ions such as coupling of a radical cation with the sensitizer radical anion and deprotonation of the radical cation also depend on the nature of the sensitizer radical anion. To study the reactivity of TPP$^•$ with molecular oxygen, we have carried out a cyclic voltammetric reduction of TPP$^+$ in the presence and absence of oxygen. For the sake of comparison, cyclic voltammograms (CVs) of DCA were also taken.

The CVs of TPP$^+$ in dichloromethane (1.5×10^{-3} mol dm^{-3}) and those of DCA (2.0×10^{-4} mol dm^{-3}) in acetonitrile are shown in Figs. 8 and 9, respectively. As shown in these Figs., both TPP$^+$ and DCA exhibit reversible behaviour in CV in the absence of oxygen. In the presence of oxygen, however, TPP$^+$ exhibits typical EC behaviour,[14] indicating that the resulting TPP$^•$ reacts with molecular oxygen. Similar heights of the reduction currents in the CVs in the presence and absence of oxygen suggest that a peroxyl radical formed by the reaction of TPP$^•$ with molecular oxygen is electrochemically inactive under the conditions employed. In striking contrast, the reduction of DCA in the presence of oxygen shows a catalytic current increase. This huge current increase is consistent with a mechanism shown in the following scheme in which DCA$^{-•}$ reduces molecular oxygen *via* one-electron transfer to afford the superoxide anion and to regenerate neutral DCA. The reverse reaction, that is, initial electrochemical reduction of molecular oxygen followed by one-electron transfer from the superoxide anion to DCA is not likely since oxygen has a large overpotential in its reduction in dichloromethane, and hence DCA is reduced at a more positive potential than molecular oxygen. The reaction sequence shown below will continue until all the oxygen molecules near the electrode are converted to the superoxide anions [eqns. (5) and (6)]. Although we have not established the structure and reactivity of the peroxyl radical, TPP–O$_2^•$, the above results clearly indicate that TPP$^•$, in contrast with DCA$^{-•}$, is highly reluctant to undergoing electron transfer to molecular oxygen to give the superoxide anion [eqns. (3)–(6)].

$$\mathrm{TPP^+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \mathrm{TPP^•} \qquad (3)$$

$$\mathrm{TPP^•} + \mathrm{O_2} \longrightarrow \mathrm{TPP{-}O_2{}^•} \qquad (4)$$

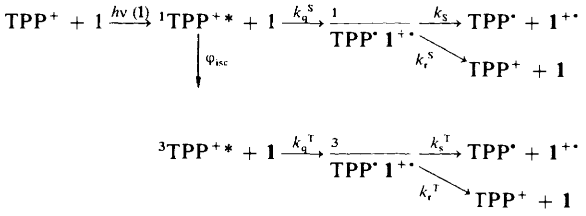
$$\mathrm{DCA} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \mathrm{DCA^{-•}} \qquad (5)$$

$$\mathrm{DCA}^{-\bullet} + \mathrm{O_2} \longrightarrow \mathrm{DCA} + \mathrm{O_2}^{-\bullet} \qquad (6)$$

Discussion

Primary Processes.—The fact that fluorescence quenching of TPP^+ by electron donors follows the Rehm–Weller equation and the large negative values of the free energy changes associated with electron transfer from the donors to the excited singlet state of TPP^+ strongly suggest that the electron transfer takes place efficiently from **1** to the excited singlet state of TPP^+. Evidence for the electron transfer was obtained by LFP experiments. Our observation of the transient absorption spectrum attributable to $\mathrm{TPP}^\bullet$ under the predominantly singlet quenching conditions indicates that the electron transfer from **1** to the excited singlet state of TPP^+ generates $\mathrm{TPP}^\bullet$ and $\mathbf{1}^{+\bullet}$.

It is of particular interest to point out that the excited triplet state of TPP^+ is also efficiently quenched by **1** ($k_q^{\mathrm{T}} = 1.2 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$) to afford $\mathbf{1}^{+\bullet}$ and $\mathrm{TPP}^\bullet$. This value combined with $k_q^{\mathrm{O}}[\mathrm{O_2}]$ ($1.3 \times 10^6\ \mathrm{s^{-1}}$) indicates that under the preparative oxygenation conditions ($[\mathbf{1}] = 0.05\ \mathrm{mol\ dm^{-3}}$), in which 76% of the excited singlet state of TPP^+ is quenched by **1**, at most *ca.* 10% of the excited singlet of TPP^+ undergoes intersystem crossing to the excited triplet state, which is completely quenched by **1** to afford $\mathbf{1}^{+\bullet}$ and $\mathrm{TPP}^\bullet$. Thus, the electron transfer from **1** not only to the excited singlet state but to the excited triplet state of TPP^+ is important as the primary process. The importance of the triplet-mediated electron transfer was further established by the results shown in Fig. 7. Fig. 7 shows that even under very low concentrations of **1**, where the quenching of the excited singlet state of TPP^+ by **1** is $<4\%$, ΔA 550 nm, the yield of the radical ion pairs still remains the same as the yield at higher concentrations ($>10^{-2}\ \mathrm{mol\ dm^{-3}}$) of **1**. Based on the results in Fig. 7, we may calculate the ratio of the radical ion yields between triplet- and singlet-mediated electron transfers. The singlet and the triplet mediated electron-transfer reactions affording the radical cations of **1** and the pyryl radicals are shown in Scheme 1.



Scheme 1

The observed ΔA by the laser flash photolysis is a summation of the ΔA_{S} and ΔA_{T} which are from the singlet and triplet radical ion pairs, respectively [eqn. (7)]. The ΔA_{S} can be expressed by

$$\Delta A = \Delta A_{\mathrm{S}} + \Delta A_{\mathrm{T}} \qquad (7)$$

eqn. (8), where I, ε and d denote light intensity, the molar extinction coefficient of the species absorbing at $\lambda = 550$ nm, and the path length (1 cm) of the cell used for the experiments, respectively.

$$\Delta A_{\mathrm{S}} = k_q^{\mathrm{S}}\tau_{\mathrm{S}}[\mathbf{1}]/(1 + k_q^{\mathrm{S}}\tau_{\mathrm{S}}[\mathbf{1}])\cdot F_{\mathrm{S}}\cdot I\cdot\varepsilon\cdot d \qquad (8)$$

$$F_{\mathrm{S}} = k_s^{\mathrm{S}}/(k_s^{\mathrm{S}} + k_r^{\mathrm{S}}) \qquad (9)$$

Similarly, ΔA_{T} can be expressed by eqn. (10) where φ_{isc} and τ_{T} are the quantum yield of the intersystem crossing of the singlet excited state of TPP^+ and the lifetime of the excited triplet state of TPP^+, respectively.

$$\Delta A_{\mathrm{T}} = \{(1 + k_q^{\mathrm{S}}\tau_{\mathrm{S}}[\mathbf{1}])^{-1}\}\cdot\varphi_{\mathrm{isc}}\cdot k_q^{\mathrm{T}}\tau_{\mathrm{T}}[\mathbf{1}]/(1 + k_q^{\mathrm{T}}\tau_{\mathrm{T}}[\mathbf{1}])\cdot F_{\mathrm{T}}\cdot I\cdot\varepsilon\cdot d \qquad (10)$$

$$F_{\mathrm{T}} = k_s^{\mathrm{T}}/(k_s^{\mathrm{T}} + k_r^{\mathrm{T}}) \qquad (11)$$

In eqn. (8), if the concentration of **1** is very large ($k_q^{\mathrm{S}}\tau_{\mathrm{S}}[\mathbf{1}]/(1 + k_q^{\mathrm{S}}\tau_{\mathrm{S}}[\mathbf{1}])$ *ca.* 1), then ΔA_{S} equals $F_{\mathrm{S}}\cdot I\cdot\varepsilon\cdot d$. Since the observed ΔA_{S} does not depend on the concentration of **1**, it is reasonable to assume that ΔA_{S} (0.14) at the highest concentration of **1** employed ($[\mathbf{1}] = 2.4 \times 10^{-2}\ \mathrm{mol\ dm^{-3}}$) reflects the absorbance of only the singlet radical pairs. Then, we may calculate $F_{\mathrm{T}}\cdot I\cdot\varepsilon\cdot d$ at each concentration of **1**, where the values of $\tau_{\mathrm{T}} = 9.6\ \mu\mathrm{s}$ and $\varphi_{\mathrm{isc}} = 0.42$ are used. The ratio $F_{\mathrm{T}}\cdot I\cdot\varepsilon\cdot d/F_{\mathrm{S}}\cdot I\cdot\varepsilon\cdot d$ means the ratio of triplet-derived free radical ions to the singlet-derived ones. The calculations show that the ratio is approximately two, indicating that the triplet quenching gives twice as many free radical ions as the singlet quenching. This finding is in sharp contrast with that in DCA- or CNA-sensitized electron-transfer oxygenation, in which only electron transfer to the excited singlet states of the cyanoaromatics from donors was proposed to occur,[15] and no direct evidence has so far been obtained for electron transfer through the sensitizer triplet states.[3]

Small oxygen effects on the decay of $\mathrm{TPP}^\bullet$ can be explained in terms of slow reactions of $\mathrm{TPP}^\bullet$ with molecular oxygen in the time scale of the laser experiments. The result is also in sharp contrast with that in CNA-sensitized oxygenation of *trans*-stilbene,[15d] in which CNA radical anions faded immediately in the presence of oxygen. The present oxygen effect thus indicates that $\mathrm{TPP}^\bullet$ is far less efficient than $\mathrm{CNA}^{-\bullet}$ in generating the superoxide anion but that $\mathrm{TPP}^\bullet$ undergoes addition to oxygen.

Oxygenation Pathways.—Previous cyclic voltammetric studies by Nelsen and co-workers[16] established that $\mathbf{1}^{+\bullet}$ reacts with molecular oxygen to afford a peroxyl radical cation, $^{+}\mathbf{1}\text{–}\mathrm{O_2}^\bullet$, which is then rapidly reduced by **1** and by the electrode to give **2** in the electrochemical time-scale used ($200\ \mathrm{mV\ s^{-1}}$). The cyclic voltammetric reduction of TPP^+ in the presence and absence of oxygen indicates that $\mathrm{TPP}^\bullet$ does not reduce molecular oxygen in the same electrochemical time-scale, but reacts with molecular oxygen to afford the peroxyl radical, $\mathrm{TPP\text{–}O_2}^\bullet$. These results imply that $\mathbf{1}^{+\bullet}$, once formed by the photoinduced electron transfer, reacts with molecular oxygen, but not with the superoxide anion. The resulting peroxyl radical cation $^{+}\mathbf{1}\text{–}\mathrm{O_2}^\bullet$, is then reduced by **1** and/or $\mathrm{TPP}^\bullet$. If the rate constant for the process $\mathrm{TPP}^\bullet + \mathrm{O_2}$ is slower than that for the process $\mathbf{1}^{+\bullet} + \mathrm{O_2}$, $\mathrm{TPP}^\bullet$ may reduce $^{+}\mathbf{1}\text{–}\mathrm{O_2}^\bullet$ before it reacts with oxygen. Also, if the reaction of $\mathrm{TPP}^\bullet$ with oxygen is reversible in a longer time-scale, some of the $\mathrm{TPP}^\bullet$ present in solution, though it is known to dimerize,[17] would reduce the peroxyl radical cation at some stage of the oxygenation. The reduction of $^{+}\mathbf{1}\text{–}\mathrm{O_2}^\bullet$ with **1** through electron transfer is supported by the observed catalytic nature of the TPP^+ as sensitizer though the quantum yields for formation of **2** are less than unity at several concentrations of **1**. A possible explanation for the low quantum yields is presumably that back electron transfer in the radical pair of $\mathbf{1}^{+\bullet}$ and $\mathrm{TPP}^\bullet$, especially in its singlet, giving **1** and TPP^+, is rapid, and hence the efficiency for the formation of free $\mathbf{1}^{+\bullet}$ is low. Since the triplet radical pairs give free radical ions twice as much as the singlet radical pairs, the majority of the product, **2**, could be formed through the triplet radical pairs, especially under a low concentration of **1**. However, this does not necessarily lead to a higher quantum yield since the low concentration of **1** retards the reaction between $^{+}\mathbf{1}\text{–}\mathrm{O_2}^\bullet$ and **1**. We suggest that reduction of $^{+}\mathbf{1}\text{–}\mathrm{O_2}^\bullet$ by **1** is more favoured than that by $\mathrm{TPP}^\bullet$ since the concentration of **1** is much higher than that of $\mathrm{TPP}^\bullet$, and $\mathrm{TPP}^\bullet$ reacts with molecular oxygen. The latter process reduces the chance of

TPP$^{\bullet}$ reacting with $^{+}\mathbf{1}$–$O_2^{\bullet}$. The proposed oxygenation pathways are summarized in eqns. (12)–(22).

$$\mathrm{TPP}^{+} \longrightarrow {}^{1}\mathrm{TPP}^{+*} \tag{12}$$

$$\mathbf{1} + {}^{1}\mathrm{TPP}^{+*} \longrightarrow {}^{1}(\mathbf{1}^{+\bullet}\mathrm{TPP}^{\bullet}) \tag{13}$$

$${}^{1}(\mathbf{1}^{+\bullet}\mathrm{TPP}^{\bullet}) \longrightarrow \mathbf{1} + \mathrm{TPP}^{+} \tag{14}$$

$${}^{1}(\mathbf{1}^{+\bullet}\mathrm{TPP}^{\bullet}) \longrightarrow {}^{3}(\mathbf{1}^{+\bullet}\mathrm{TPP}^{\bullet}) \tag{15}$$

$${}^{1}\mathrm{TPP}^{+*} \longrightarrow {}^{3}\mathrm{TPP}^{+*} \tag{16}$$

$$\mathbf{1} + {}^{3}\mathrm{TPP}^{+*} \longrightarrow {}^{3}(\mathbf{1}^{+\bullet}\mathrm{TPP}^{\bullet}) \tag{17}$$

$${}^{3}(\mathbf{1}^{+\bullet}\mathrm{TPP}^{\bullet}) \longrightarrow \mathbf{1}^{+\bullet} + \mathrm{TPP}^{\bullet} \tag{18}$$

$$\mathbf{1}^{+\bullet} + \mathrm{O}_2 \longrightarrow {}^{+}\mathbf{1}\text{–}\mathrm{O}_2^{\bullet} \tag{19}$$

$${}^{+}\mathbf{1}\text{–}\mathrm{O}_2^{\bullet} + \mathbf{1} \longrightarrow \mathbf{1}^{+\bullet} + \mathbf{2} \tag{20}$$

$${}^{+}\mathbf{1}\text{–}\mathrm{O}_2^{\bullet} + \mathrm{TPP}^{\bullet} \longrightarrow \mathrm{TPP}^{+} + \mathbf{2} \tag{21}$$

$$\mathrm{TPP}^{\bullet} + \mathrm{O}_2 \longrightarrow \mathrm{TPP}\text{–}\mathrm{O}_2^{\bullet} \tag{22}$$

Finally, a singlet oxygen mechanism for the dioxetane formation may be ruled out although **1** is known to react with singlet oxygen to give **2**.[18] Firstly, energetic considerations do not support the formation of the triplet excited state of TPP^{+} through back electron transfer in the triplet radical pairs of $\mathbf{1}^{+\bullet}$ and TPP$^{\bullet}$, since the energy of the pair (1.8 eV) is less than the triplet excitation energy of TPP^{+} (2.3 eV). Secondly, the quenching of the excited triplet state of TPP^{+} by **1** under the actual photooxygenation conditions ($[\mathbf{1}]$ = 0.05 mol dm^{-3}) can be estimated to proceed more than 400 times faster than that by dissolved oxygen on the basis of the values of k_q^{T} and $k_q^{O}[O_2]$.

In conclusion, we have demonstrated that TPP^{+} is a suitable sensitizer which can be used for studying the reactivity of radical cations of alkenes and other electron-rich substrates with molecular oxygen. This is due to two reasons. One is that the pyryl radical reacts with molecular oxygen, which will enhance the possibility of organic radical cations reacting with molecular oxygen instead of the superoxide anion. The other is that the excited triplet state of TPP^{+} may accept an electron from substrates whose oxidation potentials are up to 2 V/SCE, which will greatly reduce the amount of singlet oxygen formed through energy transfer. TPP^{+} is also useful to study the effect of spin multiplicity of a sensitizer on the reactivity of the radical pairs and radical ions since it may undergo electron transfer very efficiently through the excited triplet as well as through the excited singlet state.[19]

Further studies on electron transfer photochemistry as well as on chemistry of radical cations are being pursued in our laboratories with the use of TPP^{+} of unique properties as sensitizer.

Experimental

Materials.—Adamantylideneadamantane was prepared by the method of Schaap and Faler.[20] Its purity was confirmed by TLC on a silica gel plate and GLPC. 1,4-Dimethoxybenzene was commercially available and recrystallized twice from ethanol. TPP^{+}BF$_4^{-}$ (Fluka) was used without further purification for most of the preparative photolyses, and recrystallized twice from ethanol and dried *in vacuo* for several hours for spectroscopic studies. Tetrabutylammonium perchlorate was recrystallized twice from hexane–ethyl acetate and dried *in vacuo* at *ca.* 70 °C for several hours. Dichloromethane was treated with sulphuric acid, washed with water, and then distilled over calcium hydride. Acetonitrile was distilled over phosphorus pentoxide followed by distillation over potassium carbonate.

Photooxygenation.—Typically, 67.1 mg (0.25 mmol) of **1** and 4.7 mg (0.012 mmol) of TPP^{+}BF$_4^{-}$ were dissolved in dry dichloromethane and the resultant yellowish solution was irradiated by a 650 W tungsten–halogen lamp at running water temperature (*ca.* 20 °C) for 10 min while oxygen was bubbled through the solution. Evaporation of the solvent followed by product isolation by preparative TLC afforded **2** (25.2 mg, 36%) and recovered starting **1** (40.2 mg, 40% conversion). The products were identified by comparison of their R_F values in TLC and NMR spectra (taken on a JEOL MH-100 NMR spectrometer) with those of the authentic samples.[18,20] All other oxygenations were performed in a similar manner.

Absorption and Fluorescence Spectra.—UV spectra of **1**, TPP^{+} and the reaction mixtures were measured on a Shimadzu UV-365 recording spectrophotometer or a JASCO UVIDEC 660 spectrophotometer at room temperature. Fluorescence quenching experiments were performed on a JASCO EP-500 spectrofluorimeter at room temperature. Dichloromethane solutions were prepared in 1 cm quartz fluorescence cells and purged with dry argon for at least 15 min. Fluorescence quantum yields were measured on a Hitachi F-4000 fluorescence spectrometer at room temperature using quinine sulphate in 1 mol dm^{-3} sulphuric acid as a reference (φ_f = 0.55).[21]

Reaction Quantum Yields.—The quantum yield for the formation of **2** was measured with potassium tris(oxalato)ferrate(III) as an actinometer. Monochromatic light (λ = 366 nm) was isolated from a 400 W high pressure mercury lamp through a combination of Toshiba UVD-36B and UV-35 glass cut filters. Solutions were bubbled through with oxygen for *ca.* 15 min before irradiation and the oxygen atmosphere was kept during the reaction. Yields of **2** were obtained by determining the amount of adamantanone by GLPC (Shimadzu GC-4CMPF with a flame ionization detector, SE-30 5%). Adamantanone is quantitatively formed from **2** under GLPC conditions.

Laser Flash Photolysis.—Laser flash photolysis experiments were performed with an excimer laser (Lambda Physik EMG-101)-pumped dye laser (Lambda Physik FL-3002). In fact, nitrogen (λ = 337 nm), XeF excimer (λ = 351 nm) and excimer (XeCl) laser-pumped dye lasers (DPS, λ = 408 nm) were used (see text). A 150 W Xe lamp (Wacom KXL 151) was used as a monitoring light source. The monitoring beam, oriented perpendicularly to the exciting laser beam, was focused, after passing through a 1 cm sample cell, on an entrance slit of a monochromator (JASCO CT-25C), and detected by a photomultiplier (Hamamatsu Photonix R928). The output from the photomultiplier was then fed into a transient oscilloscope (Iwatsu TS-8123) to be digitized, and then transferred into a personal computer (NEC PC-9801) for analysis of the signals.

Cyclic Voltammetry.—Cyclic voltammetry was carried out with a standard cell equipped with a platinum disc as a working electrode, a platinum wire as a counter electrode, and a reference electrode (saturated calomel electrode). A potentiostat and a function generator were Hokuto HA-201 and Hokuto HB-104, respectively. Cyclic voltammograms were recorded on a Rikadenki RW-11 X-Y recorder. Solutions were bubbled through with argon or oxygen when necessary. Tetrabutylammonium perchlorate (0.1 mol dm^{-3}) was used as a supporting electrolyte.

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