ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 85 (1995) 53–61

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Triphenylpyrylium-salt-sensitized electron transfer oxygenation of furan derivatives. Product isolation, fluorescence quenching and laser flash photolysis studies*

N. Manoj[1], K.R. Gopidas*

Photochemistry Research Unit, Regional Research Laboratory (CSIR), Trivandrum 695 019, India

Received 5 April 1994; accepted 19 May 1994

Abstract

The 2,4,6-triphenylpyrylium-salt-sensitized photo-oxygenation of furans **1a**–**1c** and **2** is reported. Furans **1a**–**1c** give the corresponding enediones **4a**–**4c**, whereas hardly any reaction is observed for **2**. Fluorescence quenching and laser flash photolysis studies indicate that the primary process is electron transfer from the furans to the singlet or triplet excited state of the pyrylium salt. The radical cations of the furans were characterized using laser flash photolysis studies. A mechanism consistent with the experimental observations is suggested for the photo-oxygenation reactions of these furans.

Keywords: Triphenylpyrylium-salt; Electron transfer oxygenation; Furan derivatives; Fluorescence quenching; Laser flash photolysis

1. Introduction

Photoinduced electron transfer oxygenations have attracted considerable attention over the last few years [1]. In most of these reactions, a sensitizer such as 1,4-dicyanonaphthalene (DCN) or 9,10-dicyanoanthracene (DCA) is irradiated in the presence of an electron donor molecule and oxygen. Photo-oxygenation in these cases proceeds through the transfer of an electron from the donor substrate to the excited states of DCN or DCA. Electron transfer generates the radical cation of the substrate and the radical anion of the sensitizer. In one of the accepted mechanisms, the radical anion of the sensitizer reacts with molecular oxygen to produce superoxide ion [2–4]. The substrate radical cation then reacts with superoxide ion to give oxygenation products. According to a second, widely accepted mechanism, oxygenation of the substrate occurs via reaction with singlet oxygen which is produced by the interaction of photogenerated triplets of DCN or DCA with oxygen [5–9]. Oxygenation, whether mediated by singlet oxygen or superoxide ion, generally gives the same product or product distributions [10,11]. Since DCN- or DCA-sensitized photo-oxygenation can involve both superoxide ion and singlet oxygen, identification of the actual reaction mechanism usually requires further experimentation. Triphenylpyrylium-salt-sensitized (TPP^+-sensitized) photo-oxygenation, on the other hand, does not involve superoxide ion or singlet oxygen, and hence can be used for the clear identification of the mechanism of oxygenation reactions [12–16].

Although TPP^+ has been used as a sensitizer for a large number of photoinduced electron transfer reactions [17–25], only few reports are available on its use in photo-oxygenation reactions [12–16]. In this paper, we report an investigation of the TPP^+-sensitized electron transfer oxygenation of several aryl-substituted furan derivatives using steady state photolysis, quenching of TPP^+ fluorescence and laser flash photolysis. Our results show that the TPP^+-sensitized photo-oxygenation of furan derivatives proceeds by electron transfer from the furans to the singlet or triplet excited state of TPP^+ to generate the radical cation of the furan ($F^{\cdot+}$). $F^{\cdot+}$ reacts with molecular oxygen to afford the observed products. The involvement of singlet oxygen and superoxide ion is ruled out in these photo-oxygenation reactions on the basis of our own observations and reports in the literature. The furan derivatives studied include 2,5-diphenylfuran (DPF, **1a**), 2,3,5-triphenylfuran (TrPF, **1b**), 2,3,4,5-tetraphenylfuran

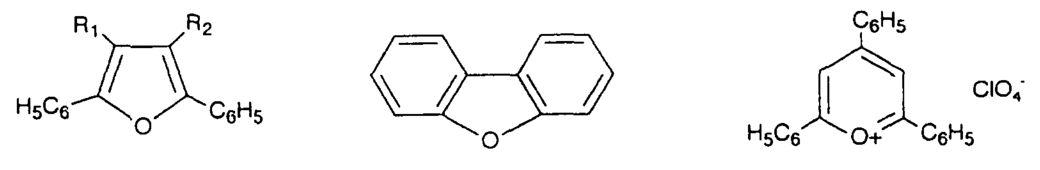
---

*Contribution No. RRLT-PRU-44 from the Regional Research Laboratory, Trivandrum.

*Corresponding author.

[1] Summer research fellow from the School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686 560, India.

SSDI 1010-6030(94)03886-Y



1a-c 2 3

1a, $R_1 = R_2 = H$
1b, $R_1 = H$, $R_2 = C_6H_5$
1c, $R_1 = R_2 = C_6H_5$

Chart 1.

(TePF, **1c**) and dibenzofuran (DBF, **2**). Their structures are shown in Chart 1 together with that of TPP^+ (**3**).

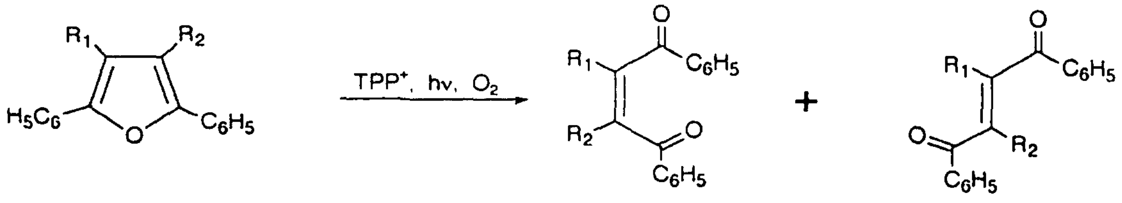
2. Results

2.1. Steady state photo-oxygenation

When a solution of DPF (**1a**) was irradiated in the presence of TPP^+ (5×10^{-5} M) in dichloromethane saturated with oxygen for 10 min at 20 °C, a mixture of enediones **4a** (5%) and **5a** (84%) was obtained (Scheme 1). Under these experimental conditions more than 90% of the light was absorbed by the sensitizer. Compound **4a** is the photo-oxygenation product and it isomerizes thermally at 20 °C to the more stable trans isomer **5a**. (Gas chromatographic analysis of the mixture immediately after photolysis showed the presence of 75% of the cis isomer **4a** and 25% of the trans isomer **5a**. The solution was kept in the dark at 20 °C for 15 min and analysed again. The chromatogram showed 6% of the cis isomer **4a** and 94% of the trans isomer **5a**, indicating that isomerization of cis to trans is a thermal process. This cis to trans ratio did not change with time.) Two types of blank experiment were carried out: one in the absence of TPP^+ and one in the absence of oxygen. In both cases the starting furan was recovered unchanged. These results indicate that TPP^+ is the light-absorbing species and, in the absence of oxygen, back electron transfer to regenerate the starting materials is the preferred pathway.

Irradiation of TrPF (**1b**) under the above conditions gave a 13% yield of **4b** and a 75% yield of the trans isomer **5b** after isolation. Blank experiments in the absence of oxygen did not yield any product. The cis isomer **4b** undergoes isomerization to the trans isomer **5b** under these irradiation conditions. Photo-oxygenation of TePF (**1c**) also gave similar results. In this case 54% of the cis isomer **4c** and 31% of the trans isomer **5c** were isolated from the photo-oxygenation reaction. Blank experiments in the absence of oxygen did not give any product.

Photo-oxygenation of DBF (**2**) in the presence of TPP^+ and oxygen did not give any product; more than 90% of the starting material was recovered in this case.



1a-c 4a-c 5a-c

1a, $R_1 = R_2 = H$
1b, $R_1 = H$, $R_2 = C_6H_5$
1c, $R_1 = R_2 = C_6H_5$

Scheme 1.

2.2. Fluorescence quenching studies

In order to gain some insight into the photophysical behaviour of the excited singlet state of TPP$^+$, quenching of TPP$^+$ fluorescence by the furan derivatives was carried out. It was observed that the bright blue fluorescence of TPP$^+$ was efficiently quenched by these furans. Plots of the fluorescence intensity vs. furan concentration were linear in all cases and fitted the Stern–Volmer equation

$$I_0/I = 1 + K_{SV}[Q] \qquad (1)$$

where K_{SV} is the Stern–Volmer constant ($K_{SV} = k_q{}^s \tau_s$). The singlet quenching rate constants $k_q{}^s$ were calculated for all furan derivatives assuming a singlet lifetime of 2.7 ns for TPP$^+$ in dichloromethane [13]. The values of K_{SV} and $k_q{}^s$ are given in Table 1. The free energy changes $\Delta G°$ associated with the transfer of an electron from the furan derivatives to the excited singlet state of TPP$^+$ were estimated according to the Weller equation [27]

$$\Delta G° \text{ (kcal mol}^{-1}\text{)} = 23.06[E_{(D^{\cdot+}/D)} - E_{(A/A^{\cdot-})} - e^2/\epsilon a] - E_{0,0} \qquad (2)$$

where $E_{(D^{\cdot+}/D)}$ and $E_{(A/A^{\cdot-})}$ are the electrochemical oxidation and reduction potentials of the donor and acceptor respectively and $E_{0,0}$ is the singlet excitation energy of the sensitizer. The term $e^2/\epsilon a$ represents the energy gained in 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 this term, since TPP$^+$ is positively charged and hence there is no net change of charge on electron transfer. The point of intersection of the absorption and emission spectra of TPP$^+$ was 440 nm and this gives $E_{0,0} = 68.4$ kcal mol^{-1}. A value of -0.28 eV (vs. a saturated calomel electrode (SCE) in dichloromethane) [13] was used for the reduction potential of TPP$^+$, and $\Delta G°$ values were calculated for those furan derivatives for which oxidation potentials were known [26]. The $\Delta G°$ values are also given in Table 1. It is evident from these values that the quenching of the excited singlet state of TPP$^+$ by these furans is diffusion controlled.

Table 1
Oxidation potentials of the furans, Stern–Volmer constants, fluorescence quenching rate constants and free energy changes associated with electron transfer from the furans to the excited singlet state of TPP$^+$

Furan	$E_{ox}{}^a$ (V)	K_{SV} (M^{-1})	$k_q{}^s$ (M^{-1} s^{-1})	$\Delta G°$ (kcal mol^{-1})
1a	1.17	75.0	2.78×10^{10}	−35.0
1b	1.18	74.8	2.77×10^{10}	−34.7
1c	1.20	64.0	2.39×10^{10}	−34.3
2	–	61.3	2.27×10^{10}	–

[a] Values vs. SCE [26].

2.3. Laser flash photolysis studies

Laser flash photolysis is one of the most powerful tools available to determine the primary events involved in photoinduced electron transfer reactions. In order to gain a deeper understanding of the primary processes occurring in the present photo-oxygenation, we carried out the flash photolysis of TPP$^+$ under various conditions.

Laser flash photolysis of TPP$^+$ (2×10^{-5} M) by the third harmonic of an Nd–YAG laser (355 nm, 70 mJ) in dichloromethane saturated with argon gave a transient absorption spectrum characterized by an absorption maximum around 470 nm and strong bleaching below 450 nm. The absorption at 470 nm was assigned to triplet TPP$^+$ in accordance with earlier observations [13,28]. The transient was quenched by oxygen with a rate constant of 5.98×10^8 M^{-1} s^{-1}.

The TPP$^+$ triplets are efficiently quenched by all the furan derivatives studied. The triplet quenching rate constants $k_q{}^T$ were obtained for **1a** and **2** by measuring the pseudo-first-order rate constants k_{obs} at different furan concentrations. $k_q{}^T$ values were then evaluated by plotting the data according to

$$k_{obs} = k_0 + k_q{}^T[F] \qquad (3)$$

The $k_q{}^T$ values are 2.35×10^{10} and 1.35×10^{10} M^{-1} s^{-1} for **1a** and **2** respectively. It should be noted that these quenching rate constants are much higher than the oxygen quenching rate constant. In the case of the other furans, quantitative evaluation of $k_q{}^T$ was not possible because, at higher concentrations, they exhibited substantial absorption of the laser light.

In order to determine the mechanism of TPP$^+$ triplet quenching by furans, the transient absorption spectra were recorded. Fig. 1 shows the transient absorption spectrum of a solution of TPP$^+$ (2×10^{-5} M) in dichloromethane containing **1a** (5×10^{-5} M) under degassed

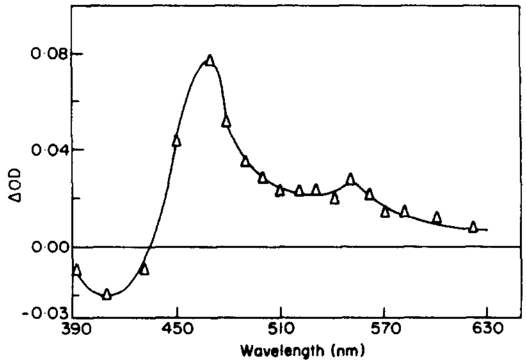


Fig. 1. Transient absorption spectrum of TPP$^+$ (2×10^{-5} M) containing **1a** (5×10^{-5} M), taken 2 μs after the laser pulse.

conditions. The transient is characterized by absorption maxima at 470 and 550 nm. Following the literature [13], we assign the 550 nm absorption to the triphenylpyranyl radical ($TPP^\bullet$) which is generated as a result of electron transfer from the furan to the triplet excited state of TPP^+

$$^3TPP^{+\bullet} + F \longrightarrow TPP^\bullet + F^{\bullet +} \qquad (4)$$

Accordingly, we assign the 470 nm absorption to the radical cation of **1a**. The decay of the 470 nm species could not be fitted to any kinetic equation. This is understandable because both $^3TPP^{+\bullet}$ and $F^{\bullet +}$ absorb in the same region and the kinetics are expected to show a mixed behaviour. The decay of the $TPP^\bullet$ species at 550 nm is second order and is due to back electron transfer to regenerate the starting materials.

Quenching of triplet TPP^+ by the other furans also leads to transient behaviour similar to that of **1a**. For **1b** and **1c**, the furan radical cation exhibits absorption maxima in the 460–470 nm region. For DBF, the radical cation is observed at 340 nm. The transient absorption spectrum obtained in this case is given in Fig. 2. The absorption maximum at 550 nm assigned to $TPP^\bullet$, is common to all cases. Even though the steady state reaction of DBF does not yield any product, the transient spectrum obtained in this case indicates that primary electron transfer also takes place in this system.

The effect of furan concentration on the yield of $TPP^\bullet$ and $F^{\bullet +}$ was checked by measuring the change in optical density (ΔOD) due to these species at various concentrations of DBF. The concentration of DBF was varied from 0.1 M to 10^{-4} M. It was observed that ΔOD increased with concentration and reached a plateau at 0.1 M of DBF for both the absorption peaks. This is shown in Fig. 3. These experiments were not possible with other furans because of their absorption of laser light at such high concentrations.

Laser flash photolysis of furan **1a** was also carried out in the presence of oxygen. This gave an identical spectrum to that in Fig. 1. The decay of the 550 nm species was affected slightly. For example, in the absence of oxygen, this species decayed with a second-order rate constant (k_2/ϵ) of 2.45×10^6 cm s^{-1}. In the presence of oxygen, the second-order rate constant (k_2/ϵ) was 3.98×10^6 cm s^{-1}. This very marginal increase in the rate constant showed that, under these experimental conditions, the reaction of the pyranyl radical with molecular oxygen is very slow and does not contribute significantly to the reaction mechanism.

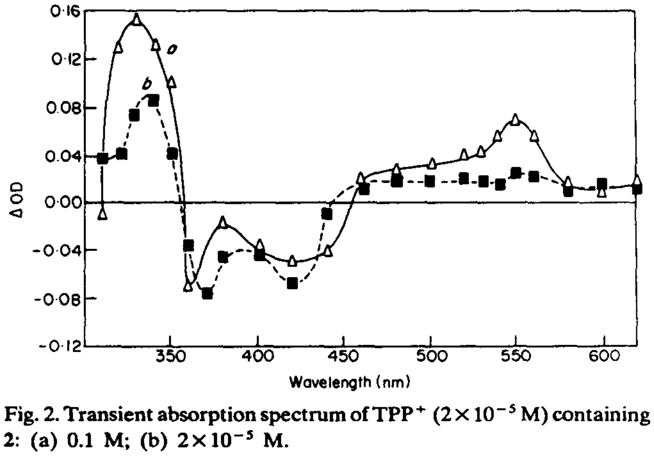


Fig. 2. Transient absorption spectrum of TPP^+ (2×10^{-5} M) containing 2: (a) 0.1 M; (b) 2×10^{-5} M.

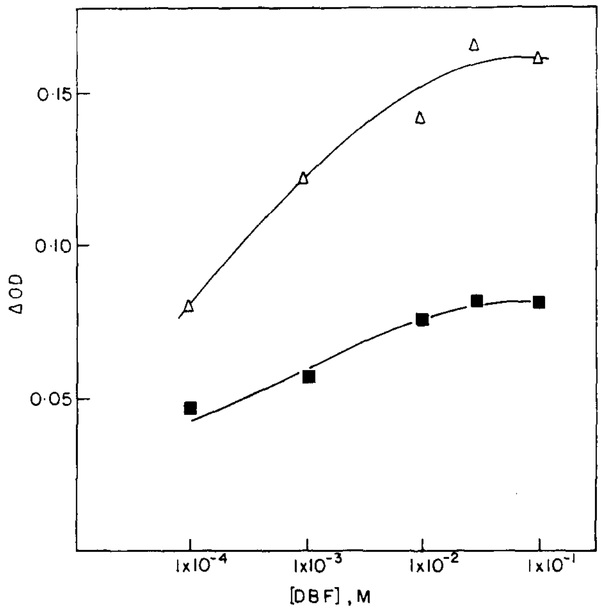


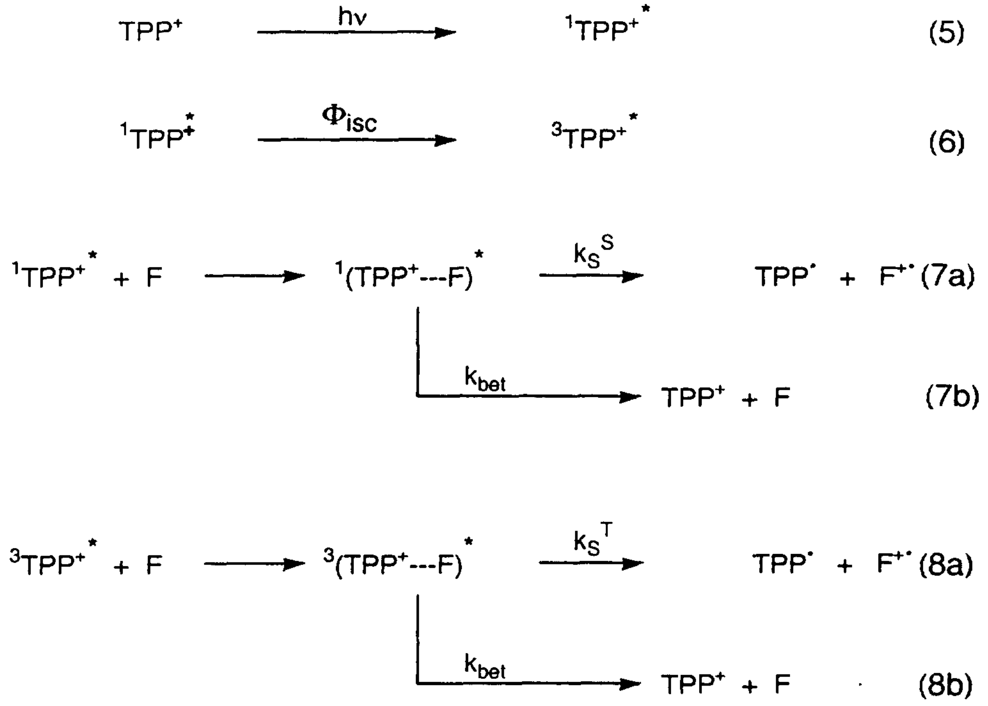
Fig. 3. Plot of ΔOD as a function of the concentration of 2: △, at 340 nm; ■, at 550 nm. The TPP^+ concentration was 2×10^{-5} M.

In order to understand the behaviour of singlet TPP^+ in the photo-oxygenation reactions, transient absorption spectra were recorded at high concentrations of DBF (0.1 M). In this case, about 90% of singlet TPP^+ was quenched by DBF. The transient absorption spectrum recorded was identical in shape to that obtained under triplet quenching conditions except for the substantial increase in the ΔOD values (see Fig. 2). This indicates that both singlet and triplet quenching lead to the same transients.

3. Discussion

3.1. *Primary process*

The fact that the fluorescence quenching of TPP^+ by furans follows the Rehm–Weller equation suggests that electron transfer takes place from the furans to the singlet excited state of TPP^+. As shown in Table 1, quenching occurs at diffusion-controlled rates. The observation of transient absorption due to $TPP^\bullet$ under predominantly singlet quenching conditions for DBF suggests that electron transfer generates $TPP^\bullet$ and $F^{\bullet +}$ through a singlet quenching pathway.



Scheme 2.

The excited triplet state of TPP^+ is also quenched efficiently by the furans at diffusion-controlled rates to afford $TPP^\bullet$ and $F^{\bullet+}$. For the photo-oxygenation reactions, the concentration of the furans was less than 1 mM. Under these conditions, less than 10% of the TPP^+ singlets will be quenched by the furans. Since $\Phi_f = 0.52$ for $^1TPP^{+*}$, approximately 40% of the remaining $^1TPP^{+*}$ will undergo intersystem crossing to yield $^3TPP^{+*}$, which is also efficiently quenched by the furans to generate $TPP^\bullet$ and $F^{\bullet+}$. Thus electron transfer from furan to the singlet and triplet excited states of TPP^+ occurs as the primary process in the photo-oxygenation reaction.

The importance of the triplet-mediated electron transfer is confirmed by the results shown in Fig. 3. The Stern–Volmer constant for DBF is 61 M^{-1}. Thus when $[DBF] = 10^{-4}$ M, only 0.6% of $^1TPP^{+*}$ will be quenched by DBF. Even under these conditions, we see the formation of a substantial amount of the radical pair (see Figs. 2 and 3). On the basis of the results given in Fig. 3, we can calculate the ratio of the radical ion yields between singlet- and triplet-mediated electron transfer. In order to do this, we must consider Scheme 2, which shows the singlet- and triplet-mediated electron transfer pathways.

The ΔOD value observed by laser flash photolysis is the sum of the radical yields from singlet (ΔOD_A) and triplet (ΔOD_T) pathways as shown in Scheme 2, i.e.

$$\Delta OD = \Delta OD_A + \Delta OD_T \tag{9}$$

From Scheme 2, it can be shown that

$$\Delta OD_A = \frac{k_q{}^s\tau_s[F]}{(1+k_q{}^s\tau_s[F])}F_sI\epsilon d \tag{10}$$

where F_s is the fraction of ion pairs formed from the singlet state, I is the light intensity, ϵ is the molar extinction coefficient of the absorbing species and d is the path length of the cell used for the experiment. F_s is given by

$$F_s = \frac{k_s{}^s}{(k_s{}^s + k_{bet}{}^s)} \tag{11}$$

ΔOD_T can be expressed similarly

$$\Delta OD_T = \frac{1}{(1+k_q{}^s\tau_s[F])}\Phi_{isc}\frac{k_q{}^T\tau_T[F]}{(1+k_q{}^T\tau_T[F])}F_TI\epsilon d \tag{12}$$

where F_T is the fraction of radical ions formed from the triplet state and is given by

$$F_T = \frac{k_s{}^T}{(k_s{}^T + k_{bet}{}^T)} \tag{13}$$

The ratio F_T/F_s, gives the ratio of the radical ion pairs formed through the triplet and singlet pathways.

When the concentration of DBF used is very high (greater than 0.1 M), $k_q{}^s\tau_s[F]/(1+k_q{}^s\tau_s[F] \approx 1$, and hence we can assume that $\Delta OD = \Delta OD_A$. It follows from Eq. (11) that $\Delta OD = F_sI\epsilon d$. Similarly, when [DBF] is very small (10^{-4} M), less than 1% of $^1TPP^{+*}$ is quenched and $\Delta OD = \Delta OD_T$. Using this value, $F_TI\epsilon d$ was calculated. The ratio $F_TI\epsilon d/F_sI\epsilon d$ was then calculated and this gives the ratio of the concentration of triplet-derived radicals to that of singlet-derived radicals. The value obtained was 1.6, which is close to that reported in the photo-oxygenation of adamantylidene adamantane by Akaba et al. [13]. This indicates that the triplet is 1.6 times more efficient in producing the radical ion pairs than the singlet excited state. This result shows that back electron transfer is more pronounced for the singlet excited state than the triplet excited state, where it is spin forbidden and occurs with a slow rate.

3.2. *Secondary processes*

In the present photo-oxygenation reaction, the fate of TPP$^\bullet$ and F$^{\bullet+}$ constitutes the secondary process. The formation of the enediones **4a–4c** and **5a–5c** suggests that the furan radical cation is intercepted by oxygen in some form. In order to obtain a clear understanding of the reaction mechanism, it is essential to determine the nature of the oxygenating species involved, which could be molecular oxygen ($^3O_2$), singlet oxygen ($^1O_2$) or superoxide ion ($O_2^{\bullet-}$). The possible reaction pathways are shown in Scheme 3.

The involvement of singlet oxygen (Eqs. (14) and (17)) in this photo-oxygenation can be ruled out on the basis of the following observations. The rate constant for the quenching of ^{3}TPP^{+*} by oxygen is approximately two orders of magnitude smaller than the rate constant of quenching by furans (see above). This means that when furan and oxygen are present in the system, the TPP$^+$ excited states are preferentially quenched by furan and not by oxygen. Even if a small amount of singlet oxygen is formed in this route, its reaction with F$^{\bullet+}$ will be slow. This is because singlet oxygen is electrophilic in nature and hence its reaction is extremely slow when the substrate is not electron rich [29–32]. Another possibility is the reaction of singlet oxygen with a ground state furan molecule. We can eliminate this possibility from observations in the literature. For example, the reaction of singlet oxygen with TePF (**1c**) has been reported to give several products [33–35] and these are not observed in the present photo-oxygenation reaction.

$$^3\mathrm{TPP}^{+*} + O_2 \longrightarrow \mathrm{TPP}^\bullet + {}^1O_2 \qquad (14)$$

$$\mathrm{TPP}^\bullet + O_2 \longrightarrow \mathrm{TPP}^+ + O_2^{\bullet-} \qquad (15)$$

$$\mathrm{TPP}^\bullet + O_2 \longrightarrow \mathrm{TPP}\text{----}O_2^\bullet \qquad (16)$$

$$\mathrm{F}^{+\bullet} + {}^1O_2 \longrightarrow \text{Products} \qquad (17)$$

$$\mathrm{F}^{+\bullet} + O_2^{-\bullet} \longrightarrow \text{Products} \qquad (18)$$

$$\mathrm{F}^{+\bullet} + O_2 \longrightarrow \text{Products} \qquad (19)$$

Scheme 3.

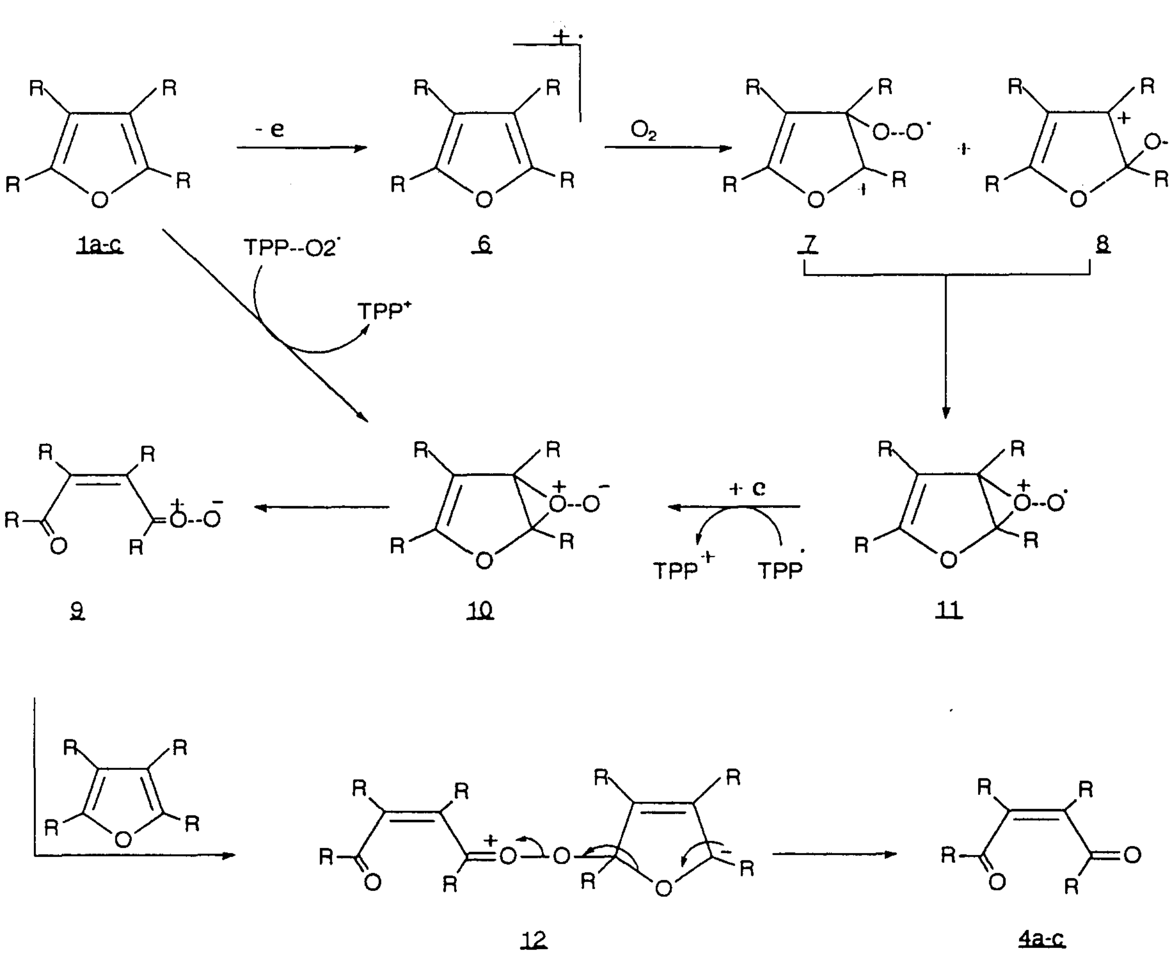
The involvement of superoxide ion in these reactions (Eqs. (15) and (18)) can also be eliminated from observations in the literature. Based on cyclic voltammetric studies, Akaba et al. [13] have shown that TPP$^\bullet$ reacts with oxygen to form a complex (TPP–O$_2^\bullet$), but this reaction does not yield superoxide ion. Our observation that the decay of TPP$^\bullet$ is not affected by oxygen supports this conclusion. Thus we can safely rule out the involvement of both singlet oxygen and superoxide ion in these photo-oxygenation reactions.

3.3. *Mechanism of oxygenation*

Assuming that the secondary process is the reaction of the furan radical cation with molecular oxygen, a possible mechanism for the formation of the observed products can be outlined as shown in Scheme 4. The attack of oxygen on the furan radical cation leads to the formation of the peroxy radical cation, the structure of which can be represented by **7** or **8**, which in turn will lead to **11**. Back electron transfer from TPP$^\bullet$ to **11** can give the perepoxide **10**. Such perepoxide intermediates have been suggested in a number of photochemical "ene" reactions [29–32]. Alternatively, the perepoxide can be formed by reaction of the furan radical cation with the TPP–O$_2^\bullet$ complex (see above), in which case the reaction proceeds in a similar manner to that described by Barton et al. [36] for the photo-oxygenation of ergosteryl acetate with trityl cation. The perepoxide can open up to give the carbonyl oxide **9**, which can add on to another molecule of furan to give the dimeric species **12**. This dimeric species can then fragment to give two molecules of the enedione **4**. It should also be noted that the formation of the carbonyl oxide and its reaction with furan to give a dimeric species similar to **12** has been proposed previously by Murray and Higley [37] and verified by Wasserman and Saito [35] in the reaction of furan derivatives with singlet oxygen.

We can also envisage the formation of 1,4-endoperoxides and 1,2-dioxetanes as intermediates from **7** and **8** in these reactions. The formation of these intermediates is well established in the singlet oxygen reactions of furan derivatives [33–35]. Decomposition of these intermediates usually gives two or three products. We have rejected the involvement of dioxetanes or endoperoxides since only the enediones are formed in the present photo-oxygenation reactions.

The lack of reactivity of DBF also deserves attention. Photo-oxygenation did not give any product in this case, even though electron transfer to the TPP$^+$ excited state



Scheme 4.

occurs to generate DBF˙+. This may be due to the fact that the formation of products similar to **4** and **5** in this case would mean the loss of aromaticity of both of the benzene rings. This would be an endothermic process and hence back electron transfer is the preferred pathway.

4. Experimental section

All melting points are uncorrected and were determined in a Buchi model 530 melting point apparatus. The IR spectra were recorded on a Perkin–Elmer model 882 IR spectrometer. The mass spectra were recorded on a Hewlett Packard model 5971 mass detector, attached to an HP 5890 series 2 gas chromatograph. All the solvents were distilled before use. Spectroscopic grade solvents were used for fluorescence and laser flash photolysis studies.

4.1. Starting materials

DPF (**1a**), (melting point (m.p.), 91–92 °C), TrPF (**1b**) (m.p., 95–96 °C) and TePF (**1c**) (m.p. 173–174 °C) were prepared by reported procedures [38,39]. DBF (**2**) was obtained from Aldrich and was recrystallized before use. Triphenylpyrylium perchlorate (**3**) was prepared by a reported procedure and was recrystallized twice before use [40].

4.2. General procedure for steady state photo-oxygenation

A solution of furan (100 mg) and TPP$^+$ (5 mg, 0.12 mmol) in dichloromethane (250 ml) was purged with oxygen for 15 min. The solution was then irradiated with 3500 Å light from a Srinivasan–Griffin Rayonet photoreactor for 10 min. Cold water was circulated during irradiation to keep the temperature below 20 °C. After irradiation, the solvent was removed at room temperature. The residue was dissolved in ether and filtered to remove TPP$^+$ and the filtrate was chromatographed either by thin layer chromatography (TLC) or column chromatography over silica gel. The products were identified by their melting points, IR spectra and mass spectra. For blank experiments in the absence of oxygen, the solutions were purged with argon for 15 min before photolysis.

4.3. Photo-oxygenation of 1a

Photolysis of **1a** (100 mg, 0.45 mmol) gave, after column chromatography over silica gel, 90 mg (84%) of *trans*-dibenzoylethylene (**5a**) (elution with petroleum ether) (m.p., 110–111 °C (mixture m.p.)) and 5 mg (5%) of *cis*-1,2-dibenzoylethylene (**4a**) (elution with a mixture (95:5) of petroleum ether and ethyl acetate) (m.p., 133–134 °C; 135 °C [41]). IR (ν_{max}): 3068 (C–H), 1651 (C=O) and 1596 (C=C).

In another experiment, photolysis of **1a** (100 mg, 0.45 mmol) was carried out in the absence of oxygen. Work-up gave 98 mg (98%) of the starting material (m.p., 89–90 °C (mixture m.p.)). In yet another experiment, photolysis of **1a** (100 mg, 0.45 mmol) was carried out in the presence of oxygen without adding TPP^+. Work-up gave 98 mg (98%) of the starting material (m.p., 89–90 °C (mixture m.p.)).

4.4. Photo-oxygenation of 1b

1b (100 mg, 0.34 mmol), after work-up by preparative TLC, gave 14 mg (13%) of *cis*-1,2-dibenzoylstyrene (m.p., 130–131 °C (mixture m.p.)) and 79 mg (75%) of *trans*-1,2-dibenzoylstyrene (m.p., 126–127 °C; 126–127°C [34]). IR (ν_{max}): 3062 (C–H), 1652 (C=O) and 1597 (C=C). Mass spectrum, *m/e* (relative intensity): 312 (M^+, 13), 235 ($M^+ - C_6H_5$, 1), 207 ($M^+ - COC_6H_5$, 5), 105 ($COC_6H_5{}^+$, 100), 77 ($C_6H_5{}^+$, 51) and other peaks.

Photolysis of **1b** (100 mg, 0.34 mmol) in the absence of oxygen gave, after work-up, 98 mg (98%) of the starting material (m.p., 95–96 °C (mixture m.p.)).

4.5. Photo-oxygenation of 1c

Photolysis of **1c** (100 mg, 0.27 mmol), after work-up by column chromatography, gave 32 mg (31%) of *trans*-1,2-dibenzoylstilbene (**5c**) (elution with petroleum ether) (m.p., 234–235 °C; 235 °C [42]). IR (ν_{max}): 3061 (C–H), 1663 (C=O) and 1597 (C=C). Mass spectrum, *m/e* (relative intensity): 388 (M^+, 3), 311 ($M^+ - C_6H_5$, 1), 283 ($M^+ - COC_6H_5$, 2), 178 ($M^+ - 2COC_6H_5$, 4), 105 ($COC_6H_5{}^+$, 100), 77 ($C_6H_5{}^+$, 35) and other peaks.

Further elution with a mixture (80:20) of petroleum ether and ethyl acetate gave 54 mg (52%) of *cis*-1,2-dibenzoylstilbene (**4a**) (m.p., 213–214 °C; 214 °C [43]). IR (ν_{max}): 3066 (C–H), 1667 (C=O) and 1597 (C=C). Mass spectrum, *m/e* (relative intensity): 388 (M^+, 3), 311 ($M^+ - C_6H_5$, 1), 283 ($M^+ - COC_6H_5$, 3), 178 ($M^+ - 2COC_6H_5{}^+$, 5), 105 ($COC_6H_5{}^+$, 100), 77 ($C_6H_5{}^+$, 35) and other peaks.

In another experiment, photolysis of **1c** (100 mg, 0.27 mmol) was carried out in the absence of oxygen. Work-up gave 95 mg (95%) of the starting material (m.p., 173–174 °C (mixture m.p.)).

4.6. Photo-oxygenation of 2

Photolysis of **2** (100 mg, 0.6 mmol), after work-up, gave 92 mg (92%) of the starting material (m.p., 84–85 °C (mixture m.p.)).

4.7. Fluorescence quenching studies

Fluorescence quenching of TPP^+ was carried out in a Spex Fluorolog F 112-X spectrofluorometer. A 2×10^{-5} M solution of TPP^+ in dichloromethane was used for these studies. TPP^+ was excited at 420 nm and the emission was monitored from 440 to 600 nm.

4.8. Laser flash photolysis studies

Laser flash photolysis experiments were carried out in an Applied Photophysics model LKS-20 laser kinetic spectrometer using a Quanta Ray GCR-12 series Nd–YAG laser. The analysing and exciting beams were fixed at right angles to each other. The laser energy was 70 mJ at 355 nm. The solutions were prepared in spectroscopic grade dichloromethane and were degassed with argon or oxygen.

5. Conclusions

Electron transfer oxygenation of aryl-substituted furan derivatives leads to the formation of enediones as products. Laser flash photolysis and fluorescence quenching studies confirm that the photo-oxygenation proceeds by electron transfer. Both singlet and triplet excited states of TPP^+ act as electron acceptors to produce radical cations of the furan derivatives. Subsequent reaction of the furan radical cations with molecular oxygen gives the observed products. Under our experimental conditions, DBF does not give any products, although it produces radical cations. Back electron transfer to generate the starting material is the preferred pathway in this case.

Acknowledgements

The authors wish to thank the Council of Scientific and Industrial Research, Government of India, and the

Regional Research Laboratory, Trivandrum, for financial support.

References

[1] L. Lopez, in J. Mattay (ed.), *Topics in Current Chemistry, Vol. 156, Electron Transfer Reactions I,* Springer, Berlin, 1990, p. 119.

[2] J. Eriksen, C.S. Foote and T.L. Parker, *J. Am. Chem. Soc., 99* (1977) 6455.

[3] L.T. Spada and C.S. Foote, *J. Am. Chem. Soc., 102* (1980) 391.

[4] J. Eriksen and C.S. Foote, *J. Am. Chem. Soc., 102* (1980) 6083.

[5] J. Eriksen and C.S. Foote, *J. Phys. Chem., 82* (1978) 2654.

[6] L.E. Manring, C.I. Gu and C.S. Foote, *J. Phys. Chem., 87* (1983) 40.

[7] D.C. Dobrowolski, P.R. Ogilby and C.S. Foote, *J. Phys. Chem., 87* (1983) 2261.

[8] P.R. Ogilby and C.S. Foote, *J. Am. Chem. Soc., 105* (1983) 3423.

[9] J. Santamaria, *Tetrahedron Lett., 22* (1981) 4511.

[10] C.S. Foote, *Tetrahedron, 41* (1985) 2221.

[11] Y. Araki, D.C. Dobrowolski, T.E. Goyne, D.C. Hanson, Z.Q. Jiang, K.J. Lee and C.S. Foote, *J. Am. Chem. Soc., 106* (1984) 4570.

[12] R. Akaba, S. Aihara, H. Sakuragi and K. Tokumaru, *J. Chem. Soc., Chem. Commun.,* (1987) 1262.

[13] R. Akaba, H. Sakuragi and K. Tokumaru, *J. Chem. Soc., Perkin Trans., 2* (1991) 291.

[14] R. Akaba, Y. Niimura, T. Fukushima, Y. Kawai, T. Tajima, T. Karugemi, A. Negishi, M. Kamata, H. Sakuragi and K. Tokumaru, *J. Am. Chem. Soc., 114* (1992) 4460.

[15] M. Kamata, Y. Kato and E. Hasegawa, *Tetrahedron Lett., 32* (1991) 4349.

[16] R. Akaba, K. Ohshima, Y. Kawai, Y. Obuchi, A. Negishi, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett., 32* (1991) 109.

[17] S.L. Mattes and S. Farid, in A. Padwa (ed.), *Organic Photochemistry,* Vol. 6, Dekker, New York, 1983, p. 233.

[18] G.J. Kavarnos and N.J. Turro, *Chem. Rev., 86* (1986) 419.

[19] H. Garcia, S. Iborra, M.A. Miranda and J. Primo, *New J. Chem., 13* (1989) 805.

[20] K. Okada, E. Hasegawa and T. Mukai, *Chem. Lett.,* (1983) 305.

[21] J. Mlcoch and E. Steckhan, *Angew. Chem., Int. Ed. Engl., 24* (1985) 412.

[22] Y. Kuriyama, T. Arai, H. Sakuragi and K. Tokumaru, *Chem. Lett.,* (1988) 1193.

[23] E. Hasegawa, K. Ishiyama, H. Kashiwazaki, T. Horaguchi and T. Shimizu, *Tetrahedron Lett., 31* (1990) 4045.

[24] R. Akaba, H. Sakuragi and K. Tokumaru, *Chem. Phys. Lett., 174* (1990) 80.

[25] K. Okada, K. Hisamitsu and T. Mukai, *Tetrahedron Lett., 22* (1981) 1251.

[26] M. Muneer, *Ph.D. Thesis,* Indian Institute of Technology, Kanpur, 1987.

[27] D. Rehm and A. Weller, *Isr. J. Chem., 8* (1970) 259.

[28] P. Valat, S. Tripathi, V. Wintgens and J. Kossanyi, *New. J. Chem., 14* (1990) 825.

[29] C.W. Jefford, *Chem. Soc. Rev.,* (1993) 59, and references cited therein.

[30] W. Adam, *Chem. Zeit., 99* (1975) 142.

[31] A.P. Schaap and K.A. Zaklika, in H.H. Wasserman and R.W. Murray (eds.), *Singlet Oxygen,* Academic Press, New York, 1979, p. 179.

[32] W. Adam, in S. Patai (ed.), *The Chemistry of Functional Groups,* Wiley, New York, 1983, p. 829.

[33] H.H. Wasserman and A. Liberless, *J. Am. Chem. Soc., 82* (1960) 2086.

[34] R.E. Lutz, W.J. Welstead, Jr., R.G. Bass and J.I. Dak, *J. Org. Chem., 27* (1962) 1111.

[35] H.H. Wasserman and I. Saito, *J. Am. Chem. Soc., 97* (1975) 905.

[36] D.H.R. Barton, G. Leclerc, P.D. Magnus and I.D. Menzies, *J. Chem. Soc., Chem. Commun.,* (1972) 447.

[37] R.W. Murray and D.P. Higley, *J. Am. Chem. Soc., 96* (1974) 3330.

[38] J.E. Lutz and R.J. Rowlitt, Jr., *J. Am. Chem. Soc., 70* (1948) 1359.

[39] D.R. Berger and K.K. Summerbal, *J. Org. Chem., 24* (1959) 1881.

[40] M.V. Baldovi, H. Garcia, M.A. Miranda and J. Primo, *Monatsch. Chem., 121* (1990) 371.

[41] J.B. Conat and R.E. Lutz, *J. Am. Chem. Soc., 45* (1923) 1303.

[42] F. Ramirez and M.B. Rubin, *J. Am. Chem. Soc., 77* (1955) 3768.

[43] D. Bar and M. Erbdebruyna, *Ann. Pharm. Tranc., 16* (1958) 235; *Chem. Abstr., 53* (1959) 4183.