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Excited-state Reactions of Triphenylpyrylium Ion with Cinnamate Derivatives: Triplet-mediated Isomerization and Singlet-mediated Dimerization

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Excited-state reactivity of 2,4,6-triphenylpyrylium ion (TPP$^+$) with cinnamates has been studied by fluorescence quenching and laser flash photolysis experiments. Electron-transfer reactions between cinnamates and excited states of TPP$^+$ are reported. The pyryl radical (TPP$^\cdot$) has been observed as an intermediate. In the singlet manifold, dimerization product(s) are reported and in the triplet manifold the *trans–cis* isomerization product is reported. Selectivity of oxygen in the product formation is observed. This is one of the few systems in which both isomerization and dimerization mechanisms are operating together through a radical cation intermediate. For the first time the dimerization of cinnamate derivatives *via* a radical cation is reported.

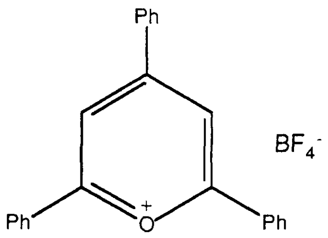
The study of solution photochemistry has grown enormously with the input of new ideas regarding the nature of the intermediates. Sometimes the prevailing ideas influence the interpretation of the mechanistic details and, occasionally, published results are reinterpreted in terms of popular intermediates. These popular intermediates include triplet states,[1] phantom triplets,[2] exciplexes[3] and radical ions.[4]

There has been a great deal of interest in the photoreactions and sensitized photoreactions of cinnamic acid and its derivatives.[5–14] Photodimerization and *E–Z* isomerization are the two basic reactions occurring in cinnamic acid derivatives. Much attention has been paid over the years to the photodimerization of cinnamic acid and its derivatives because of their use in microlithography and as photoresists.[5] The cyclodimerization of cinnamic acid in the crystalline state is one of the oldest and best known reactions in solid-state photochemistry.[6] Until the report of Egerton *et al.*[7] it was believed that the dimerization of cinnamic acid derivatives occurred more efficiently only in the solid state. Later, Shindo *et al.*[8a] explored the dynamics of the photodimerization of ethyl cinnamate in dilute solutions. Photoisomerization[8b] and photodimerization[8c] quantum yields were measured for a variety of cinnamates. Dimer formation of the alkyl cinnamates, truxinates, was also reported in organized media.[9,10]

Photosensitivity of polymeric cinnamate is limited to 330 nm and efforts have been made to sensitize beyond this wavelength. A variety of triplet sensitizers like aromatic hydrocarbons[11] and Michler's ketone[12] were used. Pyrylium and thiopyrylium ions have also been used to sensitize the polyester derivatives of cinnamic and cinnamylideneacetic acids. Energy-transfer sensitization has been reported and further support is given for this mechanism by their LCI-SCF calculation.[13,14] Since the pyrylium salts are good electron acceptors in the excited state, Williams *et al.*[5] have not ruled out the possibility of electron transfer reactions between the pyrylium salts and cinnamate derivatives.

In recent years, the triphenylpyrylium ion (TTP$^+$) has been used in the study of photosensitized oxygenation,[15] and sensitized isomerization of *cis*- and *trans*-stilbene in non-aqueous[16] and microheterogeneous[17] media. In addition to these recent studies, TTP$^+$ has been used in a number of sensitized electron-transfer reactions.[18] Nevertheless, the mechanism of sensitization of cinnamates and polymeric cinnamates by TTP$^+$ has not been unravelled.

Our interest was originally to find the mechanism of TTP$^+$-sensitized photocrosslinking of cinnamate derivatives. In this study we have taken unsubstituted triphenylpyrylium tetrafluoroborate as the sensitizer, and cinnamic acid and esters as the model systems in an acetonitrile medium.



(TPP$^+$BF$^-_4$)

$E(S_1) = 2.80$ eV;[16a]† $E(T) = 2.30$ eV[19]

$E_{TPP^+/TPP^\cdot} = -0.38$ V (*vs.* SCE)[20]

We report, herein, our findings in the steady-state and laser flash photolysis, and fluorescence quenching experiments. We observed an electron-transfer sensitization of cinnamates in contrast to the report of energy transfer by Mistr and coworkers.[13,14] So far, the occurrence of isomerization only from the singlet state of the cinnamate has been reported and the isomerization through the triplet-mediated radical pair involving cinnamates is reported here for the first time.

Experimental

2,4,6-Triphenylpyrylium tetrafluoroborate (Aldrich) was recrystallized twice from ethanol before use. All other reagents, *trans*-cinnamic acid (tCA) (Fluka), *trans*-methyl cinnamate (tMC) (Aldrich) and *trans*-ethyl cinnamate (tEC) (Aldrich) were used after purification. Acetonitrile used in this investigation was spectral grade from Fluka and Aldrich.

Steady-state photolysis experiments were carried out using a 150 W medium pressure mercury lamp of photon flux 110 mJ cm^{-2} min^{-1} with quartz jacket and water filter. Light-band selection was done using a 366 nm Oriel glass filter. Laser flash photolysis was carried out by choosing the third-harmonics of a Nd-YAG laser with the pulse energy of 20 mJ (3 ns duration); the detailed description of the facility has

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† 1 eV ≈ 1.602 18 × 10^{-19} J.

been reported elsewhere.[18] Argon was used for degassing the solutions.

Fluorescence quenching experiments were carried out using a Perkin-Elmer LS-5B spectrofluorimeter. Absorbance was maintained at *ca.* 0.1 at 355 nm. Absorption spectra were recorded on a Beckman DU7400 diode-array spectrophotometer.

Results

Steady-state Photolysis

Steady-state photolysis of a mixture of TPP$^+$ (*ca.* 1×10^{-5} mol dm^{-3}) and cinnamates (*ca.* 3×10^{-5} mol dm^{-3}) at 366 nm leads to the rapid depletion of the 275 nm absorption maximum in air-equilibrated acetonitrile and the observed spectral changes are represented in Fig. 1(*a*). In argon-saturated acetonitrile a different spectral change was observed [Fig. 1(*b*)] and a photostationary state was reached upon irradiation. A similar trend was observed for all the cinnamate derivatives in this study. Note that the 275 nm absorption is an additive absorption of both TPP$^+$ and cinnamates (Fig. 2), and mixing of the substrates does not alter the absorption spectrum, revealing that there is no ground-state interaction.

Laser Flash Photolysis

Laser flash photolysis was performed on TPP$^+$ (4.5×10^{-5} mol dm^{-3}) in the presence of varying concentrations of cinnamates (from 5.8×10^{-5} to 5.8×10^{-2} mol dm^{-3}). At lower concentrations of cinnamates, the triplet lifetime of TPP$^+$ is quenched, which results in residual absorbance in the spectral region 440–600 nm. The transient absorption spectrum, recorded at the residual absorption timescale, shows a maximum absorption at 550 nm. A representative spectrum is given in Fig. 3 spectrum B and the insert (*b*) shows the corresponding transient absorption decay at 550 nm. Absorption at 550 nm is characteristic of TPP$^•$ as reported in the literature.[20] Laser flash photolysis of TPP$^+$ with a higher concentration of cinnamates (*ca.* 6×10^{-2} mol dm^{-3}) results in a long-lived transient absorption decay [see insert (*a*) in Fig. 3] at 550 nm. The dynamics and the nature of this transient are not perturbed by the presence of oxygen and concentrations of cinnamate and TPP$^+$. The transient absorption spectrum recorded immediately after the flash, both in the presence and absence of oxygen, remains the same, and is represented in Fig. 3 spectrum A. The triplet–triplet absorption spectrum was also recorded in the absence of any quencher and is given in Fig. 3 spectrum C for comparison. This is similar to the one reported recently in the literature.[21] The oscillogram trace in insert (*a*) is attributed to the decay of TPP$^•$; spectrum A corresponds to the absorption of this radical. The trace in insert (*b*) has two components, the fast decay due to the TPP$^+$ triplet state and the slow decay due to TPP$^•$; spectrum B recorded at 10 μs is thus assigned to TPP$^•$. The difference in the absorption around 550 nm depends on the tCA concentrations; 5.85×10^{-2} mol dm^{-3} for spectrum A and 1.7×10^{-4} mol dm^{-3} for spectrum B. In the wavelength range 400–500 nm, the ground-state bleach recovery of TPP$^+$ becomes more important than the transient.

Triplet quenching experiments were carried out using various cinnamate concentrations. The quenching rate constant k_q^T of the triplet excited state of TPP$^+$ by cinnamates

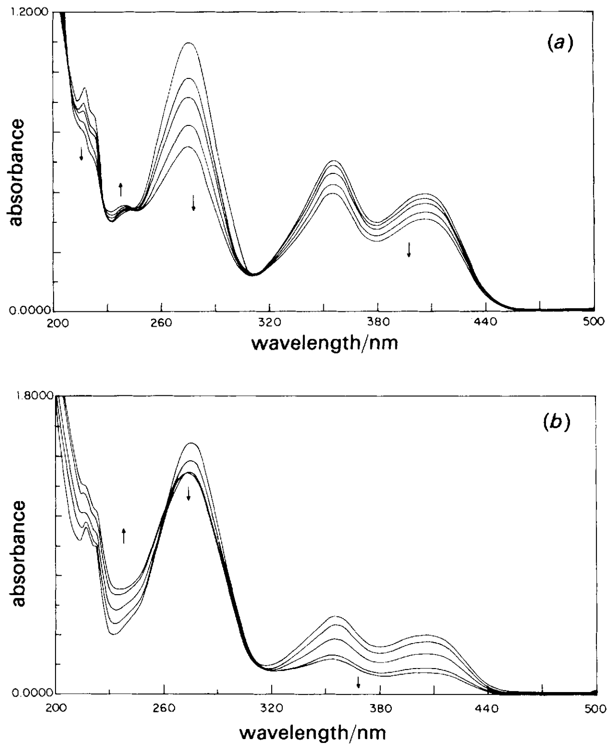


Fig. 1 Spectral changes during (*a*) photolysis of a mixture of TPP$^+$ and tCA in air-equilibrated acetonitrile for 0, 5, 15, 30 and 50 min and (*b*) photolysis of a mixture of TPP$^+$ and tCA in argon-saturated acetonitrile for 0, 2, 8, 18 and 30 min

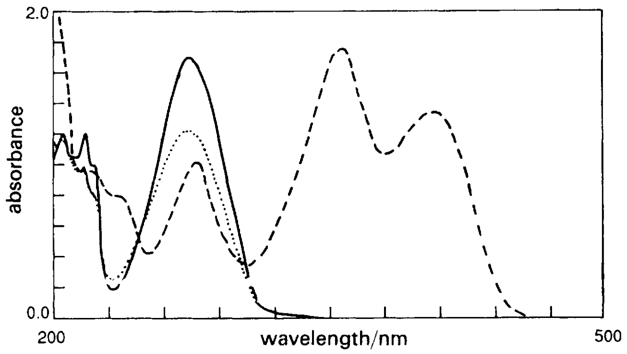


Fig. 2 Spectral comparison of TPP$^+$ (– – –), *trans*-cinnamic acid (——) and photogenerated *cis*-cinnamic acid (· · · ·) obtained by photolysis of *trans*-cinnamic acid at 366 nm for 30 min

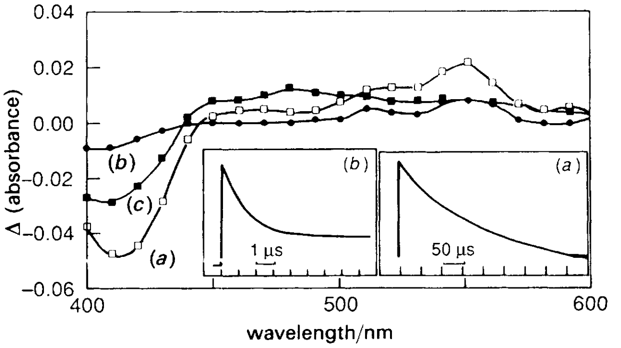


Fig. 3 Transient absorption spectrum recorded A, immediately after flash for a mixture of TPP$^+$ and tCA (5.84×10^{-2} mol dm^{-3}) in argon-saturated acetonitrile; B, at 10 μs after flash for a mixture of TPP$^+$ and tCA (1.7×10^{-4} mol dm^{-3}) in argon-saturated acetonitrile and C, triplet–triplet absorption spectrum of TPP$^+$ recorded immediately after flash in argon-saturated acetonitrile in the absence of cinnamates. Insert (*a*), radical decay corresponding to spectrum A (λ = 550 nm) and insert (*b*) transient absorption decay corresponding to spectrum B (λ = 550 nm)

was obtained using eqn. (1) by measuring the pseudo-first order rate constants at different quencher concentrations.

$$k_d = k_0 + k_q^T(Q) \qquad (1)$$

The Stern–Volmer plot of the triplet quenching is linear and the results obtained for different cinnamate derivatives are collated in Table 1. The triplet quenching experiments were carried out in argon-saturated medium. The triplet quenching by oxygen is evaluated by observing the triplet decay in air-equilibrated acetonitrile and the corresponding $k_q^T(O_2) = 7.3 \times 10^5\ s^{-1}$. The k_q^T for oxygen is obtained by taking the concentration of dissolved oxygen in acetonitrile[23] as 1.6×10^{-3} mol dm^{-3} and the magnitude of the same is 4.6×10^8 dm^3 mol^{-1} s^{-1}.

Singlet-state Quenching and Electrode Potentials

Excited singlet-state quenching of TPP$^+$ was carried out under de-aerated conditions at 25 °C, measuring the intensity of emission at 465 nm. The singlet state of TPP$^+$ is quenched effectively by the cinnamates and the quenching constants obtained for the title cinnamates are listed in Table 1. The singlet quenching constant, k_q^S, is calculated from the Stern–Volmer constant taking the literature reported[24] singlet lifetime of TPP$^+$ as 4.2 ns in acetonitrile at 25 °C. The quenching plots obey Stern–Volmer kinetics. The resulting k_q values are close to the calculated diffusion-rate limits in acetonitrile (2.9×10^{10} dm^3 mol^{-1} s^{-1}).[25] The fluorescence quenching was not accompanied by any exciplex emission.

The free energies associated with the electron transfer from the singlet as well as triplet state are obtained using the popular Rehm–Weller[26] relationship.

$$\Delta G_{S\text{ or }T} = E_{1/2\,ox}(D) - E_{1/2\,red}(A) - E_{S\text{ or }T}(A) + e_0^2/\varepsilon_a \qquad (2)$$

Since the radical ion pair generated upon electron transfer does not possess oppositely charged species, one being neutral and other cationic, and the solvent used is more polar, the last term in the above expression (contribution of Coulombic forces) is neglected.[27]

The anodic peak potential, E_{pa}, alone is reported in the literature[22] for cinnamic acid and not $E_{1/2\,ox}$. Since the oxidation potential has not been reported, ionization potentials were taken as reported[28] and converted to oxidation potentials using the following relationship.[29]

$$E_{1/2\,ox}\ (vs.\ SCE) = E_i - 6.7 \pm 0.1 \qquad (3)$$

The calculated free-energy change associated with the electron transfer from the cinnamate substrates of the excited singlet and triplet states of TPP$^+$ is exothermic, the only exception being ΔG_T for tCA (Table 1).

Discussion

Mechanism of Isomerization and Dimerization

On examining the sensitized steady-state photolysis results, we find the formation of different products in the presence and absence of oxygen. In the absence of oxygen, the nature of spectral change, shift of the absorption maximum from 275 to 273 nm, and attainment of the photostationary state reveals that the product formed is a *cis*-isomer of the cinnamate derivative. To support this, photolysis of cinnamate derivatives alone, with white light, was carried out and the similar spectral changes were observed; the product spectrum is given in Fig. 2. In the presence of oxygen, continuous depletion of the 275 nm absorption with irradiation at 366 nm is similar to dimerization spectral changes observed in the case of ethyl cinnamate, as reported in the literature.[8]

The sole formation of the isomer product in the absence of oxygen reveals that isomerization is taking place by the triplet-state reaction of the sensitizer with the cinnamates. The presence of oxygen is able to quench the triplet state of the sensitizer more effectively than when cinnamates are present at low concentration levels (*ca.* 10^{-5} mol dm^{-3}) under our photolysis experimental conditions, and this is apparent from the concentration of oxygen present in the medium and the triplet quenching constant ($k_q^T = 4.6 \times 10^8$ dm^3 mol^{-1} s^{-1}). The cinnamate, present at a low concentration level, is not sufficient to quench the singlet state of the sensitizer in the absence of oxygen. In the presence of cinnamates at high concentration (*ca.* 10^{-2} mol dm^{-3}) continuous depletion of the 275 nm absorption maximum is insensitive to oxygen, revealing that, at this concentration, cinnamates quench the singlet state of TPP$^+$ very effectively. From the fluorescence quenching data it could be estimated that 80 and 0.2% of the singlet state of TPP$^+$ is quenched at 5.84×10^{-2} and 1.7×10^{-5} mol dm^{-3} of tCA, respectively. So, the isomerization reaction does not compete with dimerization in the presence of oxygen at low and high concentration limits of cinnamates and in the absence of oxygen at low concentration limits.

The formation of TPP$^•$ was observed in the presence of cinnamates at low as well as high concentrations. At low concentrations, the triplet state of TPP$^+$ is quenched, resulting in the residual absorbance having a maximum at 550 nm. At high concentrations a long-lived transient absorption is observed owing to the reaction of TPP$^•$ formed with the other intermediate (Scheme 1). The observation of TPP$^•$ at both extremes of cinnamate concentration reveals that the electron transfer takes place from cinnamates to excited singlet and triplet states of TPP$^+$. These observations are consolidated in the reaction scheme.

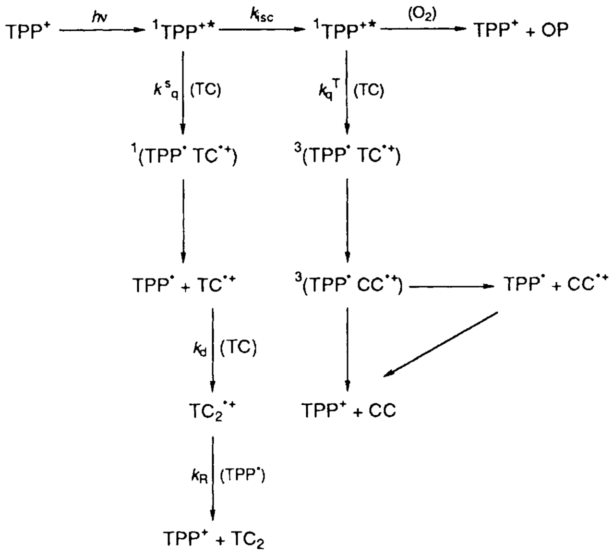
In Scheme 1, both in the presence and absence of oxygen at high concentration limits, the singlet-state-mediated electron transfer leads to a singlet radical pair and escape out of the solvent cage as TPP$^•$ and the *trans*-cinnamate radical cation (TC$^{•+}$). TC$^{•+}$ reacts with a ground-state molecule of TC, which is in excess, to give a dimeric radical cation. The decay of TPP$^•$ is due to the reaction of TPP$^•$ with the dimeric cation (TC$_2^{•+}$). Even though the clear absorptions due to TC$^{•+}$ and TC$_2^{•+}$ could not be observed. TC$^+$ and TC$_2^{•+}$ formations are proposed to explain the formation of the dimeric product and the deactivation of TPP$^•$.

On the other hand, in the absence of oxygen and at low concentration limits, the triplet state of TPP$^+$, formed by

Table 1 Thermodynamic and kinetic parameters for the quenching of the TPP$^+$ excited state by cinnamate derivatives

quencher	$E_{1/2\,ox}$ (*vs.* SCE)[a]	E_i/eV[b]	ΔG_S/eV	ΔG_T/eV	E_T/eV	ΔG_i/eV[c]	$k_q^s/10^{-10}$ dm^3 mol^{-1} s^{-1}	$k_q^T/10^{-9}$ dm^3 mol^{-1} s^{-1}	$k_R/10^{-3}$ s^{-1}
t-CA	1.95	8.70	−0.47	0.03	2.49[d]	2.33	1.62	7.27	7.72
t-MC	1.80	8.55	−0.62	−0.12	2.38[e]	2.18	1.71	3.80	7.84
t-EC[f]	—	—	—	—	*ca.* 2.49[g]	—	2.03	1.92	16.71

[a] Calculated from E; [b] ref. 22; [c] calculated using eqn. (4); [d] ref. 11(*a*) and calculated E_T is 2.79 eV; [e] ref. 19; [f] E_i and $E_{1/2\,ox}$ data are not available; [g] ref. 8(*c*).



Scheme 1 OP, oxygenated products of TPP$^+$; TC, *trans*-cinnamate; CC, *cis*-cinnamate; k_d, dimerization rate constant; k_R, radical reaction rate constant

intersystem crossing, reacts with TC resulting in the triplet radical pair. In the triplet radical pair, TC$^{•+}$ can become CC$^{•+}$ (*cis*-cinnamate radical cation) through in-cage isomerization, in competition with the cage-escape products and predominantly through back electron transfer, which results in CC (*cis*-cinnamate) and TPP$^+$.

Formation of isomer and dimer products is ruled out by the triplet energy-transfer mechanism. This can be understood by analysing Table 1 and the triplet energy[19] of TPP$^+$. Triplet energies of the cinnamates,[8c,11a,30] considered in this investigation, are well above the triplet energy of the sensitizer and, hence, the free-energy change associated with triplet-energy transfer is highly endothermic (Fig. 4).

The electron transfer to aggregated cinnamate molecules, as observed in the microheterogeneous medium, is ruled out. No deviation in the Beer's plot for the cinnamates, in the wavelength region 285–310 nm, is observed.

It is known[31] that the reaction of the alkene radical cation with neutral alkene is diffusion controlled. In addition to this, interception of the donor–acceptor radical pair by a neutral molecule of alkene resulting in a dimeric cation and the reduction of dimeric cation by back electron transfer within the geminate pair, in the case of 1,1-diphenylethylene,[32] has been reported. This sort of mechanism is not postulated by us owing to observation of the long-lived TPP$^•$.

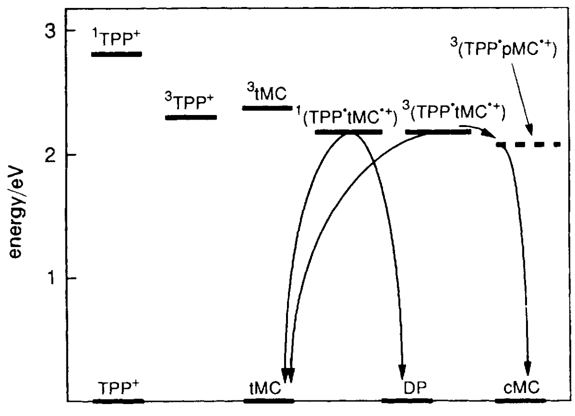


Fig. 4 Energy-level diagram for the various species of TPP$^+$ and tMC. Dotted line representation is only a tentative one. pMC represents perpendicularly oriented orbitals in methyl cinnamate cation

The proposal of formation of a dimeric radical cation by reaction of a monomeric cation with a neutral molecule is also consistent with the recent report by Akaba *et al.*[16c] In their report the *trans*-stilbene radical cation (TS$^{•+}$) is generated by electron transfer from TS to the excited state of TPP$^+$. They observed the absorption corresponding to TS$^{•+}$ and TS$_2^{•+}$. In our study such absorption for TC$^{•+}$ and TC$_2^{•+}$ could not be observed and it is possible that these absorptions are masked by absorptions due to TPP$^•$.

Role of Spin Multiplicity and Oxygen

Another subject of study was to identify the reactive excited-state spin multiplicity of cinnamates. It is known that isomerization of cinnamic acid[33] is taking place from the excited singlet state and a twisted excited state has also been proposed for cinnamates.[8b] Photoisomerization of the substituted (in the *para* position) electron-withdrawing group, methyl cinnamate, is through the triplet state, whereas that of the substituted electron donating group is through the singlet state.[33] Shindo *et al.*[8a] also reported the occurrence of dimerization through both singlet- and triplet-excited states and isomerization through singlet state for ethyl cinnamate. Triplet-sensitized dimerization has also been observed for ethyl cinnamate.[12]

Both isomerization and dimerization can occur through triplet mechanisms,[34] in which the photo-ionized electron transfer from a donor alkene to a singlet-state acceptor results in a singlet radical ion pair which undergoes reverse electron transfer to yield the locally excited alkene triplet. These isomerization and dimerization events are similar to those formed through the conventional triplet sensitization. To evaluate the possibility of this type of mechanism, the ion-pair energies are calculated using the following expression[35] [eqn. (4)] neglecting the Coulomb interaction factor and are represented in Fig. 4.

$$\Delta G_i = E_{1/2\,\mathrm{ox}}(\mathrm{D}) - E_{1/2\,\mathrm{red}}(\mathrm{A}) \qquad (4)$$

It can be seen that the energies of the ion pairs are very much below the triplet energies of cinnamates and sensitizer, and the conversion from radical pair to either triplet is endothermic.

The absence of triplet-derived dimerization, as in our present work, has been observed in the case of anethole[36] which is also an internal alkene. In addition, stilbenes[36] also fail to undergo dimerization through the triplet manifold. Recently,[16c] photo-induced dimerization has been reported for *trans*-stilbene but mention has not been made, in specific, about the multiplicity. Even though the energetics of the ion pair (TPP$^•$, TC$^{•+}$) does not allow the population of the triplet state of cinnamate, it is possible that the triplet-derived radical pair populates a radical cation, in which the orbitals are perpendicular to each other in the ion pair, which is energetically feasible,[37] and which may collapse to either the *trans* or *cis* isomer. Triplet selectivity in the oxygenation of stilbene derivatives has also been reported by Akaba *et al.*[38]

The catalytic role played by oxygen in the cyclodimerization of *N*-vinylcarbazole through the cationic intermediate is well known.[39] Such a type of catalytic activity has not been explored deeply in our present investigation. At present we observe only an assistance given by oxygen in the formation of dimeric product(s) and this occurs by quenching of the excited triplet state of TPP$^+$ by oxygen. The reactivity of the excited triplet state of TPP$^+$ with oxygen is known[40] and this leads to different oxygenated products like benzaldehyde, methylbenzoate and benzoic acid in major quantities in alcoholic solvents.

Conclusion

We have demonstrated that the photosensitized dimerization of cinnamates passes through the channel of electron transfer and this could be extended to polymeric cinnamates such as polyvinyl cinnamate, polyesters of cinnamate *etc.* Nevertheless, it needs a clear investigation of the sensitization of polymeric cinnamates with pyrylium salts. Since the triphenylpyrylium salts are good electron acceptors in the excited singlet and triplet states, it has been possible to establish the selectivity of spin multiplicity in the formation of the products. The occurrence of both isomerization and dimerization through the radical cation has been reported only in a few cases, *e.g.* *trans-N*-propenylcarbazole[41] and stilbenes,[16a,16c] and our report adds to this list.

In fact, further study of photochemically induced dynamic nuclear polarization of these systems will be able to support the involvement of radical cations and identify the nature of the cinnamate radical cation in the singlet and triplet state of TPP^+-mediated electron transfer.

The mechanism of reaction of monomeric neutral cinnamates with cationic dimeric cinnamate radicals ($TC_2^{\cdot +}$), as reported by Ledwith,[39] cannot be ruled out completely. The quantum yield investigation will be able to support such chain-reaction dimerization and this will be reported in the near future.

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