JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 10, 861–869 (1997)

THIAPYRYLIUM SALT-SENSITIZED ELECTRON TRANSFER REACTIONS OF *TRANS*-STILBENE. DIMERIZATION AND OXYGENATION

RYOICHI AKABA,[1]* MASAKI KAMATA,[2] AKIKO KOIKE,[1] KEN-ICHI MOGI[1] YASUNAO KURIYAMA[3]† AND HIROCHIKA SAKURAGI[3]

[1] *Department of Chemistry and Advanced Engineering Course of Gunma Kohsen (Gunma National College of Technology), 580 Toriba-machi, Maebashi, Gunma 371, Japan*

[2] *Department of Chemistry, Faculty of Education, Niigata University, Ikarashi, Niigata, Niigata 950–21, Japan*
[3] *Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan*

Photoinduced electron transfer reactions of *trans*-stilbene sensitized by 2,4,6-triphenylthiapyrylium tetrafluoroborate (STPP) were carried out by steady-state and laser flash pohtolysis techniques in the presence and absence of oxygen in dichloromethane. Rapid dimerization of the *trans*-stilbene cation radical with its neutral species was observed, as previously observed in 2,4,6-triphenylpyrylium tetrafluoroborate (TPP)-sensitized reactions in dichloromethane. Electrochemical and photophysical properties such as fluorescence quantum yield and T–T absorption spectrum of STPP were also studied, and the results were compared with those for TPP. The properties of STPP as an electron transfer sensitizer are discussed. © 1997 John Wiley & Sons, Ltd.

J. Phys. Org. Chem. **10**, 861–869 (1997) No. of Figures: 8 No. of Tables: 2 No. of References: 9

Keywords: thiapyrylium salt; photoinduced electron transfer; laser flash photolysis; *trans*-stilbene cation radical

Received 10 February 1997; revised 18 March 1997; accepted 21 April 1997

INTRODUCTION

Electron transfer reactions have attracted sustained interest during the last two decades.[1] Our interest in this field has been directed at the chemistry of organic cation radicals, generated by 2,4,6-triphenylpyrylium salt (TPP)-sensitized electron transfer.[2] TPP has several unique properties as an electron transfer sensitizer. First, the excited singlet state of TPP (^{1}TPP) is more electron accepting than that of frequently employed cyanoaromatics such as 9,10-dicyanoanthracene (DCA), which may allow the oxidation of substrates with higher oxidation potentials via photoinduced electron transfer.[2a] Second, a pyranyl radical (TPP$^{\bullet}$), one-electron reduced species of TPP, does not reduce molecular oxygen, and hence, superoxide anion radicals ($O_2^{-\bullet}$) may not be generated in the solution studied.[2b] Furthermore, TPP may undergo electron transfer with certain organic compounds through its excited triplet state (^{3}TPP) and also in its excited singlet state (^{1}TPP).[2e,f] DCA and other frequently used cyanoaromatics cannot meet the last two criteria.[2c]

In view of the interesting features of TPP as a sensitizer, we hoped to compare the properties of 2,4,6-triphenylthiapyrylium salt (STPP), a sulfur analog of TPP, with those of TPP. In this paper, we report some photophysical properties such as fluorescence quantum yield, lifetime of the excited singlet (^{1}STPP) and excited triplet states (^{3}STPP) and T–T absorption spectra. The results are compared with those for TPP reported previously.[2] Cyclic voltammetry of STPP was performed and semiempirical molecular orbital calculations (PM3) were carried out to obtain information about the electronic structures of STPP and its one-electron reduced species, thiapyranyl radical (STPP$^{\bullet}$). Similar calculations were also performed for TPP and TPP$^{\bullet}$ for comparison.

In addition to the photophysical and the electrochemical studies of STPP, we also undertook STPP-sensitized electron transfer reactions of *trans*-stilbene (**1**) in dichloromethane. Since we have previously reported the TPP-sensitized dimerization of **1** through its cation radical ($\mathbf{1}^{+\bullet}$),[3] it is of interest to compare the reactivity of $\mathbf{1}^{+\bullet}$ generated by STPP-sensitized electron transfer with that of TPP-sensitized electron transfer. Such a comparison will be of importance in understanding the behavior of radical ion

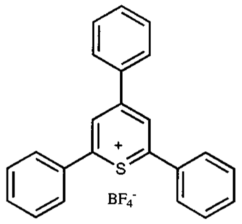
---

* Correspondence to: R. Akaba.

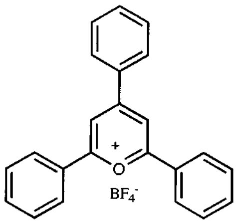
† Present address: Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, Sagamihara, Kanagawa 228, Japan.

Contract grant sponsor: Ministry of Education, Science, Sports and Culture; *Contract grant number:* 05640622; *Contract grant number:* 06640708.

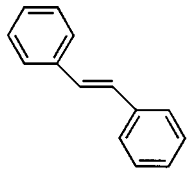
CCC 0894–3230/97/110861–09 $17.50



STPP



TPP



1

Table 1. Photophysical properties of 2,4,6-triphenylthiapyrylium tetrafluoroborate (STPP) and 2,4,6-triphenylpyrylium tetrafluoroborate

	Singlet lifetime[a] τ_s (ns)	Triplet lifetime[b] τ_t (μs)	Fluorescence quantum yield[c] (ϕ_f)
STPP	3·6	6·9	0·03
TPP	2·7[d]	9·6	0·58[d]

[a] Measured by single photon counting in dichloromethane as described in the text.

[b] Determined by the decay curves of T–T absorption as measured by LFP under argon in dichloromethane.

[c] Measured at room temperature under argon.

[d] Data from Ref. 2e.

pairs consisting of a common cation radical and a one-electron reduced species from two analogous and yet different sensitizers.

This work demonstrated that (1) STPP can be used like TPP as an efficient singlet and triplet electron transfer sensitizer which does not generate $O_2^{-\bullet}$ when used in the presence of molecular oxygen; and (2) $\mathbf{1}^{+\bullet}$ generated by STPP undergoes rapid dimerization reaction with its neutral species, as observed in TPP-sensitized reactions of **1** in dichloromethane.

RESULTS

Photophysical properties of STPP

Before we report the results of laser flash photolysis (LFP) and steady-state photolyses of STPP in the presence of **1**, the photophysical properties of STPP are presented. First, the fluorescence quantum yield (ϕ_f) of STPP was measured in dichloromethane, and found to be 0·03 at room temperature. The value is much lower than that of TPP (0·58).[2e] Second, the singlet lifetime (τ_s) was measured in dichloromethane at room temperature by the single photon counting technique, and was found to be 3·2 ns, which is similar to that observed for TPP (2·7ns).[2e] The results are summarized in Table 1.

Since both ^{3}TPP and ^{1}TPP undergo efficient electron transfer with certain organic donor molecules in solution,[2e,f] it might be expected that STPP may also similarly undergo efficient electron transfer through ^{3}TPP (some preliminary LFP work with STPP has been published[4]). Therefore, attempts were made to detect the T–T absorption spectra. Thus, LFP of STPP ($3{\cdot}9\times10^{-5}$ M) under argon gave the transient spectra shown in Fig. 1. The spectra may safely be assigned to the T–T absorption spectra since they were efficiently quenched by oxygen and aromatic donors such as **1** (see below). The triplet lifetime (τ_T) was estimated to be 6·9 μs under argon. Quenching experiments on the T–T absorption by molecular oxygen gave $k_q^{O_2}[O_2]=1{\cdot}4\times10^6\ \mathrm{s}^{-1}$. Since the oxygen concentration ($1{\cdot}07\times10^{-3}$ M at 1 atm) in dichloromethane is known,[5] the quenching rate constant $k_q^{O_2}=1{\cdot}3\times10^8\ \mathrm{s}^{-1}$. The quenching rate constant k_d^T for ^{3}STPP by **1** was determined by measuring the rate of rise of the 480 nm band due to the formation of $\mathbf{1}^{+\bullet}$ with varying concentration of **1**. The observed pseudo-first-order constant $k_d{}^T$ is plotted against the concentration of **1** in Figure 2. The slope ($k_q{}^T$) gave the quenching rate constant of ^{3}STPP by **1** as $1{\cdot}9\times10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, indicating that **1** quenches ^{3}STPP with an almost diffusion-controlled limit.

Laser flash photolysis of STPP in the presence of 1 under argon

In order to see how STPP actually works as an electron-transfer sensitizer, we carried out LFP of STPP in the presence of **1** in dichloromethane. LFP of STPP ($3{\cdot}0\times10^{-5}$ M) in the presence of **1** ($3{\cdot}4\times10^{-2}$ M) with an excimer-pumped dye laser (408 or 425 nm excitation), where *ca* 80% of ^{1}STPP was quenched by **1** as estimated by the K_{sv} value ($76{\cdot}1\ \mathrm{M}^{-1}$), gave the transient spectra shown in Figure 3. Figure 3 clearly indicates that the intensity of the 480 nm band decreases with a concomitant increase in the intensity of the 470 nm band. This spectral change corresponds to the formation of a dimer cation radical of **1** through the reaction of $\mathbf{1}^{+\bullet}$ with **1**, since the 480 and 470 nm bands are assigned to the monomer and dimer cation radicals of **1**. Similar spectral changes were observed previously in TPP-sensitized electron transfer reactions of **1** in dichloromethane.[3]

The reactions of $\mathbf{1}^{+\bullet}$ with **1** to form the dimer cation radicals could also be confirmed from time profiles of the 470 and 480 nm absorption bands, as shown in Figures 4 and 5, respectively. The 470 nm band exhibited a rise with a rate constant of $3\times10^6\ \mathrm{s}^{-1}$ whereas the 480 nm band

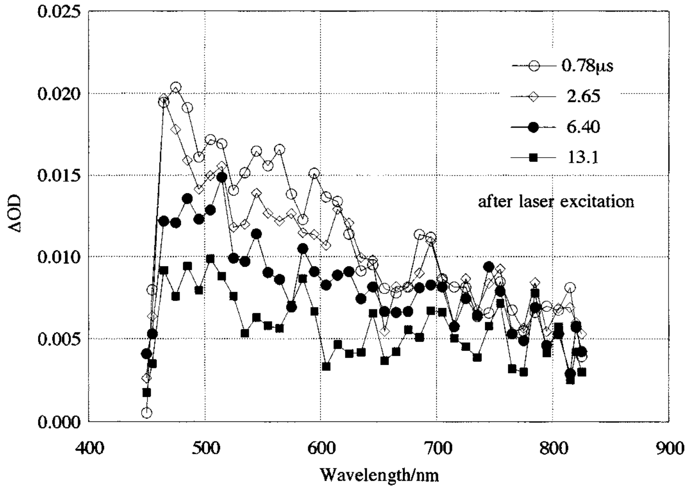


Figure 1. Transient spectra assigned to T–T absorption obtained from LFP of STPP ($3{\cdot}9\times10^{-5}$ M) in dichloromethane under argon

exhibited a decay with a rate constant of 7×10^5 s^{-1}, which would be in reasonable agreement for such closely positioned absorption bands. The rate constant for the dimer cation radical formation was then estimated by measuring the pseudo-first-order rate constant (decay at 480 and/or 485 nm) with varying concentration of **1**. It is reasonable to assume that changes in the bulk concentration of **1** would not affect the pseudo-first-order rate constant for the dimer cation radical formation since the bulk concentration of **1** (*ca* 10^{-2} M) is much higher than that of $\mathbf{1}^{+\bullet}$ ($<10^{-6}$ M) generated by pulsed laser excitation. The rate constant (k_{dim}) was found to be $1{\cdot}5\times10^{-7}$ M^{-1} s^{-1}, as shown in Figure 6, which is nearly the same as that obtained previously in the TPP-sensitized dimerization of **1** in dichloromethane (2×10^7 M^{-1} s^{-1}).[3] These results show that the dimer cation radical formation would not be dependent on the sensitizers employed.

LFP studies at lower concentrations of **1** were also carried out to see if similar dimerization reactions may be observed under such conditions. Thus, laser irradiation of STPP ($3{\cdot}9\times10^{-5}$ M) in the presence of **1** ($1{\cdot}3\times10^{-3}$ M) under argon exhibited the transient spectra shown in Figure 7. In striking contrast to the spectra shown in Figure 3, only the 480 nm band assigned to $\mathbf{1}^{+\bullet}$ was observed during the time considered. The decay (not shown) can be analyzed by second-order kinetics ($k/\varepsilon=2{\cdot}1\times10^5$ at 480 nm).

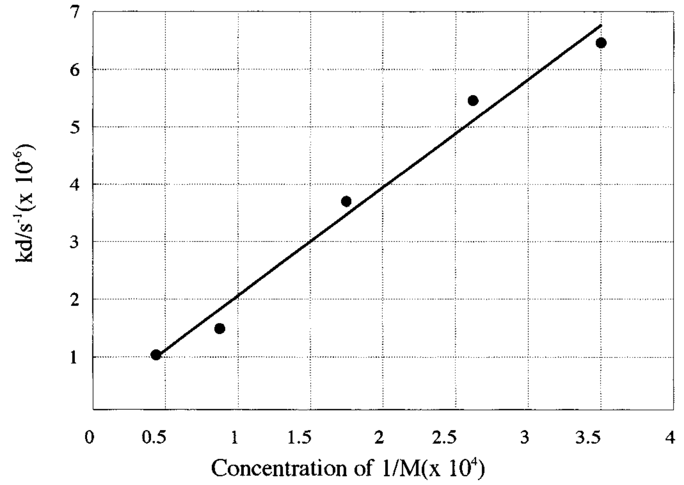


Figure 2. Plot of pseudo-first-order rate constant as a function of the concentration of **1**. The slope gave the quenching rate constant of ^{3}STPP by **1**

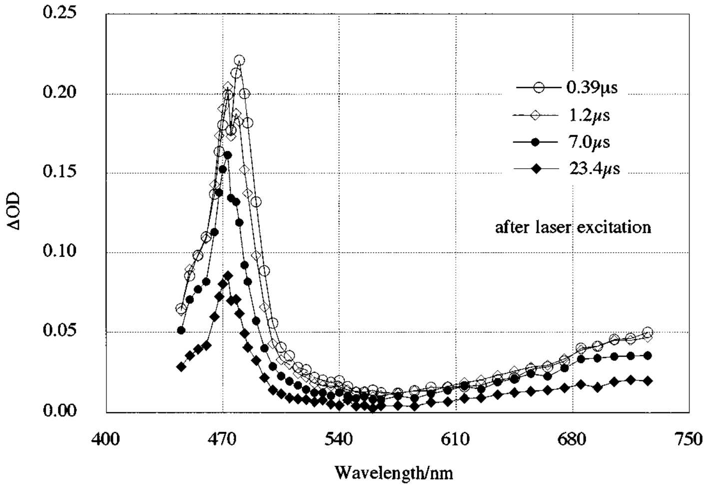


Figure 3. Transient spectra obtained from LFP of STPP ($3{\cdot}9\times10^{-5}$ M) in the presence of **1** ($3{\cdot}4\times10^{-2}$ M) in dichloromethane under argon

Laser flash photolysis of STPP in the presence of 1 under oxygen

Whether the fate of $\mathbf{1}^{+\bullet}$ is affected or not by molecular oxygen would be of interest since STPP-sensitized electron transfer reactions of **1** in the presence of oxygen gave a few oxygenation products such as benzaldehyde (see below), although in low yields. If molecular oxygen captures $\mathbf{1}^{+\bullet}$ very rapidly, it may be observed as spectral changes in the LFP experiments under oxygen. However, LFP of STPP ($3{\cdot}7\times10^{-5}$ M) in the presence of **1** ($3{\cdot}6\times10^{-2}$ M) under oxygen gave transient spectra (not shown), identical with those under argon. The decay profiles at the 475, 480 and 485 nm absorption bands under oxygen are also essentially similar to those under argon. The results suggest that addition of $\mathbf{1}^{+\bullet}$ to its neutral species is significantly faster than that to molecular oxygen, although the latter reaction cannot be completely ruled out (see below).

Cyclic voltammetry of STPP

In photoinduced electron transfer reactions, the properties of one-electron reduced species of a sensitizer are of primary importance since it is generated as a radical ion pair with a donor cation radical. Some properties of the sensitizer such as electron-accepting ability and the reactivity of the one-electron reduced species toward certain organic compounds can be measured by cyclic voltammetry (CV). As shown by Saeva and Olin,[7] cyclic voltammograms (not shown) of STPP in acetonitrile indicate that not only

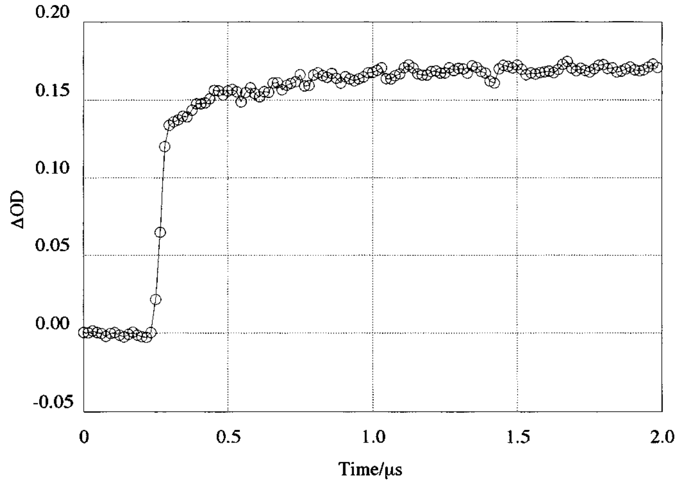


Figure 4. Rise of the absorption band at 470 nm in LFP of STPP ($3{\cdot}9\times10^{-5}$ M) in the presence of **1** ($3{\cdot}4\times10^{-2}$ M) in dichloromethane under argon

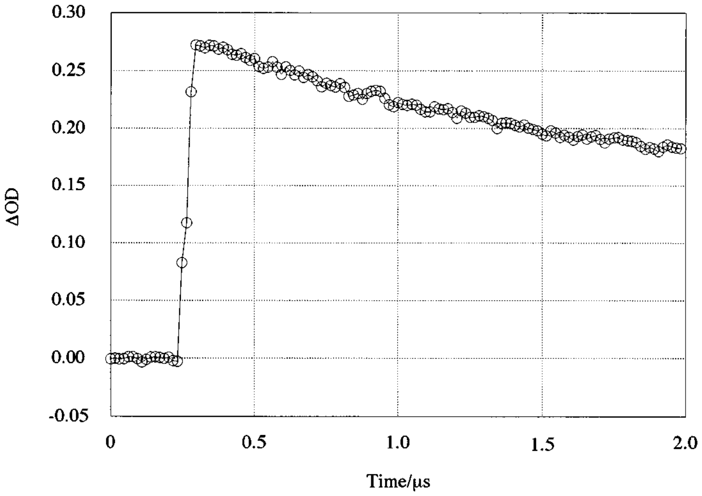


Figure 5. Decay of the absorption band at 480 nm in LFP of STPP ($3{\cdot}9\times10^{-5}$ M) in the presence of **1** ($3{\cdot}4\times10^{-2}$ M) in dichloromethane under argon

STPP$^{\bullet}$ generated at the first reduction wave but also a thiapyranyl anion (STPP^{-}) generated at the second reduction wave are stable on the CV time-scale (200 mV s^{-1}) at room temperature. The results (Table 2) show that the first reduction potential (E_p^{red1}) of STPP ($-0{\cdot}21$ V vs Ag/AgCl reference electrode) is *ca* 0·10 V more positive than that of TPP ($-0{\cdot}30$ V), and the second reduction potential (E_p^{red2}) of STPP was found to be much more positive ($-1{\cdot}19$ V) than that of TPP ($-1{\cdot}46$ V).

Bubbling oxygen through the solution caused a significant change in the CV curve, the first reduction wave becoming irreversible, showing typical EC behavior.[7] This indicates that STPP$^{\bullet}$ reacts with molecular oxygen to afford a peroxyl radical. No evidence was obtained for electron transfer from STPP$^{\bullet}$ to molecular oxygen on the CV time-scale.

Semiempirical molecular orbital calculations (PM3) for STPP and its one-electron reduced species

As described in a previous section, the properties and reactivity of a sensitizer and its one-electron reduced species play important roles in controlling the fate of photogenerated radical ion pairs. To obtain a deeper understanding of the electronic structures and equilibrium geometries of STPP and STPP$^{\bullet}$ we carried out PM3

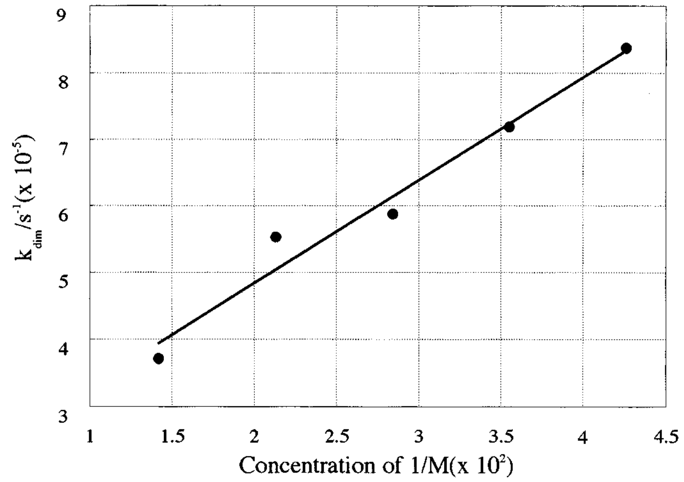


Figure 6. Plot of the pseudo-first-order rate constant as a function of the bulk concentration of **1**. The slope of the plot gave the dimerization rate constant $k_{\text{dim}}=1{\cdot}5\times10^{7}$ M^{-1} s^{-1} (see text)

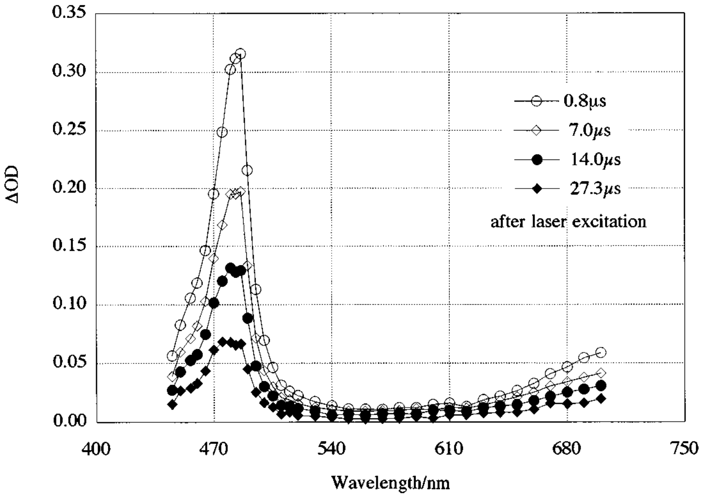


Figure 7. Transient spectra obtained from LFP of STPP ($3{\cdot}9\times10^{-5}$ M) in the presence of **1** ($1{\cdot}3\times10^{-3}$ M) in dichloromethane under argon

calculations for these species.[7] Similar calculations were also performed for TPP and TPP$^{\bullet}$ for comparison. The LUMO energies of STPP, TPP, TPP$^{\bullet}$ and STSPP$^{\bullet}$ thus obtained are given in Table 2. The LUMO energies of STPP and STPP$^{\bullet}$ are lower than those of TPP and TPP$^{\bullet}$, respectively, which is consistent with the electrochemical results.

The spin densities of STPP$^{\bullet}$ and TPP$^{\bullet}$ were also calculated, and the results are illustrated in Figure 8. We found contrasting results between STPP and TPP. STPP$^{\bullet}$ has significant spin density on the C-3 and C-5 carbons on the thiapyranyl ring and *ipso* and *meta* carbons on the phenyl rings. Note that the sulfur atom carries the highest spin density (1·01). In striking contrast, the highest spin densities of ring carbons in TPP$^{\bullet}$ were found on the C-2, C-4 and C-6 carbons in the pyranyl ring and *ortho, meta* and *para* carbons in the phenyl rings. A very low spin density (0·09) was found on the oxygen atom in TPP$^{\bullet}$. Although the results strongly suggest that addition of molecular oxygen occurs at different sites between STPP$^{\bullet}$ and TPP$^{\bullet}$, detailed discussion about the structures and reactivity of the peroxyl radicals must wait until full experimental results are obtained.

Concerning the equilibrium geometries, PM3 calculations indicate that all three phenyl rings are planar to the pyrylium or the thiapyrylium ring in both STPP and TPP. The planarity is also retained in the STPP$^{\bullet}$ and TPP$^{\bullet}$ radicals.

Table 2. LUMO energies[a] and experimental reduction potentials[b] of TPP, TPP$^{\bullet}$, STPP and STPP$^{\bullet}$

Pyrylium salt	E_p^{red1}	E_p^{red2}	LUMO of cations	LUMO of radicals
O	−0·30	−1·46	−5·66	−0·52
S	−0·21	−1·19	−6·06	−1·27

[a] In eV, calculated by PM3 calculations (see text).
[b] In V vs Ag/AgCl reference electrode.

Product studies

It would be of interest to see whether oxygenation products are actually formed or not, although no oxygen effect was observed on the formation of the dimer cation radical **1–1**$^{+\bullet}$ in the LFP experiments. Typically, **1** was irradiated in dichloromethane for 2 h at a substrate concentration of *ca* 5×10^{-2} M and a sensitizer (STPP) concentration of 1×10^{-3} M with >360 nm radiation, which selectively excited the sensitizer (see Experimental for details). Gas chromatographic (GC) examination of the reaction mixture indicates that benzaldehyde (**2**) was formed in 13% yield [based on **1** consumed (51%)]. The yields of the oxygenation products from **1** are low and the mass balance is not very good. However, we found that **2** was consumed under the photooxygenation conditions to give benzoic acid as one of the reaction products. For example, irradiation of a dichloromethane solution of **2** (5×10^{-2} M) in the presence of STPP (5×10^{-3} M) for 2 h with bubbling oxygen under otherwise same conditions led to the consumption of **2** and the formation of benzoic acid. The conversion of **2** and the yield of benzoic acid varied; however, at least *ca* 40% of **2** was consumed under the experimental conditions. The results may partly account for the low yield of **2** in the STPP oxygenation of **1**.

We also studied the oxygenation of **1** at low concentrations (1×10^{-3}–5×10^{-3} M) where the quenching ratio of ^{1}STPP by **1** was also low (7–28% calculated based on the K_{sv} value), and hence a significant amount of ^{3}STPP would be quenched by **1** to afford **1**$^{+\bullet}$ and the thiapyranyl radical. Even under such circumstances, **2** was still formed, although the yields were low (9–12%).

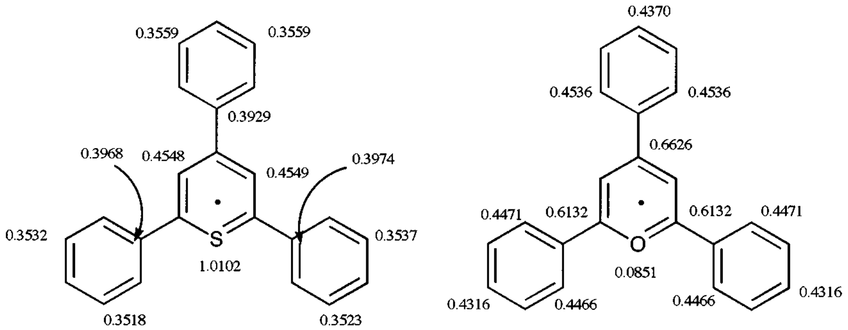


Figure 8. Spin density distributions in STPP$^{\bullet}$ and TPP$^{\bullet}$ obtained by semi-empirical molecular orbital calculations (PM3).

DISCUSSION

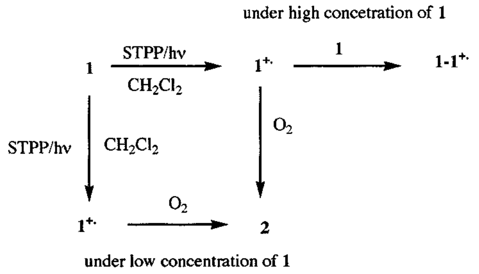
As shown in Table 1, the fluorescence quantum yield of STPP is significantly lower than that of TPP although their singlet lifetimes (τ_s) are not very different. The results suggest that other deactivation pathways such as radiationless deactivation and/or intersystem crossing may be more important in ^{1}STPP than in ^{1}TPP, probably owing to the heavy atom effect of sulfur. Concerning the electron-accepting ability of STPP, the electrochemical results (Table 2) indicate that STPP, which is more easily reduced to its one-electron reduced species than TPP, is more electron accepting than TPP. The fluorescence of STPP was also quenched by several olefins involving **1** in the diffusion-controlled limit,[8] suggesting that the electron-accepting ability of ^{1}STPP is similar to that of ^{1}TPP. As shown in Figure 1, we also observed the T–T absorption and its quenching by **1** within the diffusion-controlled limit. All these results indicate that STPP is an electron transfer sensitizer suitable for generating radical ion pairs in both singlet and triplet excited states and for comparing the difference in their reactivities ascribed to the spin multiplicity.

Concerning the reactivity of $\mathbf{1}^{+\bullet}$, we might expect the rate constant for the dimer cation radical formation to be different between STPP- and TPP-sensitized reactions, since the physical properties of STPP$^{\bullet}$ and TPP$^{\bullet}$, such as polarizability, charge and spin distribution, which may influence the degree of interaction of these radicals with $\mathbf{1}^{+\bullet}$, may be different from each other. Actually, it was found that the pattern of the spin distribution in STPP differs from that of TPP$^{\bullet}$. However, the rate constants for the dimer cation radical formation between TPP- and STPP-sensitized reactions were found to be very similar to each other. The results suggest that (i) the dimer cation radical formation that we observed is the reaction of the free cation radical $\mathbf{1}^{+\bullet}$ with the bulk neutral species (**1**) and (ii) the different reactivities and properties between STPP$^{\bullet}$ and TPP$^{\bullet}$ as component radicals in the respective radical ion pairs may not influence such reactions of the free cation radicals in dichloromethane. On a shorter time-scale such as in the pico- and nanosecond region, we may observe differences between the two systems in the quantum yields for the formation of solvent-separated radical ion pairs from the contact radical ion pairs, and in the quantum yields for the formation of the free cation radical ($\mathbf{1}^{+\bullet}$) from the solvent-separated radical ion pairs.

The dimerization of $\mathbf{1}^{+\bullet}$ with **1** may be relevant for the mechanism of the oxygenation of **1**. The dimerization of **1** through its radical cation has been reported by several workers.[9] Although we have not established the structure of the dimer cation radicals, Tojo *et al.*[9c] have recently reported LFP and γ-radiolysis studies on the dimerization of $\mathbf{1}^{+\bullet}$ and cyclo-reversion of cation radicals of cyclobutane dimers of **1**. They have shown that $\mathbf{1}^{+\bullet}$ undergoes dimerization with **1** to give a π-dimer cation radical which has absorptions in the 460–470 nm region in solution. They also noted that the tetraphenylcyclobutane dimer cation radicals (two stereoisomers) generated by γ-radiolysis from the corresponding neutral species undergo bond fission to give π-dimer cation radicals, which would be further converted upon warming to σ-dimer cation radicals with absorption bands at 370, 550 and 770 nm. Based on these results, our dimer cation radical may be assigned to the π-dimer cation radical. The σ-dimer cation radical cannot be clearly observed under our experimental conditions, although the absorption bands assigned to the σ-dimer cation radicals may be hidden under the absorptions of $\mathbf{1}^{+\bullet}$, π-dimer cation radicals and/or TPP.

We suggest that rapid dimerization of $\mathbf{1}^{+\bullet}$ with **1** to give the π-dimer cation radicals decreases the yield of **2** because it decreases the extent of the reaction of $\mathbf{1}^{+\bullet}$ with molecular oxygen. Although there may be oxygenation pathways from **1** to **2** involving the dimer cation radical $(\mathbf{1}–\mathbf{1})_2^{+\bullet}$,[9a] the fact that **2** is still formed at low concentrations of **1** where no dimerization was observed by LFP supports the contention that there may be reaction channels to **2** which involve the reactions of $\mathbf{1}^{+\bullet}$ with molecular oxygen.[2f] Participation of $O_2^{-\bullet}$ in the oxygenation pathways is unlikely since CV of STPP clearly indicates that STPP$^{\bullet}$ formed upon electron transfer reacts with molecular oxygen instead of reducing it.

In conclusion, we have shown that STPP can be employed as an electron transfer sensitizer in both singlet and triplet manifolds. Although the dimerization of *trans-*



stilbene cation radical with its neutral species was not affected by the sensitizer (STPP or TPP) employed, comparison of photoinduced electron transfer reactions sensitized by STPP with those by TPP for other substrates may open the way to finding different reaction courses on efficiency of the generated cation radicals and the radical ion pairs. STPP also has the advantage that its one-electron reduced species, $STPP^{\cdot}$, has no absorption in the 500–600 nm range, which increases the possibility of observing transient absorptions at these wavelengths.[4]

Further studies on electron transfer oxygenation with STPP and TPP would provide a more detailed understanding of photoinduced electron transfer reactions in general, and are being actively pursued in our laboratories.

EXPERIMENTAL

Materials. *trans*-Stilbene (**1**) is commercially available and was recrystallized from ethanol before use. STPP was synthesized according to the method of Saeva and Olin[7] and its purity was confirmed by elemental analyses, m.p., ^{1}H NMR and cyclic voltammetry in CH_3CN.

Measurements. ^{1}H NMR spectra were recorded on a JEOL FX-90 NMR spectrometer and IR spectra on a JASCO A-102 infrared spectrophotometer. GC analyses of the reaction mixtures were performed with a Shimadzu GC-7A gas chromatograph equipped with a thermal conductivity detector or with a Shimadzu GC-4M gas chromatograph equipped with a flame ionization detector. Laser flash photolyses were carried out with an excimer (Lambda Physik EMG-101, XeCl 308 nm)-pumped dye laser (Lambda Physik FI-3002, DPS dye, 10 mJ per pulse) at room temperature; a detailed description of the apparatus was given elsewhere.[2e] Single photon counting to measure the singlet lifetime of STPP was carried out on a Horiba-NAES 1100 spectrofluorimeter at room temperature. Cyclic voltammetry was carried out with a four-necked CV cell with a platinum disk as a working electrode, a platinum wire as a counter electrode and a saturated calomel or Ag/AgCl electrode as a reference electrode. A Hokuto HA501 potentiostat/galvanostat, a Hokuto HB 104 function generator and a YEW Model XY recorder were used for the measurements. GC–MS analyses were performed on a Hitachi M-80A GC–MS system with an ionization voltage of 70 eV.

Photooxygenation procedures. Photosensitized electron transfer oxygenation was carried out in dichloromethane at a substrate concentration of *ca* $0{\cdot}1\times10^{-2}$–5×10^{-2} M and a sensitizer concentration (STPP) of 1×10^{-3} M. The solution was placed in a Pyrex tube of *ca* 15 mm i.d. immersed in a water-cooled bath. A Riko 400 W high-pressure mercury lamp was used as an excitation light source and Toshiba L-39 glass filters ($>$360 nm) were used for the selective excitation of the sensitizers. Yields of the photoproducts were determined by GC with internal references, and the sensitivity differences for thermal conductivity or flame ionization detection between the references and the products were corrected. The structures of the oxygenation products were established by co-injections of authentic samples with two different columns and/or GC–MS analyses.

Molecular orbital calculations. PM3 calculations were performed with a SiliconGraphics INDY workstation with the SPARTAN program (Version 4.0). All the calculations were performed with geometry optimization. The spin densities reported were calculated by NBO (natural bond orbital) population analysis contained in the SPARTAN software.

ACKNOWLEDGEMENTS

We thank Professor S. Tajima and Mr K. Ogino of the Chemistry Department (Maebashi) for carrying out the GC–MS measurements. Thanks are also due to Professor T. Arai and Mr M. Ikegami for their help in measuring the fluorescence quantum yields. This work was partly sponsored by Grants-in-Aid for Scientific Research (05640622 and 06640708) to R.A. from the Minsitry of Education, Science, Sports, and Culture.

REFERENCES

1. (a) G. J. Kavarnos and N. J. Turro, *Chem. Rev.* **86**, 419 (1986); (b) S. L. Mattes and S. Farid, in *Organic Photochemistry*, edited by A. Padwa, Vol. 6, pp. 233–326. Marcel Dekker, New York (1983); (c) M. A. Fox, *Adv. Photochem.* **13**, 237–327 (1986); (d) L. Lopez, in *Photoinduced Electron Transfer I* edited by J. Mattay, pp. 117–166. Springer, Berlin (1990); (e) R. Billing, D. Rehorek and H. Henning, in *Photoinduced Electron Transfer II*, edited by J. Mattay, pp. 151–199. Springer, Berlin (1990).
2. (a) R. Akaba, Y. Niimura, Y. Kawai, T. Tajima, T. Kuragami, A. Negishi, M. Kamata, H. Sakuragi and K. Tokumaru. *J. Am. Chem. Soc.* **114**, 4460–4465 (1992); (b) R. Akaba, M. Kamata, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.* **33**, 8105–8108 (1992); (c) R. Akaba, M. Kamata, H. Itoh, A. Nakao, S. Goto, K. Saito, A. Negishi, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.* **33**, 7011–7014 (1992); (d) R. Akaba, S. Aihara, H. Sakuragi and K. Tokumaru, *J. Chem. Soc., Chem. Commun.* 1262–1263 (1987); (e) R. Akaba, H. Sakuragi and K. Tokumaru, *J. Chem. Soc., Perkin Trans. 2*, 291–297 (1991); (f) R. Akaba, K. Ohshima, Y. Kawai, Y. Obuchi, A. Negishi, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.* **32**, 109–112 (1991).

3. R. Akaba, H. Sakuragi and K. Tokumaru, *Chem. Phys. Lett.* **172**, 80–84 (1990).
4. R. Akaba, M. Kamata, Y. Kuriyama, H. Sakuragi and K. Tokumaru, *Chem. Lett.* 1157–1160 (1993).
5. S. L. Murov, I. Carmichael, and G. L. Hug, *Handbook of Photochemistry*, 2nd ed., p. 129. Marcel Dekker, New York (1993).
6. R. S. Nicholson and I. Shain, *Anal. Chem.* **36**, 706 (1964).
7. F. Saeva and C. R. Olin, *J. Am. Chem. Soc.* **102**, 299–303 (1980).
8. R. Akaba, unpublished results.
9. (a) F. D. Lewis, A. M. Bedell, R. E. Dykstra, J. E. Elbert, I. R. Gould and S. Farid, *J. Am. Chem. Soc.* **112**, 8055–8064 (1990); (b) Y. Kuriyama, H. Sakuragi, K. Tokumaru, Y. Yoshida and S. Tagawa, *Bull. Chem. Soc. Jpn.* **66**, 1852–1855 (1993); (c) S. Tojo, K. Morishima, A. Ikeda, T. Majima and S. Takamuku, *Bull. Chem. Soc. Jpn.* **68**, 958–966 (1995); (d) S. Tojo, S. Toki and S. Takamuku, *J. Org. Chem.* **56**, 6240–6243 (1991).