

Photosensitization of Stilbene Isomerization by Palladium and Platinum Porphyrins, an Intermolecular Quantum Chain Process¹

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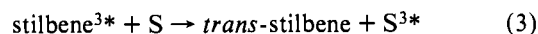
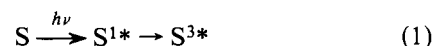
Abstract: The sensitization of stilbene isomerization by the strongly solution phosphorescent palladium(II) and platinum(II) porphyrins has been investigated. These complexes, which have relatively long triplet lifetime and triplet energies well below the spectroscopic triplets of the stilbenes, are efficient sensitizers. Although sensitization of the 1,2-diphenylpropenes appears "normal", sensitization of the stilbenes results in quantum yields for the *cis* to *trans* process greater than unity and *trans*-rich photostationary states. The results can be explained by a quantum chain process in which the metalloporphyrin serves both as an energy donor and an acceptor. In contrast to quantum chain processes previously observed with conjugated dienes which involve interchange of acceptor triplets and occur at relatively high concentrations, the phenomena observed here occur at relatively low donor and acceptor concentrations. The results suggest the intermediacy of a sensitizer-acceptor cage-encounter complex which may have different preferred geometry and altered nonradiative decay properties compared to the free stilbene triplet.

Introduction

Although it is one of the most thoroughly studied of all photoreactions occurring in solution, the triplet sensitized photoisomerization of the stilbenes continues as the subject of several current investigations.² Perhaps the two most intriguing features of the sensitized stilbene isomerization are the sensitization promoted by sensitizers having triplet energies lower than the spectroscopic triplets of the stilbenes and the variety of mechanisms for quenching of stilbene triplets by different substances. It has been shown in several cases that sensitization by energy transfer to the *cis*-stilbenes, both isomers of the 1,2-diphenylpropenes, and several other nonrigid systems with sensitizers having low-lying triplets can occur with rate constants considerably greater than predicted on the basis of the energies of spectroscopic states of the donors and acceptors.³⁻⁶ Although the phenomenon can be regarded as well established, several of the mechanistic details regarding "nonvertical" energy transfer remain unresolved.^{5,7} While much has been inferred about the role of the acceptor in these processes, relatively little has been determined regarding the role of the sensitizer triplet. Excited states of several olefins such as the 1,2-diphenylpropenes are indicated to have short lifetimes and a nonplanar geometry, and the dominant and often exclusive channel for return to the ground state is rapid radiationless decay of the twisted state intermediate in geometry between *trans* and *cis* isomers. The stilbene triplet has a measurable (ca. 110 ns) lifetime⁸ and it can be quenched in solution by interaction with a variety of substances including oxygen,^{9,10} nitroxides,^{13,14} azulene,^{2,4,15} and β -carotene.¹⁷ The consequence of quenching is quencher dependent. The latter two quenchers, which have very low-lying triplets, are believed to quench by triplet energy transfer; quenching results in selective formation of *trans*-stilbene.^{2,16} Oxygen quenches the stilbene triplet without altering the *cis*/*trans* decay ratio⁹ while di-*tert*-butyl nitroxide quenches with a slight enhancement of the *cis*/*trans* decay ratio.^{13,14} The simplest explanation consistent with these observations is that oxygen and the nitroxide quench the twisted stilbene triplet by a process not involving energy transfer while β -carotene and azulene quench a transoid triplet in an energy transfer process.²

The possibility of energy transfer from a transoid stilbene triplet to a potential triplet energy acceptor coupled with the occurrence of rapid energy transfer from "energy-deficient" triplet sensitizers to *cis*-stilbene allows the possibility of a

quantum chain process for photoisomerization as indicated by eq 1-3.^{17,18}



While quantum chain processes, although rare, have been observed in other systems,¹⁹⁻²³ there has until now not been clear-cut evidence for the importance of this process in intermolecular cases. We were able to observe its intramolecular counterpart in a study of zinc and magnesium porphyrin complexes with the stilbene-like pyridyl ligands 1-(α -naphthyl)-2-(4-pyridyl)ethylene (NPE) and 4-stilbazole.^{18,24} With these complexes, the coupling of rapid ligand exchange with efficient intramolecular occurrence of steps 2 and 3 as shown above permits a quantum chain and photocatalytic process to occur with a quantum efficiency, $\phi_{c \rightarrow t} \approx 7$.²⁴ A study of the process using flash spectroscopy indicates that essentially all triplets of the ligand-olefin are deactivated by step 3 such that the quantum yield is limited only by decay of the metalloporphyrin; a kinetic analysis of the process leads to the relationship given by eq 4 where k_{et} is the rate constant for the intramolecular analogue of step 2 and k_d is the reciprocal of the porphyrin triplet lifetime. The measured values and those calculated by eq 4 agree well.

$$\phi_{c \rightarrow t} = \frac{\phi_{isc}^{mp} k_{et}}{k_d} \quad (4)$$

The ready occurrence of a quantum chain process via intramolecular energy transfer encouraged us to examine the possibility that more general intermolecular counterparts should occur. In principle such a process should occur readily provided that the energetics of the stilbene derivative and sensitizer allow reactions 2 and 3 to occur with high efficiency. In the intermolecular case, however, the short lifetime of the stilbene triplet should permit such a process to occur only at high sensitizer concentrations or in solvents where a strong solvent cage exists since rapid unassisted decay of the "free" stilbene triplet should break the chain. Furthermore, the sensitizer triplet should have a sufficient lifetime and energy to permit efficient operation of step 2. Although a number of sensitizers having energies in the 40-45 kcal/mol range could

potentially mediate such a process, the palladium(II) and platinum(II) porphyrins appeared to be particularly attractive candidates for use in such a study for a number of reasons. These complexes, in which the porphyrin is bound to a d^8 metal ion, are very stable as square planar complexes and there is little tendency in the ground state to bind additional ligands. The strong phosphorescence of these complexes in fluid media coupled with their long excited state lifetimes indicate that even relatively slow bimolecular energy transfer processes should occur with moderate efficiency and be readily detectable.²⁵⁻²⁷ In the present paper we report a study of the photosensitization of stilbene and 1,2-diphenylpropene isomerization by palladium and platinum porphyrins. Results of this study indicate that an intermolecular quantum chain process can indeed occur for the *cis*- to *trans*-stilbene isomerization but that, surprisingly, the intermolecular excited state interaction between sensitizer and stilbene appears more complex than its intramolecular counterpart. Thus while simple energy transfer steps can account for all the phenomena in the latter case, the intermolecular case appears to involve the introduction of new decay channels not present in either sensitizer or acceptor alone.

Experimental Section

Materials. The *trans*-stilbene was either Baker Ultrex or zone refined from James Hinton. Since the *cis*-stilbene obtained from Aldrich contained a yellow impurity, it was chromatographed on reagent alumina and then vacuum distilled. Purity of the olefins was determined to be greater than 99.2% by vapor phase chromatography. Samples of purified *trans*- and *cis*-1,2-diphenylpropene were supplied by Dr. D. A. Hunter and used without further purification.

Octaethylporphyrin was a gift of Dr. Fred Hopf. *meso*-Tetra-phenylporphyrin was prepared by the Adler²⁸ modification of the Rothemond method.²⁹ Since the porphyrin obtained by this method is contaminated by small amounts of *meso*-tetraphenylchlorin, the crude product was purified³⁰ by refluxing with 2,3-dichloro-5,6-dicyanobenzoquinone. The porphyrins were metalated by the method of Eisner and Harding.³¹ The bisbenzonitrile palladous chloride and bisbenzonitrile platinum chloride used in the metalation reaction were prepared from Alfa Ventron PdCl₂ and PtCl₂, respectively.³² Palladium octaethylporphyrin (PdOEP) was purified by column chromatography on alumina by elution with 6% methylene chloride, 94% benzene; palladium tetraphenylporphyrin (PdTPP) was chromatographed on alumina using a 3:2 solution of benzene and chloroform. Both palladium porphyrins were recrystallized from chloroform-methanol. Owing to difficulty in separating the platinum tetraphenylporphyrin (PtTPP) from the porphyrin starting material by conventional column chromatography, the reaction mixture was dissolved in benzene and purified by medium-pressure liquid chromatography on Woelm silica gel using chloroform as the eluent, followed by recrystallization from chloroform-methanol. Purity of the palladium and platinum porphyrins was checked by UV-visible spectroscopy and by emission spectroscopy to ensure that no free base porphyrin was present.

Thiophene-free benzene and spectroquality pentane used as solvents were stirred over sulfuric acid until the acid layer no longer turned yellow. They were then neutralized, washed with distilled water, and dried over magnesium sulfate before passing through a column filled with alumina. This was followed by distillation from P₂O₅.

All samples were degassed by six or more cycles of freeze-pump-thaw on a vacuum line in Pyrex ampules made from 13 × 100 mm lipless test tubes with standard taper ground-glass joints fused at the top for connection on the vacuum line. The solutions were sealed at a final pressure of less than 5×10^{-6} Torr.

Quenching Rate Studies. Emission spectra for Stern-Volmer plots were obtained using a Hitachi MPF-2A spectrofluorimeter equipped with a R446 phototube. Solutions of palladium or platinum porphyrins which were not degassed did not show any emission.

Flash Spectroscopic Studies. Quenching rate constants were also determined from flash spectroscopic studies³³ of emission lifetimes of the palladium and platinum porphyrin triplets. Between the flash lamp and the sample, Corning 3-73, 4-72, and 4-74 filters were used to eliminate the wavelengths of stilbene and 1,2-diphenylpropene

absorbance and metalloporphyrin phosphorescence. First-order rate constants for triplet decay (k_d) were obtained from plots of the ln of the oscilloscope deflection at time t after an arbitrary time t_0 after the flash vs. t . Triplet lifetimes were calculated as $\tau = 1/k_d$.

Photoisomerization Studies. For photostationary state measurements the samples were placed in a water bath in a merry-go-round and irradiated with a Hanovia 450-W medium-pressure mercury lamp in a Pyrex sieve. Corning 3-73 filters were used to eliminate the wavelengths which the stilbenes and 1,2-diphenylpropenes absorb. The solutions were irradiated for 1 week in the case of the palladium porphyrins and 2 weeks in the case of the platinum porphyrin to ensure that the photostationary state had been reached. Absorption spectroscopy using a Perkin-Elmer 576 ST spectrophotometer showed that porphyrin decomposition did not occur upon lengthy irradiation. The extent of *cis*-*trans* isomerization was obtained by vapor-phase chromatography using a Varian 1400 Aerograph with a 6 ft × 1/8 in. 10% W-98 on Diatoport S column or a Hewlett-Packard 5750 gas chromatograph with a fluorosilicate 10 ft × 1/8 in. 5% FS1265 Chromosorb G column. Both gas chromatographs were equipped with a flame ionization detector. Mass balance analysis showed that the lengthy irradiation did not cause decomposition of the stilbenes.

The quantum yield studies of isomerization were carried out by irradiating the samples in the water bath of a merry-go-round with a Hanovia 450-W medium-pressure mercury lamp surrounded by a Pyrex sleeve using Corning 3-70 and 4-97 filters to isolate the 545-nm mercury line and Corning 3-73 and 5-58 filters to isolate the 435-nm mercury line. The intensity of the exciting light was monitored by Reinecke salt actinometry³⁴ using either a Bausch & Lomb spectronic 210 UV spectrophotometer or a Perkin-Elmer 576 ST spectrophotometer. Isomerizations were carried to very low conversions to prevent appreciable back-reaction and a back-reaction correction³⁵ was made. The extent of isomerization was determined by vapor phase chromatography under the same conditions described for the photostationary state measurements. The amount of *trans*-stilbene present after the *cis* → *trans* isomerization was compared to an internal standard of anthracene added after irradiation to check for linear detector response.

Results

The palladium and platinum porphyrins are conveniently excited using the mercury lines at 435 or 545 nm where the porphyrins have strong absorption (Figure 1). At this wavelength there is no measurable absorption by either the stilbenes or 1,2-diphenylpropenes. Irradiation of metalloporphyrin solution containing stilbenes or 1,2-diphenylpropenes in benzene or pentane leads to isomerization of the olefin as the only detectable reaction. Even prolonged irradiation leads to no net decomposition of either porphyrin or olefin. Photostationary states of essentially identical composition are achieved by prolonged irradiation starting from either isomer. The measured photostationary state values for the various olefin-sensitizer-solvent combinations are given in Table I. As data in Table I indicate, there is little difference in the photostationary state composition for a given olefin-sensitizer-solvent combination for different concentrations of sensitizer or olefin over the range studied; the values thus can probably be regarded as concentration independent.

As mentioned earlier, the platinum(II) and palladium(II) porphyrins exhibit room temperature phosphorescence in solution and have relatively long triplet lifetimes. Consequently, it is possible to investigate triplet quenching processes either via steady-state luminescence quenching or via flash photolysis. Both techniques were used for quenching of the metalloporphyrin triplet by the stilbenes and 1,2-diphenylpropenes. In contrast to the intramolecular olefin-metalloporphyrin complexes²⁴ it was found that both stilbenes and 1,2-diphenylpropenes quench the metalloporphyrin triplets with rate constants in the range 10^5 - 10^6 M⁻¹ s⁻¹. No new transients were detected either by conventional (microsecond) flash photolysis or by luminescence spectroscopy. Metalloporphyrin lifetimes and quenching constants obtained in this study are given in Table II.

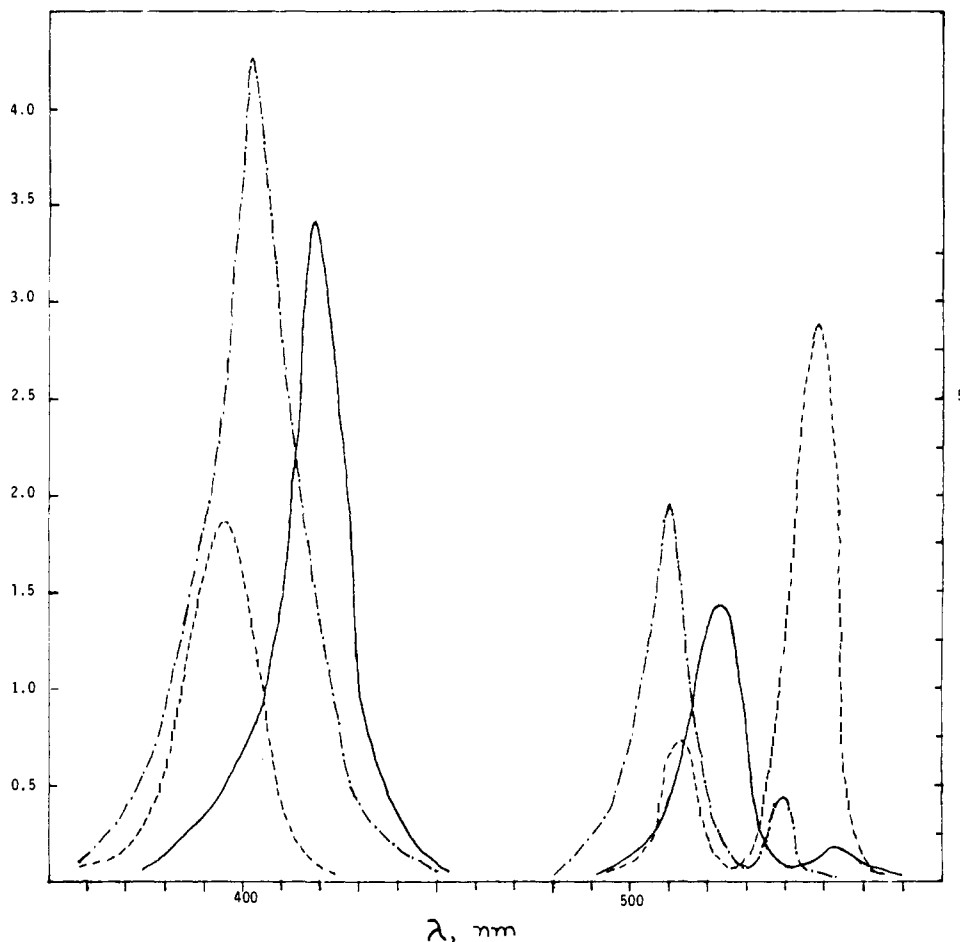


Figure 1. Absorption spectra of metalloporphyrins in benzene: (—) PdTPP, (---) PdOEP, (- · - ·) PtTPP. Left-hand ordinate is extinction coefficient at the Soret (350-450-nm range) $\times 10^{-5}$. Right ordinate is extinction coefficient in visible range (480-600 nm) $\times 10^{-4}$.

Quantum yields for metalloporphyrin-sensitized isomerization were measured for benzene solutions with concentrations of olefin great enough to quench all sensitizer triplets. These values are listed in Table III. Quantum yield experiments were carried only to low conversions; however, a back-reaction correction³⁵ was applied for both $\phi_{c \rightarrow t}$ and $\phi_{t \rightarrow c}$. Although quantum yields from trans to cis are moderate, the quantum yields in the reverse direction exceed unity for all three porphyrins. In contrast the PdOEP sensitized cis to trans isomerization of *cis*-1,2-diphenylpropene in benzene was found to proceed with $\phi_{c \rightarrow t} = 0.37$.

Discussion

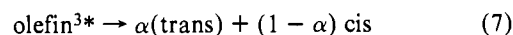
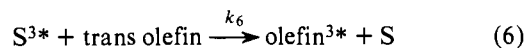
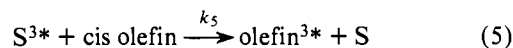
PdOEP Sensitization of 1,2-Diphenylpropene Isomerization.

In contrast to the behavior observed with the stilbenes in previous photosensitization studies, photosensitized isomerization of the 1,2-diphenylpropenes appears to be a relatively simple process.^{3,4} Evidently the 1,2-diphenylpropene triplet is non-planar and it cannot be quenched by substances having low-lying excited states such as azulene.^{4,15} The simpler behavior of the 1,2-diphenylpropenes and other trisubstituted diarylethenes is due to the presence of only a single minimum on the triplet surface corresponding to a twisted geometry; the triplet minimum is close to a ground state maximum such that very rapid radiationless decay occurs and competitive quenching via energy transfer is improbable.

Although the PdOEP triplet sensitized isomerization of the 1,2-diphenylpropenes was not extensively investigated, enough data were obtained to indicate that the sensitization in this case is apparently a "normal" process in which no reverse energy transfer occurs. The PdOEP triplet was quenched by both isomers of 1,2-diphenylpropene with rate constants very close

to those obtained for other sensitizers having similar triplet energies.³ For example, the values obtained for 1-acetylstyrene ($E_T = 45.5$ kcal/mol) and 7,12-dimethylbenz[*a*]anthracene ($E_T = 44.3$ kcal/mol) fall respectively slightly above the slightly below those given in Table II for the 44.8 kcal/mol PdOEP triplet.³

For a "normal" sensitized isomerization the simplest mechanism is given by eq 1, 5-7.



From this mechanism, it can easily be shown that the trans/cis ratio in the photostationary state is given by

$$\left(\frac{t}{c}\right)_{\text{PSS}} = \frac{k_5}{k_6} \left(\frac{\alpha}{1 - \alpha}\right) \quad (8)$$

It has been well established that α for the 1,2-diphenylpropenes is 0.44;^{3,4} the "predicted" value for the photostationary state using eq 8 and the measured quenching constants is 78% cis, which is in fair agreement with the measured values of 67% cis. For the scheme outlined above it can be shown that the initial quantum yields are given by $\phi_{c \rightarrow t}^0 = \phi_{\text{isc}}^s \alpha$ and $\phi_{t \rightarrow c}^0 = \phi_{\text{isc}}^s (1 - \alpha)$ under conditions where all the sensitizer triplets are captured by the olefin. For the palladium and platinum porphyrins intersystem crossing efficiencies have not been determined precisely, although for the palladium porphyrins estimates in the range 0.7-0.9 have been made using different techniques.³⁶

Table I. Photostationary States for Metalloporphyrin Sensitized Isomerization of Stilbenes and 1,2-Diphenylpropenes

Sensitizer ^a	Starting substrate	Substrate concn × 10 ³ M	Solvent	% cis, pss
PdOEP	<i>cis</i> -Stilbene	0.65	Pentane	25.3
		1.30		27.4
		1.95		28.6
PdOEP	<i>trans</i> -Stilbene	0.84	Pentane	25.8
		1.37		27.1
		2.31		27.1
PdOEP	<i>cis</i> -Stilbene	1.84	Benzene	18.4
		3.68		18.3
		5.52		18.5
PdOEP	<i>trans</i> -Stilbene	7.36	Benzene	18.1
		1.01		16.5
		2.41		16.7
PdTPP	<i>cis</i> -Stilbene	4.13	Benzene	16.5
		15.4		17.2
		25.6		16.5
PdTPP	<i>trans</i> -Stilbene	35.8	Benzene	16.9
		46.1		17.3
		16.5		16.1
PtTPP	<i>cis</i> -Stilbene	23.4	Benzene	16.0
		44.1		17.2
		63.2		17.8
PtTPP	<i>trans</i> -Stilbene	13.2	Benzene	37.1
		20.0		37.3
		26.8		36.9
PdOEP	<i>cis</i> -1,2-Diphenylpropene	27.0	Benzene	36.1
		34.0		38.4
		78.5		37.4
PdOEP	<i>trans</i> -1,2-Diphenylpropene	120	Benzene	37.3
		145		37.0
		8.7		68.7
PdOEP	<i>cis</i> -1,2-Diphenylpropene	21.8	Benzene	69.0
		32.7		68.5
		40.9		68.8
PdOEP	<i>trans</i> -1,2-Diphenylpropene	6.5	Benzene	66.6
		18.7		66.9
		39.1		66.3

^a Degassed solutions, sensitizer concentrations 5–50 × 10⁻⁶ M; Corning 3-73 filter used to remove UV absorbed by substrate.

Table II. Quenching of Metalloporphyrin Triplets by Stilbenes and 1,2-Diphenylpropenes^a

	Sensitizer			
	PdOEP (pentane)	PdOEP (benzene)	PdTPP (benzene)	PtTPP (benzene)
τ^0 , μ s	555	500	358	54
Method	I^0/I^b	I^0/I^b	I^0/I^b	I^0/I^b
<i>cis</i> -Stilbene		τ^0/τ^c		
k_q	3.28×10^6	1.37×10^6	1.75×10^5	6.68×10^5
Correlation coefficient	1.00	0.993	0.995	
<i>trans</i> -Stilbene				
k_q	3.34×10^6	1.52×10^6	5.32×10^5	1.03×10^5
Correlation coefficient	0.999	0.982	0.946	0.986
<i>cis</i> -1,2-Diphenylpropene				
k_q		1.98×10^5	9.69×10^4	
Correlation coefficient		1.00	0.809	
<i>trans</i> -1,2-Diphenylpropene				
k_q		6.81×10^5		
Correlation coefficient		0.995		

^a Degassed solutions; rate constants determined by linear regression analysis. ^b Measured by phosphorescence intensity quenching. ^c Measured by reduction of triplet lifetime as determined by flash photolysis.

Comparison of the value $\phi_{c \rightarrow t} = 0.37$ obtained with PdOEP and *cis*-1,2-diphenylpropene with $\alpha = 0.44$ gives $\phi_{isc}^s = 0.84$, which appears to be a reasonable value.

Pd and Pt Porphyrins Sensitization of Stilbene Isomerization. Both isomers of the stilbenes quench triplets of the three porphyrins used as sensitizers with rate constants which are in the same range as those obtained for the stilbenes and other sensitizers having triplet energies in the 42–45 kcal/mol

range.^{3,4} Interestingly there is little variation observed between quenching constants for *cis* and *trans* isomers with any of the three sensitizers; in contrast k_6/k_5 is 3.02 for 1-acetylpyrene and 1.86 for 7,12-dimethylbenz[*a*]anthracene,³ the sensitizers closest in energy to PdOEP and PtTPP, for which the values are 1.05 and 0.76, respectively. Evidence that a simple sensitization and radiationless deactivation/isomerization process as outlined in eq 1, 5–7 is not occurring comes from a com-

Table III. Quantum Yields for Metalloporphyrin Sensitization of Stilbene Isomerization

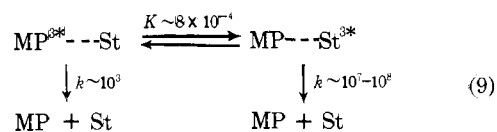
Process ^a	PdOEP	Sensitizer PdTPP	PtTPP
$\phi_{c \rightarrow t}$	1.58 ± 0.03 ^b	1.36 ± 0.3 ^c	1.34 ± 0.01 ^e
$\phi_{t \rightarrow c}$	0.30 ± 0.01 ^b	0.24 ± 0.01 ^d	

^a Degassed benzene solutions, porphyrin concentrations 5–100 × 10⁻⁵ M; irradiation wavelengths 435 nm for PtTPP and 546 nm for PdOEP and PdTPP. ^b Concentration 0.186 M. ^c Concentration 1.44 M. ^d Concentration 0.646 M. ^e Concentration 2.84 M.

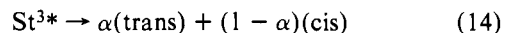
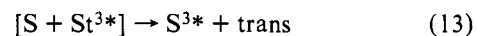
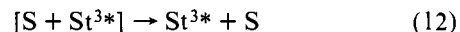
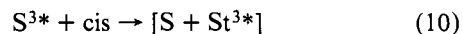
parison of predicted and measured photostationary states. For the three sensitizers the values predicted for (t/c)_{PSS} in benzene using eq 8 are 0.66, 1.01, and 0.91 for PdOEP, PdTPP, and PtTPP, respectively. The measured values are 4.49, 4.88, and 1.67 for the same sensitizers; in each case the stationary states are far richer in trans isomer than predicted. The reason for this is readily apparent when the quantum yields are examined. The measured $\phi_{t \rightarrow c}$ values are slightly lower than would be predicted for a simple isomerization proceeding only by unassisted decay of the stilbene triplet, but the values for $\phi_{c \rightarrow t}$ exceed unity in each case. Although the measured quantum yields for the intermolecular metalloporphyrin sensitized isomerization are not as dramatically large as those observed with intramolecular sensitization,¹⁹ it appears clear that in the intermolecular sensitization a quantum chain process is also occurring.

Although the larger than unity quantum efficiencies indicate that a simple sensitization as described above for the 1,2-diphenylpropenes is not occurring, it is clear that the mechanism for the intermolecular sensitization is not quite so simple as that used to explain the intramolecular metalloporphyrin sensitization of stilbene-like ligands. In the latter case, no quenching of metalloporphyrins triplets was observed, the photostationary states were >90% trans, and the cis to trans process overwhelmed the reverse. Thus for the intramolecular case, it is evident that nonradiative decay of olefin triplets is relatively unimportant. The presence of a sizable fraction of cis isomer in the photostationary state for the intermolecular process indicates that decay of olefin triplets must be competitive with quenching of the stilbene triplet to trans ground state by the metalloporphyrin. This is also consistent with the observation that encounters between metalloporphyrin triplets and stilbene ground states result in a net excited state quenching. That this is reasonable for the metalloporphyrins and stilbene can readily be seen. As mentioned earlier, if an energy transfer occurred between porphyrin triplet and stilbene to produce kinetically "free" stilbene triplets, there would be no possibility for a chain process with the porphyrin concentrations used (10⁻⁴–10⁻⁶ M) since the stilbene triplet would not survive long enough to be quenched. That the chain process is observable indicates either that a complex is formed between the sensitizer and acceptor or that a solvent cage holds the sensitizer and acceptor together long enough to permit multiple energy transfer events to occur.

If the metalloporphyrin triplet and stilbene are held together long enough to permit an equilibration as indicated in eq 9, it would be anticipated that the major decay path would be radiationless decay of the stilbene triplet by a factor of perhaps 10 to 1, since despite the unfavorable equilibration constant for excitation on the olefin (estimated from the difference in "spectroscopic" triplets of *trans*-stilbene and PdOEP), the much more rapid decay of the stilbene triplet would dominate slow decay from the porphyrin. The observation that decay of "free stilbene" triplets is competitive but not dominant suggests that the stilbene potential surface may be modified in the presence of the porphyrin or that perhaps a complex is formed as will be discussed below.



The simplest kinetic model that will explain the observed results is given by eq 1, 10–15.^{37,38}



Using the usual steady state approximations the following expressions can be derived for initial quantum yields (under conditions where triplet porphyrin quenching is complete) and photostationary state ratios.

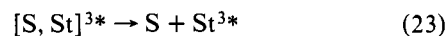
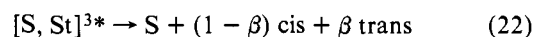
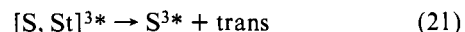
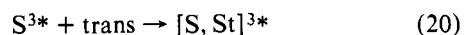
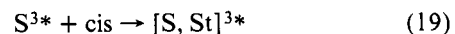
$$\phi_{c \rightarrow t} = \phi_{\text{isc}}^s \frac{k_{13} + \alpha k_{12}}{k_{12}} \quad (16)$$

$$\phi_{t \rightarrow c} = \phi_{\text{isc}}^s (1 - \alpha) \quad (17)$$

$$\frac{(\text{trans})}{(\text{cis})\text{PSS}} = \frac{k_{10} \alpha + k_{13}/k_{12}}{k_{11} (1 - \alpha)} \quad (18)$$

Since measured quenching constants are nearly equal for the two isomers for all three sensitizers, the photostationary state ratios should be approximately equal to the ratio $\phi_{c \rightarrow t}/\phi_{t \rightarrow c}$. For PdOEP the quantum yield ratios predict a photostationary state of 16% cis while the measured value is ~17%; the predicted and measured values for PdTPP are 15 and 17%, respectively. The quantum yield expressions, eq 16 and 17, predict a "normal" quantum yield for the trans → cis process but a value which can exceed unity for the reverse reaction depending upon the relative magnitude of the "propagation" step, k_{13} , and the "termination" step, k_{12} . If we use the value $\phi_{\text{isc}}^s = 0.84$ for PdOEP determined from 1,2-diphenylpropene isomerization and $\alpha = 0.40$,⁴ we obtain from eq 16 the ratio, $k_{13}/k_{12} = 1.4$, for partitioning of the species [S + St^{3*}].

The above mechanism is attractive for its simplicity and for the fact that it allows for a quantum chain process. However, there is at least one aspect of the results that suggests that interaction between excited metalloporphyrin and stilbene may involve somewhat more than a cage encounter complex. As mentioned above, eq 17 predicts a "normal" value for $\phi_{t \rightarrow c}$. Since $(1 - \alpha) \approx 0.6$ for the stilbene triplet, values for $\phi_{t \rightarrow c}$ should be in the range 0.48–0.54, assuming ϕ_{isc}^s values of 0.8–0.9 for the palladium porphyrins. The measured values are clearly substantially lower. Since kinetically free stilbene triplets in benzene are well established to decay with $\alpha = 0.40$,⁴ it appears that there must be an additional process occurring in which nonradiative decay, presumably of stilbene triplets, occurs to give a greater fraction of *trans*-stilbene. There have been previous observations of energy wastage in photosensitized isomerization of the stilbenes with other sensitizers;^{39,40} in the case of the fluorenone-sensitized reaction an exciplex intermediate has been proposed.³⁹ A mechanism, modified to account for this would replace eq 10–13 by eq 19–23



where $[S, St]^{3*}$ is probably best described as a complex in which at least the properties of the triplet stilbene are modified.⁴¹ Although a detailed kinetic analysis of this mechanism is a bit more complicated, the essential features are the addition of a new decay channel or "termination" step in which decay of the complex gives ground state stilbene with a different decay ratio than obtained for free stilbene triplets. The propagation/termination ratio is now given by $k_{21}/(k_{22} + k_{23})$. It is not possible from the available data to estimate relative values of k_{22} and k_{23} , but the three limiting cases can be analyzed. If $\beta = 1$ (all decay within the "complex" leads to formation of *trans*-stilbene), $\phi_{t \rightarrow c} = \phi_{isc}^s [(1 - \alpha)k_{23}]/(k_{22} + k_{23})$, leading to a value for $k_{23}/(k_{22} + k_{23}) = 0.6$. Analysis of the expression for $\phi_{c \rightarrow t}$ leads to the prediction that $k_{21}/k_{23} = 1.6$. The second limiting case would have $k_{23} \ll k_{21}$ and k_{22} such that no "free" stilbene triplets are formed. In this case, we obtain comparable values for k_{21} and k_{22} and $\beta = 0.74$, the fraction transformed by nonradiative decay of the complex $[S, St]^{3*}$. The third limiting case where $k_{22} \ll k_{21}$ and k_{23} is identical with the simpler mechanism described by eq 1, 10–15.

Although it is not possible to determine quantitatively the precise mechanism, the results can be satisfactorily explained in terms of the complex $[S, St]^{3*}$ having the stilbene in a different geometry from that preferred by "free" stilbene triplets. Saltiel has analyzed the results of several studies involving quenching of the stilbene triplet by azulene, oxygen, and *tert*-butyl nitroxide to indicate that the "free" stilbene triplet exists in a preferred twisted geometry.² Quenching by oxygen and the nitroxide can occur without requiring the stilbene triplet to obtain a transoid configuration. The strong dependence of azulene quenching on viscosity has been interpreted in terms of an equilibration between twisted and transoid forms in the presence of azulene which is followed by energy transfer from the transoid form to azulene.² For the intermolecular chain process with the metalloporphyrins where the porphyrin is both the sensitizer and quencher, it appears that the complex formed must have the stilbene preferentially in a nearly transoid configuration. In such a complex, an altered potential surface for the stilbene triplet could result in a net lowered rate of decay by virtue of a smaller population of twisted triplets. While rapid quenching of the stilbene triplet by the metalloporphyrin to permit the quantum chain process should occur, nonradiative decay of a transoid stilbene triplet in the complex should lead to a greater fraction *trans* than for the free twisted triplet.⁴²

In summary, these investigations using long-lived low-energy sensitizers to both sensitize the formation of and quench acceptor triplets indicate that substantial intermolecular quantum chain processes of this sort can indeed occur. Interestingly, the quantum chain processes observed here can occur at much lower substrate concentrations than those at which the mechanistically different sensitized diene isomerization quantum chain process occurs.^{19–23} However, the occurrence of the quantum chain process in these cases is due to formation of a relatively long-lived complex which modifies to some extent the behavior and properties of the stilbene triplet. Thus, although it should be possible to induce similar processes with other sensitizer-acceptor systems, it would not be surprising to find a considerable dependence of these phenomena on the nature and structure of the sensitizer.⁴⁴

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References and Notes

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