

Photochemical Generation, Isomerization, and Oxygenation of Stilbene Cation Radicals

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Abstract: The cation radicals of *cis*- and *trans*-stilbene and several of their ring-substituted derivatives have been generated in solution directly by means of pulsed-laser-induced electron transfer to singlet cyanoanthracenes or indirectly via electron transfer from biphenyl to the singlet cyanoanthracene followed by secondary electron transfer from the stilbenes to the biphenyl cation radical. Transient absorption spectra of the *cis*- and *trans*-stilbene cation radicals generated by secondary electron transfer are similar to those previously obtained in 77 K matrices. Quantum yields for radical ion-pair cage escape have been measured for direct electron transfer from the stilbenes to three neutral and one charged singlet acceptor. These values increase as the ion-pair energy increases due to decreased rate constants for radical ion-pair return electron transfer, in accord with the predictions of Marcus theory for highly exergonic electron transfer. Cage-escape efficiencies are larger for *trans*- vs *cis*-stilbene cation radicals, possibly due to the greater extent of charge delocalization in the planar *trans* vs nonpolar *cis* cation radicals. Cage-escaped stilbene cation radicals can initiate a concentration-dependent one way *cis* → *trans*-stilbene isomerization reaction. In the presence of oxygen, isomerization is inhibited and oxidative cleavage of either *trans*- or *cis*-stilbene to benzaldehyde occurs. Correlation of the measured quantum yields for oxygenation and isomerization with quantum yields for cage escape establishes that oxygenation is a nonchain process whose efficiency shows little variation with stilbene substituent or configuration, whereas isomerization is a chain process whose chain length is dependent upon substituent.

Introduction

Photoinduced electron transfer results in the formation of a radical ion pair that in polar solvent can diffuse apart to form free radical ions in competition with return electron transfer.^{1,2} Both the ion pair and free ions can also undergo chemical reactions (Scheme I).³ The return electron transfer process has attracted attention from experimentalists^{2,4,5} seeking to establish the energy gap dependence of electron-transfer rates in the "Marcus inverted region".⁶ Understanding the return electron-transfer process is also of crucial importance in optimizing the yield of electron-transfer-initiated reactions, since reactions within the radical ion pair and its separation to yield free radical ions must compete with return electron transfer.

We report here the results of our collaborative investigation of the cage-escape, isomerization, and oxygenation efficiencies of a series of ring-substituted derivatives of *trans*- and *cis*-stilbene.⁷⁻⁹ Cage-escape efficiencies are dependent upon the energy gap for return electron transfer, in accord with the prediction of Marcus theory, but are systematically larger for *trans* vs *cis* isomers. Quantum yields for the one-way *cis* → *trans* isomerization of the substituted *cis*-stilbene cation radicals are found to be dependent upon both the cage-escape efficiency and the chain length of the subsequent cation radical-initiated isomerization process.⁸ Quantum yields for photooxygenation are dependent upon cage-escape efficiency but display relatively little variation with stilbene substituent or configuration. These results permit the first extensive correlation of cage escape and reaction efficiency for chain and nonchain processes initiated by photoinduced electron transfer.

Results

Fluorescence Quenching. Excited-state lifetimes and energies, and ground-state reduction potentials for three cyanoanthracene singlet acceptors, 9-cyanoanthracene (CA), 9,10-dicyanoanthracene (DCA), and 2,6,9,10-tetracyanoanthracene (TCA), and one positively charged singlet acceptor, *N*-methylacridinium hexafluorophosphate, (MA) are given in Table I. Half-wave reduction potentials for the cyanoanthracenes in acetonitrile solution were measured in our laboratories vs Ag/AgI with the oxidation of ferrocene ($E_{1/2} = 0.875$ V) as an external reference.

Scheme I

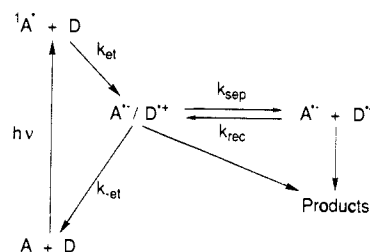


Table I. Excitation Energies and Reduction Potentials for Several Singlet Acceptors

| acceptor | τ_s , ^a ns | E_s , ^b eV | E_{red} , ^c V |
|-------------------------------------|----------------------------|-------------------------|----------------------------|
| 9-cyanoanthracene (CA) | 16.9 | 3.00 | -0.98 |
| 9,10-dicyanoanthracene (DCA) | 14.9 | 2.90 | -0.43 |
| 2,6,9,10-tetracyanoanthracene (TCA) | 16.6 | 2.87 | +0.03 |
| <i>N</i> -methylacridinium (MA) | 36 | 2.77 | +0.02 |

^a Singlet lifetimes in deoxygenated acetonitrile solution. ^b Singlet energies from refs 3a, 4d, and 4e. Values for the cyanoanthracenes are the average energies of the zero-zero transitions of the absorption and emission spectra. ^c Half-wave potential for reversible reduction in acetonitrile solution vs Ag/AgI.

Table II. Quenching of Excited Electron Acceptors by *trans*- and *cis*-Stilbene

| acceptor ^a | stilbene | $-\Delta G_{et}$, eV | $k_q\tau$, ^b M ⁻¹ | $10^{10}k_q$, ^c M ⁻¹ s ⁻¹ |
|-----------------------|----------|-----------------------|--|---|
| CA | t-S | -0.11 | 61 | 0.36 |
| CA | c-S | 0.0 | 3.6 | 0.021 |
| DCA | t-S | -0.55 | 316 | 1.9 |
| DCA | c-S | -0.44 | 287 | 1.7 |
| TCA | t-S | -0.96 | 370 | 2.2 |
| TCA | c-S | -0.85 | 315 | 1.9 |

^a See Table I for abbreviations. ^b Slope of linear Stern-Volmer plot for fluorescence or triplet quenching in acetonitrile solution. ^c Calculated from lifetime data in Table I.

The literature value of $E_{1/2}$ for MA vs SCE has been converted to the Ag/AgI electrode by addition of 0.39 V.

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(1) (a) Weller, A. Z. Phys. Chem. (Wiesbaden) 1982, 130, 129. (b) Weller, A. Z. Phys. Chem. (Wiesbaden) 1982, 133, 93.

Table III. Stilbene Oxidation Potentials and Quenching of 9,10-Dicyanoanthracene Fluorescence by Substituted Stilbenes

| stilbene | E_{ox} , eV | $k_q\tau$, ^b M ⁻¹ | $10^{10}k_q$, ^c M ⁻¹ s ⁻¹ |
|---------------------------------|------------------|---|--|
| <i>trans</i> -4,4'-dimethoxy | 1.45 | 365 | 2.2 |
| <i>trans</i> -4-methoxy | 1.53 | 361 | 2.1 |
| <i>trans</i> -4,4'-dimethyl | 1.76 | 294 | 1.7 |
| <i>trans</i> -4-methyl | 1.83 | 288 | 1.7 |
| <i>trans</i> -stilbene | 1.95 | 316 | 1.9 |
| <i>trans</i> -4-chloro | 1.98 | 268 | 1.6 |
| <i>trans</i> -4-cyano | 2.18 | 255 | 1.5 |
| <i>trans</i> -4-trifluoromethyl | 2.17 | 256 | 1.5 |
| <i>cis</i> -4-methoxy | 1.61 | 257 | 1.5 |
| <i>cis</i> -4,4'-dimethyl | 1.88 | 263 | 1.6 |
| <i>cis</i> -4-methyl | 1.95 | 242 | 1.4 |
| <i>cis</i> -stilbene | 2.06 | 287 | 1.7 |
| <i>cis</i> -4-chloro | 2.13 | 218 | 1.3 |
| <i>cis</i> -4-cyano | 2.23 | 212 | 1.3 |

^a Peak potential for irreversible oxidation in acetonitrile solution vs Ag/AgI. ^{b,c} See footnotes to Table II.

Quenching of CA, DCA, or TCA fluorescence by *trans*-stilbene (*t*-S) or *cis*-stilbene (*c*-S) results in Stern-Volmer plots that either were linear or exhibited slight upward curvature. The initial slopes of the plots are reported in Table II as $k_q\tau$ values along with values of k_q calculated from measured values for τ (Table I). Values of $k_q\tau$ and τ obtained for *t*-S with CA and DCA are in excellent agreement with those previously reported by Eriksen and Foote.¹⁰ Also reported in Table II are values of ΔG_{et} , the free energy of electron transfer, calculated from Weller's equation (eq 1).^{1b}

$$\Delta G_{et} = E_{ox} - E_{red} - E^* - 0.06 \text{ eV} \quad (1)$$

Values of k_q are near the rate of diffusion in acetonitrile solution ($1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$)¹¹ except in the case of singlet CA with *t*-S and *c*-S for which ΔG_{et} is less exergonic than in the other cases.

Fluorescence quenching of DCA by a series of substituted *trans*- and *cis*-stilbenes has also been investigated. Values of $k_q\tau$ and k_q are given in Table III. Values of $k_q > 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ are observed in all cases. Also included in Table III are the peak potentials for oxidation of the stilbenes in acetonitrile solution measured with cyclic voltammetry and a scan rate of 100 mV/s. Under these conditions, the more readily oxidized *trans*-stilbenes are reversibly oxidized but some of the *trans*- and all of the *cis*-stilbenes are irreversibly oxidized. The oxidation potentials of *trans*- and *cis*-stilbenes in acetonitrile solution have also been measured by

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(5) (a) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057. (b) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673. (c) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080. (d) Irvine, M. P.; Harrison, R. J.; Beddard, G. S.; Leighton, P.; Sanders, J. K. M. *Chem. Phys.* **1986**, *104*, 315.

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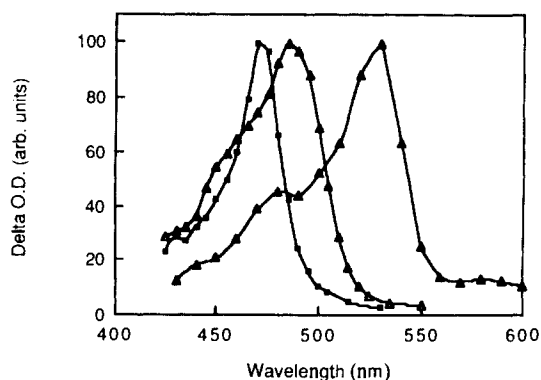
(7) For previous reports of isomerization, oxygenation, and cage-escape efficiencies of unsubstituted *trans*- and *cis*-stilbene, see refs 8 and 9.

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**Figure 1.** Normalized absorption spectra of the cation radicals of *trans*-stilbene (■), *trans*-4-methoxystilbene (△), and *trans*-4,4'-dimethoxystilbene (▲) in acetonitrile solution.**Table IV.** Absorption Spectral Data for Stilbene Neutrals and Cation Radicals

| stilbene | neutral ^a | | cation radical ^b | |
|------------------------------|----------------------|---------------------|-----------------------------|------------|
| | λ_{max} , nm | ϵ | λ_{max} , nm | ϵ |
| <i>trans</i> -4,4'-dimethoxy | 324 | 35 300 | 530 | 65 500 |
| <i>trans</i> -4,4'-dimethyl | 302 | 32 200 | 500 | 60 600 |
| <i>trans</i> -4-methoxy | 306 | 29 100 ^c | 485 | 60 600 |
| <i>trans</i> -4-methyl | 300 | 29 100 | 480 | 66 500 |
| <i>trans</i> -stilbene | 297 | 28 200 | 472 | 59 600 |
| <i>trans</i> -4-chloro | 301 | 30 200 ^c | 490 | 68 500 |
| <i>trans</i> -4-cyano | 323 | 35 300 ^c | 480 | 50 500 |
| <i>cis</i> -4,4'-dimethyl | 286 | 13 200 | 530 | 16 200 |
| <i>cis</i> -4-methoxy | 290 | 13 100 ^c | 520 | 10 100 |
| <i>cis</i> -4-methoxy | 284 | 7 960 | 520 | 26 300 |
| <i>cis</i> -stilbene | 276 | 10 200 | 508 | 21 400 |
| <i>cis</i> -4-chloro | 283 | 11 800 ^c | 520 | 16 000 |

^a Data for cyclohexane solution. ^b Data for acetonitrile solution.

^c Data from ref 16.

Amatore¹² under conditions of full reversibility. The values obtained for *trans*- and *cis*-stilbene (1.98 and 2.09 V vs Ag/AgI, respectively) are essentially the same as those reported in Table III. Values of ΔG_{et} calculated from eq 1 range from -0.27 eV for *cis*-4-cyanostilbene to -1.05 eV for *trans*-4,4'-dimethoxystilbene.

Exciplex fluorescence is not observed in acetonitrile solution for any of the acceptor-stilbene pairs but is observed for DCA with several of the stilbenes in benzene solution.^{8,13} Absorption spectra of mixtures of CA or DCA (10^{-4} M) and the stilbenes ($<10^{-1}$ M) are strictly additive; however, mixtures of TCA (10^{-4} M) and *t*-S or *c*-S (0.05 M) display broad absorption above 400 nm, indicative of charge-transfer complex formation. A Benesi-Hildebrand plot for the TCA-*t*-S (0.02-0.2 M) complex provided an association constant of $7 \pm 1 \text{ M}^{-1}$.

Cation-Radical Formation. Characterization of the *trans*-stilbene cation radical (*t*-S^{•+}) formed upon photoinduced electron transfer to CA or DCA by means of transient absorption spectroscopy was previously reported by Spada and Foote.¹⁴ Air saturation serves to remove the small but observable contribution of CA^{•-} or DCA^{•-} to the transient absorption spectrum in the visible region by means of exergonic electron transfer to oxygen, forming superoxide, which is transparent in the visible region. We have obtained the transient absorption spectra of *t*-S^{•+} and several of its ring-substituted derivatives formed either directly, by electron-transfer quenching of DCA (10^{-5} M) by stilbene (0.1 M) or indirectly, by means of initial electron transfer from biphenyl (0.1 M) to DCA followed by exergonic secondary electron transfer from stilbene (5×10^{-4} M) to the biphenyl cation radical ($E_{ox} = 2.40$ V). This indirect method of generating stilbene cation radicals results in higher quantum yields for generation of the free

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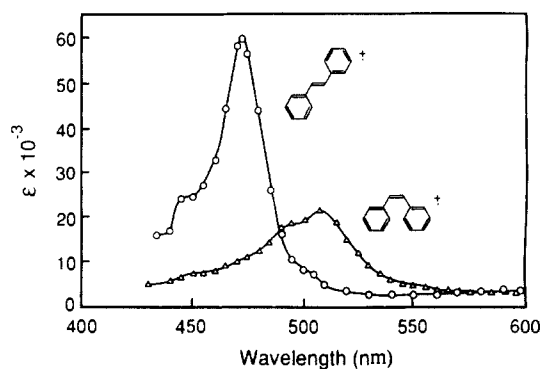


Figure 2. Transient absorption spectra of *trans*- and *cis*-stilbene cation radical in acetonitrile solution at room temperature obtained 0.5 μ s after excitation.

cation radicals and hence improved signal/noise in the transient-absorption spectra.⁹ The time-resolved decay of the biphenyl cation-radical spectrum ($\lambda_{\max} = 640$ nm) is accompanied by growth of the stilbene cation-radical absorbance at shorter wavelength with a time constant of ca. 200 ns. This corresponds to a rate constant of ca. $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for exergonic electron transfer from the stilbenes to biphenyl cation radical.

Normalized absorption spectra for *t*-S^{•+} and its 4-methoxy and 4,4'-dimethoxy derivatives recorded 0.5 μ s after the excitation pulse are shown in Figure 1. Extinction coefficients for the stilbene cation radicals were determined with the cation radical of tritylamine ($\lambda_{\max} = 668$ nm, $\epsilon = 26\,200^{15}$), generated under identical secondary-electron-transfer conditions, as an actinometer. Absorption spectral data for stilbene neutrals in cyclohexane solution and cation radicals in acetonitrile solution are summarized in Table IV. Absorption data for several of the monosubstituted stilbenes have previously been reported by Jungmann et al.¹⁶

Secondary electron transfer has also been employed to generate *c*-S^{•+} without concomitant formation of *t*-S^{•+}.⁹ The transient absorption spectrum obtained 0.5 μ s following laser flash photolysis of DCA with 0.1 M biphenyl and 5×10^{-4} M *c*-S is shown in Figure 2 along with the spectrum of *t*-S^{•+} obtained under comparable conditions. The energies, band shapes, and relative extinction coefficients of *t*-S^{•+} and *c*-S^{•+} obtained by photoinduced electron transfer are similar to those obtained by Shida and co-workers¹⁷ by means of radiolysis in 77 K halocarbon matrices. Decay of the stilbene cation radicals generated by secondary electron transfer is predominantly second order. Absorption due to *c*-S^{•+} decreases by ca. 1 order of magnitude in 10 μ s following the excitation pulse. During this period, the spectral band shape of *c*-S^{•+} remains essentially unchanged either at ambient temperature or at 60 °C, with only a slight shoulder appearing at ca. 470 nm, the absorption maximum of *t*-S^{•+}. No change in band shape with time is observed for *t*-S^{•+}. Similar results were obtained with the substituted *cis*-stilbenes, except in the case of the 4-methoxy derivative for which the initially observed spectrum ($\lambda_{\max} = 520$ nm) changed to that of the *trans* isomer ($\lambda_{\max} = 485$ nm) within 10 μ s.

Quantum yields for separation of the initially formed radical ion pair to generate free stilbene cation radicals (Φ_{sep}) were determined by laser flash photolysis of deoxygenated acetonitrile solutions containing $(2-4) \times 10^{-5}$ M acceptor, 0.05 M stilbene, and 5×10^{-4} M *trans*-4,4'-dimethoxystilbene. Secondary electron transfer to the free stilbene cation radical from 4,4'-dimethoxystilbene yields the same transient species from each of the stilbenes, allowing relative values of Φ_{sep} to be determined directly. Absolute

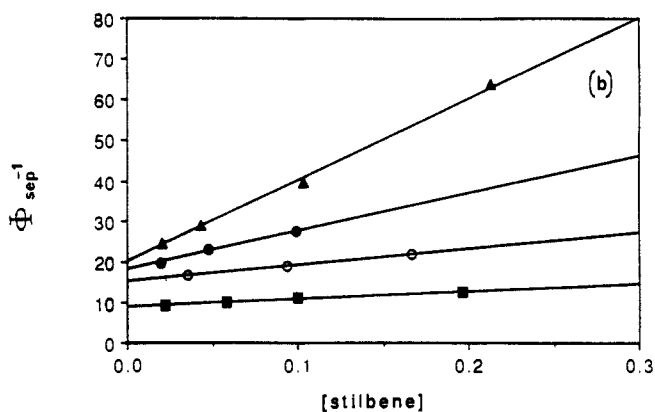
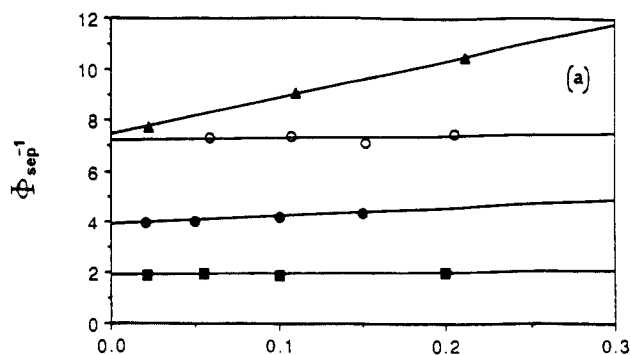


Figure 3. Concentration dependence of free-ion formation. (a) Key: dicyanoanthracene with *trans*-4-methylstilbene (\blacktriangle), *cis*-stilbene (\circ), *trans*-stilbene (\bullet), and *trans*-4-cyanostilbene (\blacksquare). (b) Key: tetracyanoanthracene with *trans*-4-methylstilbene (\blacktriangle), *trans*-4-chlorostilbene (\bullet), *cis*-4-chlorostilbene (\circ), and *trans*-4-cyanostilbene (\blacksquare).

Table V. Quantum Yields for Formation of Stilbene Cation Radicals in Acetonitrile Solution

| stilbene | acceptor ^a | Φ_{sep} (trans) | $-\Delta G_{\text{et}}$, V (trans) | Φ_{sep} (cis) | $-\Delta G_{\text{et}}$, V (cis) |
|-------------------|-----------------------|--------------------------------|--|------------------------------|--------------------------------------|
| 4-methoxy | DCA | 0.052 | 1.96 | 0.032 | 2.04 |
| | TCA | 0.029 | 1.50 | 0.023 | 1.58 |
| 4,4'-dimethyl | DCA | 0.095 | 2.19 | 0.048 | 2.31 |
| | TCA | 0.043 | 1.73 | 0.022 | 1.85 |
| 4-methyl | DCA | 0.14 | 2.26 | 0.077 | 2.38 |
| | TCA | 0.048 | 1.80 | 0.019 | 1.92 |
| stilbene | CA | 0.71 | 2.93 | <i>b</i> | |
| | DCA | 0.26 | 2.38 | 0.14 | 2.49 |
| | TCA | 0.053 | 1.92 | 0.027 | 2.03 |
| | MA | 0.054 | 1.93 | 0.023 | 2.04 |
| 4-chloro | DCA | 0.27 | 2.41 | 0.019 | 2.56 |
| | TCA | 0.057 | 1.95 | 0.029 | 2.10 |
| 4-cyano | DCA | 0.53 | 2.61 | 0.39 | 2.66 |
| | TCA | 0.11 | 2.15 | 0.054 | 2.20 |
| 4-trifluoromethyl | DCA | 0.48 | 2.60 | | |

^aSee Table I for abbreviations. ^bInsufficient singlet quenching to permit measurement.

values of Φ_{sep} are obtained by using the benzophenone triplet state as an actinometer.^{4c} Plots of Φ_{sep}^{-1} vs stilbene concentration are shown in Figure 3 parts a and b for several stilbenes with DCA and TCA, respectively. The concentration dependence is far more pronounced for TCA vs DCA and for stilbenes with electron-donating vs electron-withdrawing substituents. Values of Φ_{sep} in the limit of low stilbene concentration obtained from the intercepts of plots such as those shown in Figure 3 are reported in Table V along the values for ΔG_{et} calculated from the sum of the stilbene oxidation potentials and acceptor reduction potentials. The value of Φ_{sep} for DCA with *t*-S decreases slightly from 0.26 in argon-saturated solution to 0.22 with air saturation and 0.20 with oxygen saturation.

Stilbene Isomerization. As previously reported by one of our laboratories,⁸ irradiation of DCA with *c*-S or *t*-S results in *cis,trans*

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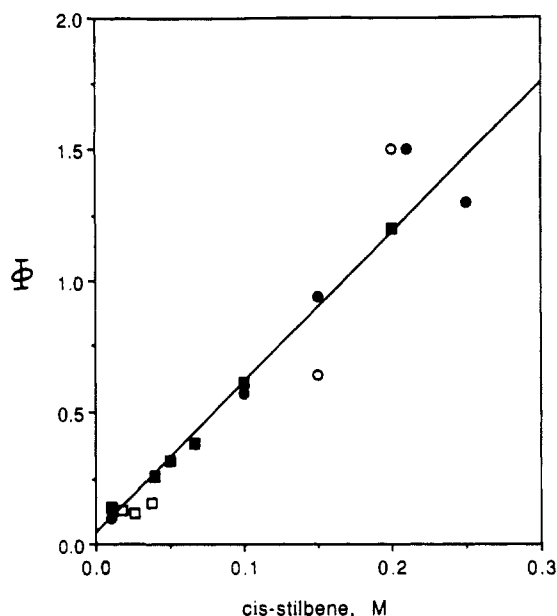


Figure 4. DCA-sensitized isomerization as a function of concentration of *cis*-stilbene in acetonitrile solution. Symbols represent four different data sets.

Table VI. Quantum Yields for Dicyanoanthracene-Sensitized Isomerization in Acetonitrile Solution^a

| stilbene | $\Phi_{t \rightarrow c}$ | $\Phi_{c \rightarrow t}$ | % <i>t</i> -S ^b | $\Phi_{c \rightarrow t} / \Phi_{sep}$ |
|-------------------|--------------------------|--------------------------|----------------------------|---------------------------------------|
| 4-methoxy | 0.001 | 0.12 | <i>c</i> | 6.0 ^d |
| 4,4-dimethyl | 0.006 | 0.35 ^e | <i>c</i> | 7.3 |
| 4-methyl | 0.001 | 0.14 | 99.9 | 2.8 |
| stilbene | 0.002 | 0.32 | 98.8 | 2.5 |
| 4-chloro | 0.006 | 2.5 | 96.0 | 17 |
| 4-cyano | 0.002 | 13.0 | 98.8 | 34 |
| 4-trifluoromethyl | <i>c</i> | <i>c</i> | 98.8 | |

^a Values obtained for 365- or 420-nm irradiation of deoxygenated solutions of 0.05 M stilbene and 10^{-4} M DCA on a merry-go-round apparatus. ^b Photostationary state obtained from *trans* and *cis* isomers. ^c Not determined. ^d Calculated from an estimated value of $\Phi_{sep} = 0.02$. ^e Value for 0.02 M stilbene.

isomerization. Values of $\Phi_{t \rightarrow c}$ are low (0.002) and independent of *t*-S concentration, whereas $\Phi_{c \rightarrow t}$ increases from ca. 0.1 for 0.01 M *c*-S to >1.0 for *c*-S concentrations above 0.2 M. A least-squares fit to the four independent data sets shown in Figure 4 has an intercept of 0.04 and a slope of 5.7 ($R^2 = 0.994$). Kuriyama et al.¹⁸ report similar results for *c*-S concentrations above 0.1 M and an essentially constant value of $\Phi_{c \rightarrow t} = 0.02$ at lower *c*-S concentrations. Our previously reported method for the measurement of $\Phi_{c \rightarrow t}$ provides reproducible results as long as *c*-S from the same commercial batch and the same light intensity are used.⁸ A higher value of $\Phi_{c \rightarrow t}$ (0.75 for 0.05 M *c*-S) was obtained from freshly chromatographed *c*-S irradiated at 404 nm on an optical bench with lower light intensity ($I_a = 2 \times 10^{-8}$ vs 8×10^{-8} einstein s^{-1} for the merry-go-round apparatus.) Erratic results were encountered at low conversions (<2%), plausibly due to the consumption of traces of oxygen or other adventitious quenchers (vide infra). Quantum yields were also observed to decrease at conversions of *c*-S >10%. Addition of 0.025 or 0.05 M *t*-S reduces the initial value of $\Phi_{c \rightarrow t}$ from 0.32 to 0.16 or 0.10, respectively.

Values of $\Phi_{t \rightarrow c}$ and $\Phi_{c \rightarrow t}$ for the DCA-sensitized isomerization of the stilbenes and several *para*-substituted derivatives at a single stilbene concentration (0.05 M) are summarized in Table VI. Values of $\Phi_{t \rightarrow c} < 0.006$ were obtained for all of the *trans* isomers. Values of $\Phi_{c \rightarrow t}$ are dependent upon the substituent, increasing from 0.12 for *cis*-4-methoxystilbene to 13.0 for *cis*-4-cyanostilbene. Isomerization efficiencies were observed to increase with stilbene

Table VII. Cage Separation and Isomerization Quantum Yields for *cis*-Stilbene with Singlet Acceptors

| acceptor | $-\Delta G_{et}$, ^a eV | Φ_{sep} | $\Phi_{c \rightarrow t}$ | $\Phi_{c \rightarrow t} / \Phi_{sep}$ |
|-------------------------------------|---------------------------------------|--------------------|--------------------------|---------------------------------------|
| 9-cyanoanthracene (CA) | 3.04 | (0.6) ^c | 1.5 | 2.5 |
| 9,10-dicyanoanthracene (DCA) | 2.49 | 0.14 | 0.32 | 2.3 |
| 2,6,9,10-tetracyanoanthracene (TCA) | 2.03 | 0.020 | 0.02 | 1.0 |
| <i>N</i> -methylacridinium (MA) | 2.04 | 0.023 | 0.012 | 0.5 |

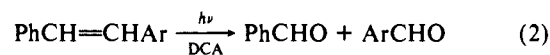
^a Calculated from the sum of the donor and acceptor redox potentials. ^b See Table VI, footnote *a* for reaction conditions. ^c Estimated value, see text.

concentration. Photostationary states highly enriched in the *trans* isomer were obtained upon prolonged irradiation of either the *trans* or *cis* isomer of most of the substituted stilbenes (Table VI). Attempts to obtain photostationary states for the DCA-sensitized isomerization of *p*-methoxystilbene were hampered by the low quantum yields and by the slow consumption of DCA, which also occurred to varying degrees upon prolonged irradiation, with other substituted stilbenes.

Quantum yields for isomerization of 0.05 M *c*-S in acetonitrile solution were determined from several electron acceptors in addition to DCA. Values of $\Phi_{c \rightarrow t}$ for 1.0×10^{-3} M 9-cyanoanthracene, 6×10^{-5} M 2,6,9,10-tetracyanoanthracene, and 5×10^{-4} M *N*-methylacridinium are given in Table VII. The value of $\Phi_{c \rightarrow t}$ obtained from CA is corrected for incomplete quenching (ca. 15%) by 0.05 M *c*-S. No correction is needed for DCA, TCA, or MA. Plots of $\Phi_{c \rightarrow t}^{-1}$ vs $[c-S]^{-1}$ for CA- and DCA-sensitized isomerization have intercepts (reciprocal of the quantum yield in the limit of high stilbene concentration) near 0.

Stilbene Oxygenation. As previously reported by Foote and co-workers,¹⁹ DCA-sensitized irradiation of either *t*-S or *c*-S in the presence of oxygen results in the formation of benzaldehyde (BA) and lesser amounts of stilbene oxides (SO) and several other oxidation products. At low conversions (<10%) of 0.05 M *t*-S or *c*-S, the only products that can be quantitatively analyzed by GC are BA and SO. These are also the only products detected by ¹H or ¹³C NMR for samples irradiated at either 25 or 0 °C at <30% conversion. An induction period is observed for the formation of SO (but not BA) but can be eliminated by the addition of 0.01 M BA prior to irradiation. When solutions of *t*-S are irradiated with continuous air purging, no isomerization (<0.5%) is observed. When *c*-S solutions containing ca. 0.1% *t*-S are irradiated, the *t*-S concentration rapidly increases to 1.5% but does not increase further with irradiation time. Added *n*-dodecanethiol (0.001–0.03 M) inhibits SO formation but has little effect on the yield of BA.

The DCA-sensitized photooxygenation of several *mono*-*para*-substituted derivatives of *t*-S and *c*-S were also investigated. The major products of these reactions were BA and substituted BA (eq 2). The two aldehydes are formed in a 1:1 ratio except in



the case of *p*-methoxystilbene, which yields a 2:1 ratio of anisaldehyde/BA. This apparent anomaly requires further investigation.

Quantum yields for formation of total BA (substituted plus unsubstituted) determined for air-saturated solutions of 0.05 M *t*-S, *c*-S, and substituted stilbenes were measured with monochromatic 404-nm irradiation on an optical bench in 1-cm cuvettes continuously bubbled with air. The results are reported in Table VIII along with values of Φ_{BA} obtained from 9-cyanoanthracene and 2,6,9,10-tetracyanoanthracene as electron acceptors. All of the stilbenes in Table VIII quench singlet DCA with rate constants near the rate of diffusion in acetonitrile solution, and 0.05 M stilbene is sufficient to quench >90% of singlet DCA in oxygen-saturated solutions (Table III).

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(19) (a) Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455. (b) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083.

Table VIII. Quantum Yields of Benzaldehyde Formation and Cage Separation of Substituted Stilbenes

| stilbene | acceptor | Φ_{BA}^a | Φ_{sep}^b | Φ_{BA}/Φ_{sep} |
|-----------------------------|----------|---------------|----------------|------------------------|
| <i>trans</i> -4-methoxy | DCA | 0.02 | 0.034 | 0.59 |
| <i>trans</i> -4,4'-dimethyl | DCA | 0.04 | 0.085 | 0.47 |
| <i>trans</i> -4-methyl | DCA | 0.08 | 0.13 | 0.62 |
| <i>trans</i> -stilbene | DCA | 0.17 | 0.25 | 0.68 |
| <i>trans</i> -stilbene | CA | 0.60 | 0.71 | 0.85 |
| <i>trans</i> -stilbene | TCA | <0.002 | 0.050 | <0.04 |
| <i>trans</i> -4-chloro | DCA | 0.19 | 0.27 | 0.70 |
| <i>trans</i> -4-cyano | DCA | 0.19 | 0.51 | 0.37 |
| <i>trans</i> -4-cyano | TCA | <0.002 | 0.10 | <0.02 |
| <i>cis</i> -4,4'-dimethyl | DCA | 0.04 | 0.048 | 0.83 |
| <i>cis</i> -4-methyl | DCA | 0.05 | 0.077 | 0.64 |
| <i>cis</i> -stilbene | DCA | 0.08 | 0.13 | 0.61 |

^aQuantum yield for air-saturated acetonitrile solutions containing 0.05 M stilbene and 3×10^{-4} M cyanoanthracene. 404-nm irradiation.

^bValues from Table V for deoxygenated solutions.

Table IX. Effect of Trimethoxybenzene and Oxygen upon Benzaldehyde Formation and Isomerization of *cis*-Stilbene

| TMB, M | O ₂ , M | $\Phi_{c \rightarrow t}^a$ | Φ_{BA}^a |
|--------------------|--------------------|----------------------------|---------------|
| 0 | 0 | 0.75 | 0.0 |
| 2×10^{-5} | 0 | 0.25 | 0.0 |
| 1×10^{-4} | 0 | 0.05 | 0.0 |
| 0 | 1×10^{-6} | 0.04 | 0.06 |
| 0 | 1×10^{-3} | 0.03 | 0.08 |
| 1×10^{-4} | 1×10^{-3} | <0.01 | <0.01 |

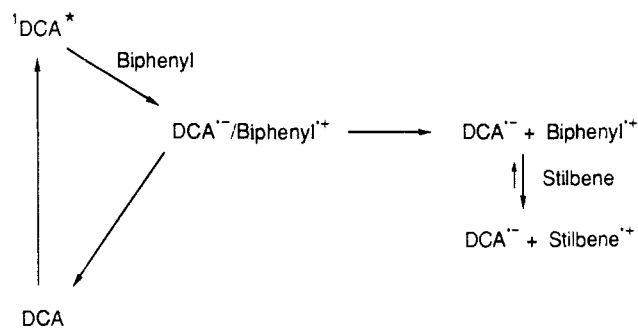
^aAcetonitrile solutions containing 0.05 M *c*-S and 3×10^{-4} M DCA irradiated on an optical bench at 404 nm.

The values of Φ_{ba} obtained for *t*-S and *c*-S (Table VIII) are similar to those previously reported for 365-nm irradiation on a merry-go-round apparatus.⁸ These values show little variation with light intensity ($(0.2-1.6) \times 10^{-8}$ einstein s⁻¹). The value of Φ_{BA} is independent of *t*-S concentration when sufficient *t*-S is present to quench >90% of singlet DCA (>0.04 M *t*-S), but decreases at lower *t*-S concentrations. Most of this decrease can be accounted for by incomplete quenching of DCA by *t*-S and by competitive quenching of DCA by oxygen ($k_{q\tau} = 300$ M⁻¹ s⁻¹). The dependence of Φ_{BA} upon oxygen concentration was investigated for solutions purged with mixtures of air and prepurified nitrogen. Oxygen concentrations were calculated from the mixing ratios of air/nitrogen, assuming that the concentration of oxygen in air-saturated acetonitrile is ca. 1×10^{-3} M.^{20,21} The value of Φ_{BA} decreases only slightly, from 0.17 to 0.15, over an oxygen concentration range of 10^{-3} – 10^{-6} M, but is <0.01 in nitrogen-purged solutions. Analogous results were obtained with *c*-S.

The electron donor 1,2,4-trimethoxybenzene (TMB) (10^{-3} M) was reported by Eriksen and Foote^{19b} to quench 94% of the DCA-sensitized photooxygenation of *t*-S. The effect of added TMB upon the quantum yields for BA formation and isomerization of *c*-S is reported in Table IX. Both O₂ (10^{-3} M) and TMB (10^{-4} M) separately quench ca. 90% of the isomerization of 0.05 or 0.10 M *c*-S. The combination of O₂ and TMB results in nearly total suppression of both reactions. Added *trans*-4,4'-dimethoxystilbene also is an efficient quencher of *c*-S isomerization, a concentration of 5×10^{-4} M being sufficient to quench ca. 95% of *t*-S formation.

Discussion

Transient Absorption Spectra. The cation radicals of *trans*- and *cis*-stilbene and several of their methylated derivatives have previously been generated by means of radiolysis in frozen matrices and their electronic absorption spectra investigated by Shida and

Scheme II

co-workers.¹⁷ The absorption spectrum of *t*-S^{•+} observed in the matrix consists of long-wavelength bands at 759 nm ($\epsilon = 5.55 \times 10^3$) and 482 nm ($\epsilon = 3.34 \times 10^4$) assigned to transitions from a filled π -orbital to the half-filled HOMO (A band) and from the HOMO to the LUMO (B band), respectively. Corresponding transitions for *c*-S^{•+} in the matrix occur at 750 nm ($\epsilon = 2.61 \times 10^3$) and 518 nm ($\epsilon = 1.0 \times 10^4$). The decrease in energy and oscillator strength of the higher energy band for *c*-S^{•+} vs *t*-S^{•+} is attributed to the effect of geometrical changes upon the absorption band.^{17c} Several calculations indicate that *t*-S^{•+} is essentially planar, whereas *c*-S^{•+}, like neutral *c*-S, is nonplanar.^{17c,22}

Photoinduced electron transfer provides a method of generating *t*-S^{•+} in solution. Transient absorption^{9,14,18,23-25} and resonance Raman spectroscopy²⁶ have been used to probe the formation and decay of *t*-S^{•+}, and its ESR spectrum has been obtained by means of steady-state irradiation.^{22c} Transient absorption spectra obtained in solution are somewhat broader than the matrix spectra¹⁷ but have similar band shapes. We find that improved signal/noise can be achieved when *t*-S^{•+} is generated indirectly by means of initial electron transfer to singlet DCA from biphenyl (BP) followed by secondary electron transfer from *t*-S to BP^{•+} rather than by direct electron transfer to DCA from *t*-S. The cosensitized path (Scheme II) benefits from the higher quantum yield for separation of the DCA^{•-}/BP^{•+} ($\Phi_{sep} = 0.75^{4d}$) vs DCA^{•-}/*t*-S^{•+} (Table V) radical ion pair. The measured rate constant for highly exergonic electron transfer from *t*-S ($E_{ox} = 1.95$ V) to BP^{•+} ($E_{ox} = 2.40$ V) is $\sim 1.5 \times 10^{10}$ M⁻¹ s⁻¹, and the equilibrium in Scheme II lies far on the side of *t*-S^{•+}, resulting in quantitative conversion of BP^{•+} to *t*-S^{•+} within 0.5 μ s.}}

Indirect cosensitized photoinduced electron transfer (Scheme II) has also been used to generate *c*-S^{•+}. The transient absorption spectrum of *c*-S^{•+} shown in Figure 2 is similar in λ_{max} and band shape to the B band observed by Shida and co-workers¹⁷ under steady-state matrix-radiolysis conditions. Noticeably lacking is a shoulder near 472 nm, the absorption maximum of *t*-S^{•+}. The ratio of *c*-S^{•+} vs *t*-S^{•+} B-band intensities in solution (Table IV) is 0.35, similar to the matrix value of 0.30 obtained by Shida and co-workers.¹⁷ Thus, a relatively small component (ca. 10%) due to *t*-S^{•+} would have been readily detected in the spectrum of *c*-S^{•+}. Under the indirect electron-transfer conditions used to generate the stilbene cation radicals (Scheme II), their decay is mainly second order. After 10 μ s, when the absorption due to the *c*-S^{•+} has decreased by ca. 1 order of magnitude, the spectrum is essentially unchanged at either 25 or 60 °C, with only a slight shoulder observable at ca. 470 nm, near the absorption maximum of the *t*-S^{•+}.

All of the substituted *cis*-stilbene cation radicals were observed to be configurationally stable on the microsecond time scale except for the 4-methoxy derivative. Takamuku and co-workers²⁷ have

(20) (a) On the assumption that ³O₂ is a diffusion-controlled quencher ($k_q \sim 2 \times 10^{10}$ M⁻¹ s⁻¹) of ¹DCA*,^{20b} the concentration of oxygen in air-saturated acetonitrile solution is ca. 3×10^{-3} M. (b) Beriman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, London, 1971; p 58.

(21) (a) A value of 1.7×10^{-3} M can be calculated from the reported value of 8.1×10^{-3} M for oxygen-saturated acetonitrile solution.^{21b} (b) Achord, J. M.; Hussey, C. L. *Anal. Chem.* **1980**, *52*, 601.

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recently studied the formation of $c\text{-S}^{+\bullet}$ and its 4-methoxy derivative by means of pulse radiolysis and observe that $c\text{-S}^{+\bullet}$ is configurationally stable at room temperature in dichloroethane solution but that its 4-methoxy derivative isomerizes with a rate constant of $2.3 \times 10^6 \text{ s}^{-1}$. This substituent effect is attributed by Takamuku and co-workers²⁷ to a decrease in the barrier to unimolecular isomerization of the cation radical resulting from localization of the electron hole on the methoxy oxygen.

Both electron-donating and -withdrawing substituents cause a bathochromic shift in the HO \rightarrow LU transitions of *trans*- and *cis*-stilbene neutrals and cation radicals (Table IV). A larger shift for the cation radical vs neutral of 4,4'-dimethylstilbene was previously observed by Suzuki et al.^{17b} This effect was attributed to the greater stabilization of the HOMO vs LUMO upon substitution, as a consequence of the larger C_4 atomic orbital coefficient in the HOMO. Values of λ_{max} for the *cis*-stilbene cation radicals are all 30–40 nm to the red of their *trans* isomers. The 4-CN substituent is unique in causing a larger bathochromic shift for the neutral vs the cation radical. Also noteworthy is the fact that the shift for 4,4'-dimethoxystilbene is greater than double the shift for methoxystilbene neutral and cation radical.

The effect of substituents upon the electrochemical oxidation potentials^{28–30} and gas-phase photoelectron³¹ spectra of several 4-substituted and 4,4'-disubstituted stilbenes has previously been investigated. Values of E_{ox} increase as the electron-withdrawing ability of the substituent increases, providing a reasonably good fit to a Hammett correlation with σ^+ , in accord with the ability of substituents such as *p*-OCH₃ to provide resonance delocalization of the positive charge. The extent of odd-electron delocalization in planar *trans*-stilbene cation radicals is indicated by the larger hyperfine coupling constant for methyl vs vinyl protons in the ESR spectrum of 4,4'-dimethylstilbene.^{22c} Values of E_{ox} are larger for *cis* vs *trans* isomers by amounts ranging from 0.15 to 0.05 V, the smallest differences being observed for methoxy and cyano substituents.

Cage Escape Efficiencies. Previous investigations have established that quantum yields for the formation of free radical ions (Φ_{sep}) via photoinduced electron transfer are dependent upon the solvent polarity, the redox potentials of the donor and acceptor, the molecular dimensions of the radical ions, the light-absorbing species (monomer vs charge-transfer complex), and the spin state of the radical ion pair.^{1–6,32} In the present investigation, a single solvent (acetonitrile) and three neutral and one cationic singlet acceptor (CA, DCA, TCA, and MA) of similar molecular dimension and singlet energy were employed (Table I).

Electron transfer from singlet DCA or CA to the stilbenes occurs predominantly via diffusive quenching, as evidenced by the absence of a significant dependence of Φ_{sep} upon stilbene concentration (Figure 3a). In contrast, the more powerful acceptor TCA forms a ground-state complex ($K \sim 7 \text{ M}^{-1}$) with *t*-S and presumably with the other stilbenes. Hence, quenching of TCA fluorescence by the stilbenes will have both a static and a dynamic component. The static component is expected to result in a lower value of Φ_{sep} than the dynamic component as a consequence of the formation of a contact radical ion pair upon excitation of a charge-transfer complex vs a solvent-separated radical ion pair upon diffusive quenching.^{4c} Since return electron transfer can compete with solvation of the contact radical ion pairs, values of Φ_{sep} can be substantially smaller for static vs dynamic electron-transfer quenching. Goodman and Peters²³ have determined values of $k_{\text{-et}} = 7.6 \times 10^9 \text{ s}^{-1}$ and $k_{\text{sol}} = 1.3 \times 10^9 \text{ s}^{-1}$ for the excited *t*-S-fumaronitrile charge-transfer complex. Thus, only 20% of the initially formed contact radical ion pair survives to form the solvent-separated radical ion pair. Values of Φ_{sep} for dynamic

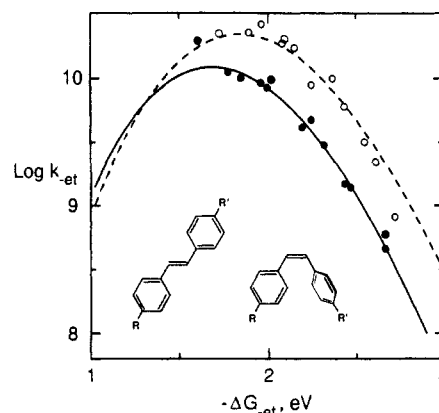


Figure 5. $\log k_{\text{-et}}$ for return electron transfer within geminate ion pairs of DCA or TCA with *trans*-stilbenes (●) or *cis*-stilbenes (○) vs the free energy change for the reaction.

quenching of TCA by the stilbenes (Table V) have been obtained by extrapolation of the observed values (Figure 3b) to 0 stilbene concentration. It should be noted that the magnitudes of the slopes in Figure 3 parts a and b parallel the anticipated strength of the ground-state donor-acceptor interaction and are greater for TCA vs DCA, *trans*- vs *cis*-stilbenes, and stilbenes with electron-donor vs -acceptor substituents.³³

We have also measured Φ_{sep} values for *t*-S and *c*-S with the cationic singlet acceptor *N*-methylacridinium. The values obtained (Table V) are nearly the same as those for TCA, a neutral acceptor of similar oxidation potential (Table I). This result is in agreement with a recent report from one of our laboratories for a series of alkylated benzene donors.^{4d} Evidently the absence of Coulombic attraction between the MA radical and stilbene cation radical does not result in a higher value of Φ_{sep} than that for the cyanoanthracene-stilbene radical ion pairs.

Values of Φ_{sep} obtained for the stilbenes from CA, DCA, TCA, and MA as singlet acceptors are summarized in Table V. Comparison of these values establishes that Φ_{sep} is larger for the weaker acceptor (CA > DCA > TCA or MA), for *trans*- vs *cis*-stilbenes, and for stilbenes with electron-withdrawing vs -donating substituents. According to the mechanism shown in Scheme I, Φ_{sep} is determined by the competition between separation and return electron transfer in the singlet radical ion pair ($\Phi_{\text{sep}} = k_{\text{sep}} / (k_{\text{sep}} + k_{\text{-et}})$). Investigations in one of our laboratories have established that $k_{\text{sep}} \sim 5 \times 10^8 \text{ s}^{-1}$ for structurally related cyanoaromatic acceptor-aromatic donor geminate radical ion pairs and is independent of redox potentials.⁴ Thus, the observed values of Φ_{sep} are determined primarily by the variation of $k_{\text{-et}}$ with donor-acceptor pairs and can be used with k_{sep} to calculate approximate values for $k_{\text{-et}}$.

Calculated values of $k_{\text{-et}}$ are plotted in Figure 5 vs the free energy for return electron transfer, $\Delta G_{\text{-et}}$. In order to compare this data with that of previous studies from one of our laboratories,⁴ the $\Delta G_{\text{-et}}$ values summarized in Table V were normalized to those of the previous conditions.⁴ The oxidation potential of *trans*-stilbene and the reduction potential of DCA were measured under the previous conditions (for details see ref 4e), and a value of -2.44 V was obtained for $\Delta G_{\text{-et}}$. The $k_{\text{-et}}$ data in Figure 5 are thus plotted against the $\Delta G_{\text{-et}}$ values in Table V, after addition of 0.06 V in each case. The data for the *trans*- and *cis*-stilbenes fall on roughly parallel curves; however, in both cases $k_{\text{-et}}$ decreases as $\Delta G_{\text{-et}}$ becomes more exergonic, as expected for electron transfer in the "Marcus inverted region".^{4–6} The curves that are superimposed on the data in Figure 4 represent theoretical fits to a semiclassical description of electron-transfer rates as described in ref 4e. The fit superimposed upon the *trans*-stilbene data is

(33) A reviewer has suggested that the concentration dependence of Φ_{sep} might result from reaction of the ion pair with a second molecule of stilbene. While there is ample precedent for such a reaction,³⁶ it would be most likely to occur for the longest lived ion pairs, e.g., those formed between the weakest donor-acceptor pairs, whose Φ_{sep} values are independent of concentration.

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that obtained previously for radical ion pairs of DCA and TCA with substituted naphthalenes, biphenyls, and fluorene as radical cations, whereas the fit superimposed upon the *cis*-stilbene data is that obtained from substituted benzenes as donors with the cyanoanthracene acceptors.^{4c} The worst fit is observed for the strongest donor-acceptor pair (TCA-*trans*-4-methoxystilbene) for which the extrapolated value of Φ_{sep} is subject to the largest error.

A plausible explanation for the smaller k_{ct} values for *trans*- vs *cis*-stilbenes of comparable oxidation potential is provided by the previously noted difference in planarity between the *trans* and *cis* cation radicals. In the planar *t*-S^{•+}, the electron hole is delocalized over a conjugated system similar in size to that in naphthalene or biphenyl. Delocalization should be less extensive in the nonplanar *c*-S^{•+}. Localization of the electron hole on a single benzene ring would result in a cation radical similar in effective size to that of a substituted benzene.

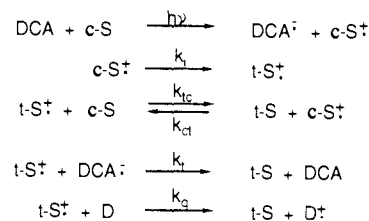
Isomerization. As previously reported by one of our laboratories,⁸ irradiation of *t*-S with DCA results in inefficient isomerization, whereas irradiation of *c*-S with DCA results in efficient, concentration-dependent isomerization (Figure 4). Double-reciprocal plots for the dependence of $\Phi_{\text{c} \rightarrow \text{t}}$ vs [*c*-S] for CA- and DCA-sensitized isomerization have intercepts near 0 indicative of very large quantum yields in the limit of high *c*-S concentration. Results obtained for several substituted stilbenes at a fixed stilbene concentration (0.05 M) are summarized in Table VI. Values of $\Phi_{\text{t} \rightarrow \text{c}}$ are uniformly low, while values of $\Phi_{\text{c} \rightarrow \text{t}}$ increase with increasing stilbene oxidation potential, attaining values distinctly higher than 1.0 for chloro- and cyanostilbenes. Photostationary states consisting of >96% *trans* isomer have been obtained for all of the substituted stilbenes except those of lowest oxidation potential for which approach to the photostationary state is very slow.

A cation-radical chain process in which free *c*-S^{•+} formation is the chain-initiating step was proposed to account for this one-way isomerization process.⁸ As previously reported,⁸ the chain isomerization occurs only in polar solvents in which separation of the initially formed radical ion pair can occur. Additional evidence for *c*-S^{•+} as the chain-initiating species is provided by the effects of added electron donors or oxygen upon the isomerization efficiency (Table IX). We have used exergonic secondary electron transfer from the stilbene cation radicals to *trans*-4,4'-dimethoxy stilbene (DMS) as a method of determining Φ_{sep} (Table V) and observe that 5×10^{-4} M DMS is sufficient to intercept essentially all of the free *c*-S^{•+} generated by laser-induced electron transfer to DCA within 0.5 μs of its generation. This concentration of DMS is also sufficient to quench >95% of *c*-S isomerization in steady-state experiments.

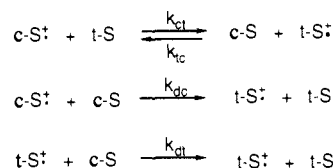
Further evidence supporting free *c*-S^{•+} as the chain-initiating species is provided by a comparison of the effect of acceptor upon Φ_{sep} and $\Phi_{\text{c} \rightarrow \text{t}}$. Assuming that the rate constants for chain propagation and termination are independent of the acceptor, values of $\Phi_{\text{c} \rightarrow \text{t}}$ should be determined primarily by the efficiency of cage escape. Cage-escape efficiencies have been measured in the case of DCA, TCA, and MA sensitization (Table V). A value of $\Phi_{\text{sep}} = 0.6 \pm 0.1$ for the CA^{•-}/*c*-S^{•+} ion pair can be estimated from the value of 0.71 for CA^{•-}/*t*-S^{•+}. Calculated values of $\Phi_{\text{c} \rightarrow \text{t}}/\Phi_{\text{sep}}$ for the three cyanoaromatic acceptors and MA are reported in Table VII. Considering the substantial error in measurement of the $\Phi_{\text{c} \rightarrow \text{t}}$ values, the variation in $\Phi_{\text{c} \rightarrow \text{t}}/\Phi_{\text{sep}}$ with acceptor is relatively small. The similar values of Φ_{sep} and $\Phi_{\text{c} \rightarrow \text{t}}$ for the neutral TCA and positively charged MA indicate that neither cage escape nor propagation vs termination is more efficient for the radical-cation-radical pair MA^{•+}/*c*-S^{•+} than for the radical-ion pair TCA^{•-}/*c*-S^{•+}. Low values of $\Phi_{\text{c} \rightarrow \text{t}}$ have also been reported for the charged singlet acceptors triphenylpyrylium ($E_{\text{red}} = +0.10$ V vs Ag/AgI)^{34a} and for methylviologen.^{34b}

Although the variation in $\Phi_{\text{c} \rightarrow \text{t}}/\Phi_{\text{sep}}$ for *c*-S with different acceptors is much smaller than the variation in the observed $\Phi_{\text{c} \rightarrow \text{t}}$

Scheme III



Scheme IV

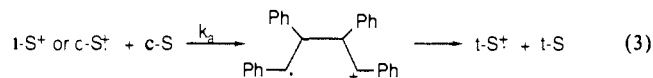


values, this is not the case for the substituted *cis*-stilbenes with a single acceptor, DCA (Table VI). Evidently, substituents influence the chain length of the cation-radical one-way isomerization process as well as the cage-escape efficiency. Both electron-donating and electron-withdrawing substituents appear to increase the chain length.

One of us previously proposed the mechanism for cation-radical-initiated one-way isomerization of *c*-S outlined in Scheme III.⁸ The chain-propagating steps in this mechanism are exergonic unimolecular isomerization of *c*-S^{•+} to *t*-S^{•+} (k_i) followed by endergonic electron transfer from *c*-S to *t*-S^{•+} (k_{tc}). Termination can occur via reduction of *c*-S^{•+} or *t*-S^{•+} by DCA^{•-} or an electron donor (D) present either as an impurity or as added quencher.

The observation that *c*-S^{•+} is configurationally stable under the conditions of our laser flash photolysis and Takamuku's pulse radiolysis experiments²⁷ sets an upper limit of ca. 10^4 s⁻¹ for k_i . The significantly higher value of Φ_{sep} (0.14) vs $\Phi_{\text{c} \rightarrow \text{t}}$ in the limit of low *c*-S concentration (0.04 from Figure 4 and 0.02 from ref 18) indicates that $k_i < k_t$. However, kinetic analysis of the quantum yield data in Figure 4 and Table IX according to Scheme III requires a value of $k_i > 10^5$ s⁻¹. The observed decrease in $\Phi_{\text{c} \rightarrow \text{t}}$ with added *t*-S is also incompatible with this mechanism. Thus, we conclude that the unimolecular isomerization mechanism of Scheme III cannot account for our experimental results. It is possible that this mechanism does apply in the case of *cis*-4-methoxystilbene or other substituted *cis*-stilbenes.

The observation of *c*-S^{•+} configurational stability under laser flash photolysis conditions led us to consider alternative mechanisms for the *c*-S concentration-dependent isomerization process. One plausible alternative is the reversible addition of *c*-S^{•+} or *t*-S^{•+} to neutral *c*-S to form an acyclic dimer cation radical that reverts to reactants with loss of stereochemistry (eq 3). There is ample

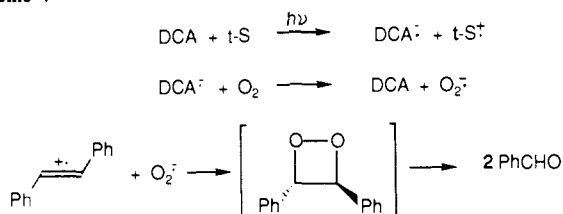


precedent for the formation of dimer cation radicals as intermediates in the cation-radical dimerization and oxygenation of terminal aryl olefins such as 1,1-diphenylethylene.^{3a} Thermochemical cycles (Appendix I) suggest that formation of an acyclic dimer cation radical from the reaction of *t*-S^{•+} with *c*-S is exergonic by ca. 8 kcal/mol and that the acyclic dimer cation radical is more stable than its cyclic isomer by ca. 7 kcal/mol.

A mechanism for the isomerization of *c*-S via the formation of a dimer cation radical is summarized in Scheme IV. The initiation and termination steps are the same as in Scheme III and thus have been omitted. This mechanism is fully consistent with the observed variation in $\Phi_{\text{c} \rightarrow \text{t}}$ with *c*-S concentration (Figure 4) and its dependence upon added electron donors (Table IX) or *t*-S. A value of $k_{\text{ct}}/k_{\text{tc}} = 73$ can be estimated from the difference in *c*-S vs *t*-S oxidation potentials (Table III). A similar equilibrium constant and a rate constant of 2×10^9 M⁻¹ s⁻¹ have recently been reported for the cation radicals of *cis*- and *trans*-1,2-bis(*N*-methyl-4-pyridyl)ethylene.³⁵ By use of this value and the quantum

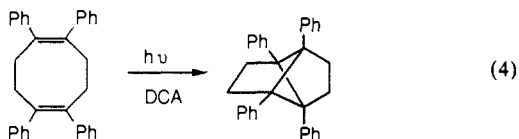
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Scheme V



yield data, values of the bimolecular rate constants $k_{dc} = 8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{dt} = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ are obtained. These values are distinctly smaller than those previously reported for the cation radicals of terminal olefins, but are similar to those for other internal olefins.^{36,37} The smaller value for k_{dt} vs k_{dc} may reflect the greater stability of the planar, delocalized *t*-S cation radical.

While dimer cation-radical formation appears thermodynamically and kinetically plausible, the experimental evidence remains inconclusive. Our efforts to detect stilbene dimers as products of DCA-sensitized irradiation have been unsuccessful. However, intramolecular 2 + 1 cyclization has been observed in DCA-sensitized irradiation of 1,2,5,6-tetraphenyl-1,5-cyclooctadiene (eq 4).³⁸ Our efforts to trap the stilbene dimer cation radical with



oxygen or nucleophiles have been unsuccessful, as have our efforts to trap the cation radical formed by the photooxygenation of tetraphenylcyclobutanes.^{37b} The latter reaction results in the formation of stilbenes as the only primary products, either in the absence or in the presence of oxygen.

Oxygenation. Investigations by Foote and co-workers^{19,39} of the DCA-sensitized photooxygenation of *t*-S over the past decade have led to the proposed mechanism for the formation of the major product, benzaldehyde, outlined in Scheme V. We admit to some misgivings about a mechanism that requires the combination of two reactive intermediates (present in very low concentrations in steady-state experiments) in which cycloaddition to form a dioxetane (which has eluded detection by low temperature spectroscopy) effectively competes with return electron transfer. While our results neither confirm nor disprove this oxidative cleavage mechanism, they do support the formation of $t\text{-S}^{\cdot+}$ as the initial step in BA formation and provide the first quantitative data for the efficiency of cage escape and subsequent oxygenation.

Quantum yields for benzaldehyde formation and stilbene cation radical cage escape are summarized in Table VIII. The values of Φ_{sep} were determined in deoxygenated solution and thus may be slightly higher than values in air-saturated solution. In the case of *t*-S and the values of Φ_{sep} obtained in argon- and air-saturated solutions are 0.26 and 0.22, respectively. Thus, the calculated values of Φ_{BA}/Φ_{sep} may slightly underestimate the efficiency of BA formation from the cage-escaped stilbene cation radicals. These values do serve to establish several important features of the photooxygenation reaction.

First, the larger value of Φ_{BA} for *t*-S vs *c*-S is due primarily to the more efficient cage escape of *t*-S.

Second, the total range of Φ_{BA}/Φ_{sep} values for CA or DCA sensitization is small compared to the range in Φ_{BA} values. Thus, the efficiency of oxygenation of cage-escaped stilbene cation radicals is much less dependent upon substituent than is cation-

radical-initiated isomerization (Table VI). This is consistent with the nonchain nature of the oxygenation process, which is evidenced by its lack of stilbene concentration dependence.

Third, another notable feature of the data in Table VIII is the low values of Φ_{BA} obtained by use of TCA as the sensitizer. The comparison of photooxygenation efficiency with DCA vs TCA as a sensitizer has been proposed as a mechanistic probe for the involvement of $\text{O}_2^{\cdot-}$ in photooxygenation reactions.⁴⁰ Since secondary electron transfer from $\text{DCA}^{\cdot-}$ to O_2 is exergonic whereas electron transfer from $\text{TCA}^{\cdot-}$ to O_2 is endergonic, formation of $\text{O}_2^{\cdot-}$ should occur with DCA but not TCA as an electron-transfer sensitizer. However, comparison of product formation quantum yields for cage escape may be misleading since the quantum yields for cage escape should be larger for ion pair of $\text{DCA}^{\cdot-}$ vs $\text{TCA}^{\cdot-}$ due to the larger energy gap for return electron transfer and the formation of ground-state complexes with TCA but not DCA (Table V). We have measured both Φ_{BA} and Φ_{sep} for DCA and TCA with *t*-S and its cyano derivative, a weaker donor with higher cage-escape efficiency, and find that the reaction of the stilbene cation radicals is at least 20 times more efficient for DCA vs TCA sensitization. This result, if correctly interpreted, supports the involvement of $\text{O}_2^{\cdot-}$ in the photooxidation mechanism.

If the Foote mechanism (Scheme V) is indeed correct, the value of $\Phi_{BA}/\Phi_{sep} = 0.68$ can be used to estimate the efficiency of product formation upon encounter of $t\text{-S}^{\cdot+}$ with $\text{O}_2^{\cdot-}$. Since two molecules of benzaldehyde would be formed from this reaction, at least one-third of such encounters must lead to product formation—even more if some of the $t\text{-S}^{\cdot+}$ reacts with electron-donor impurities. According to the FMO analysis of Yamaguchi,⁴¹ the $t\text{-S}^{\cdot+}/\text{O}_2^{\cdot-}$ singlet pair can undergo stepwise or concerted cycloaddition or return electron transfer to yield *t*-S and $^1\text{O}_2$, while the triplet pair can only undergo stepwise cycloaddition or return electron transfer to yield *t*-S and $^3\text{O}_2$. On a spin statistical basis, charge recombination of $t\text{-S}^{\cdot+}$ with $\text{O}_2^{\cdot-}$ should yield a 3:1 mixture of triplet and singlet radical pairs, and thus not all of the product can be accounted for by a concerted singlet mechanism.

An interesting feature of the photooxygenation of *c*-S is the ability of as little as 10^{-6} M O_2 to limit the formation of *t*-S to ca. 1.5% of total stilbene and reduce the value of $\Phi_{c \rightarrow t}$ from 0.75 to 0.04 (measured at ca. 1% conversion of *c*-S, Table IX). A plausible explanation for this observation is provided by rapid reversible electron transfer from $c\text{-S}^{\cdot+}$ to *t*-S (Scheme IV). This process reaches dynamic equilibrium when the stilbene concentration ratio $[\text{c-S}]/[\text{t-S}] = 66$ is approximately equal to the value of $k_{ct}/k_{tc} = 73$ calculated from the difference in stilbene oxidation potentials. At this ratio the concentrations of $c\text{-S}^{\cdot+}$ and $t\text{-S}^{\cdot+}$ should be nearly equal. Evidently, consumption of *t*-S becomes faster than its formation when $[\text{c-S}]/[\text{t-S}] < 66$. Even at this low steady-state concentration of *t*-S, much of the photooxygenation of *c*-S may actually occur via $t\text{-S}^{\cdot+}$, thus accounting for the similar values of Φ_{BA}/Φ_{sep} for cis and trans isomers (Table VIII).

Several alternative mechanisms for the oxidative cleavage of stilbene have been considered. We judge the reaction of a dimer cation radical (eq 3) with $^3\text{O}_2$ to be the most attractive of these on the basis of both the precedent for its occurrence in the photooxygenation of 1,1-diarylethylenes^{36,42} and its kinetics, which are first order in reactive intermediate. Its involvement in the photooxygenation of *t*-S appears to be inconsistent with the observed absence of Φ_{BA} dependence upon either stilbene or oxygen concentration and with the larger values of Φ_{BA}/Φ_{sep} for DCA vs TCA sensitization. We cannot offer it as a preferred alternative to Foote's mechanism for the photooxygenation of stilbene in the absence of direct evidence for the formation of a dimer cation radical from *t*-S.

Photooxygenation of *t*-S or *c*-S yields, in addition to BA, *trans*-stilbene oxide (SO) and lesser amounts of benzil, benzoin,

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and benzoin benzoate.^{37b} The formation of SO displays a short induction period suggestive of its formation via a secondary photoprocess. When 0.01 M BA is added to a solution of 0.05 M *t*-S and DCA prior to irradiation, the induction period is eliminated. The initial yield of benzoin benzoate is also increased while the yield of benzil is decreased. The addition of *n*-dodecanethiol (0.01–0.1 M) to the reaction mixture results in a modest increase in the yield of BA and essentially complete inhibition of the formation of SO and the other minor oxygenation products. On the basis of this evidence, we propose that SO is formed via a free-radical process involving the benzoyl radical that can be scavenged by added thiol or react with oxygen to form the benzoylperoxy radical, a known nonstereospecific olefin epoxidizing agent.⁴³

Concluding Remarks

The efficiency of photoinduced reactions in which radical ions are reactive intermediates is dependent upon both the efficiency of formation of the radical ion and the efficiency of its subsequent reactions (Scheme I). The measurement of both the cage-escape efficiency and the quantum yield for one-way isomerization and photooxygenation of a series of substituted *cis*- and *trans*-stilbenes allows for the first time the analysis of cage-escape and reaction efficiencies as a function of stilbene configuration and substitution. Cage-escape efficiencies are dependent upon the energy gap for return electron transfer. Thus, for a given acceptor, the highest cage-escape quantum yield is obtained from the weakest donor: that is, the stilbene with the strongest electron-withdrawing substituent. The more efficient cage escape of *trans*- vs *cis*-stilbenes with comparable oxidation potentials is tentatively attributed to more effective charge delocalization in the planar *trans* vs nonplanar *cis* cation radicals.

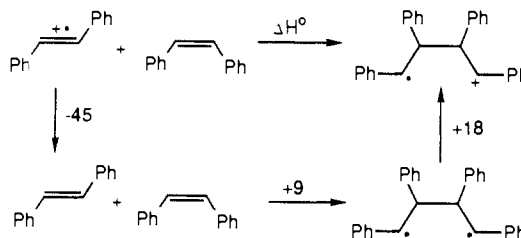
The maximum cage-escape and product-formation quantum yields for a given stilbene donor are obtained from the weakest possible singlet acceptor. Use of stronger acceptors is counterproductive, due to both more rapid return electron transfer in the solvent-separated radical ion pair and the formation of ground-state charge-transfer complexes for which return electron transfer competes with solvation. The use of high donor or acceptor concentrations also favors ground-state complex formation and thus is counterproductive. The use of charged vs neutral singlet acceptors offers no special advantage.

Strategies for optimizing cage-escape efficiencies that have been previously employed include cosensitization (Scheme II)^{4e} and the use of triplet electron-transfer sensitizers. While cosensitization is effective, it requires the use of higher concentrations of the cosensitizer than the secondary donor, thus complicating product purification. Return electron transfer in triplet radical ion pairs is spin forbidden, and thus cage escape would be expected to be more efficient than for singlet radical ion pairs.³² Kuriyama et al.^{34a} report values of $\Phi_{c \rightarrow t}$ 0.11 and 0.003, respectively, for triplet and singlet triphenylpyrylium-sensitized isomerization of *c*-S. We obtained a value of $\Phi_{c \rightarrow t} = 0.09$ using triplet chloranil as the acceptor.^{37b} While these values are significantly higher than obtained from a strong singlet acceptor such as TCA, they are distinctly lower than those obtained from the weaker singlet acceptors, DCA or CA. It is possible that ground-state complex formation reduces the efficiency of cage escape for these very strong triplet acceptors.

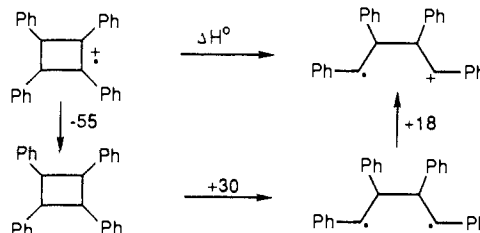
Experimental Section

Materials. *cis*-Stilbene (Aldrich, 97%) was purified (>99.5%) by means of chromatography on silica gel. *trans*-Stilbene (Aldrich) was recrystallized from ethanol and benzene. *trans*-Methoxystilbene (Aldrich) was used as received. The other stilbenes were synthesized from literature procedures.⁴⁴ *cis*-Stilbenes were generated by irradiating a solution of 1 g of the corresponding *trans*-stilbene in 200 mL of nitro-

Scheme VI



Scheme VII



gen-purged benzene with 300-nm light with a Rayonet Model RPR-100 reactor. Irradiation for 4 h generally gave 70–80% conversion to the *cis* isomers. The *cis*-stilbenes were isolated in >98% purity by column chromatography on alumina with 1:10 benzene/hexane as the eluent. 9,10-Dicyanoanthracene (DCA, Kodak) was recrystallized from ethanol and sublimed under vacuum. 9-Cyanoanthracene was recrystallized from ethanol. Acetonitrile (Aldrich spectroscopic grade) was refluxed over calcium hydride and distilled prior to use.

Steady-State Measurements. Fluorescence quenching data were obtained for nitrogen-purged solutions of 1.4×10^{-5} M DCA and stilbenes (usually 0.001–0.005 M) with a Perkin-Elmer MPF-44A fluorescence spectrometer. Quantum yields for stilbene isomerization were determined for nitrogen-purged solutions of 3×10^{-4} M DCA and 0.05 M stilbenes irradiated on a merry-go-round apparatus at 25 °C. Light intensities were analyzed by Aberchrome 540 actinometry.⁴⁵ Monochromatic 365-nm light was provided by the filtered light (Corning 7-54 and 0-52 glass filters) of a 450-W Hanovia medium-pressure mercury lamp enclosed in a water-cooled Pyrex lamp well. Monochromatic 420-nm light was provided by a Rayonet reactor with Type 216 lamps. Alternatively, quantum yields were measured on an optical bench with an Oriel lamp housing and power supply with a high-pressure 300-W mercury-xenon lamp and a Bausch and Lomb 0.25 M monochromator at 404 nm. Light intensities were determined with ferrioxalate actinometry.¹¹ Solutions were analyzed for product formation by use of a 6 ft \times 0.125 in. column containing 4% SF-96 on Chromosorb G or a J&W fused-silica megabore column coated with DB-1 on a Varian 3700 or a Hewlett-Packard 5890A gas chromatograph equipped with flame ionization detector.

Photooxygenation experiments were performed on the optical bench apparatus by use of a stirred, thermostated cell holder. Oxygen concentrations were varied with calibrated Cole-Palmer flow meters to introduce nitrogen and air into a mixing chamber prior to continuous bubbling of the stilbene-containing solution. Light intensities were measured with ferrioxalate actinometry¹¹ and monitored during irradiation with an Atomic Laboratories photon meter. The intensity of 404-nm irradiation was varied by changing the monochromator slit widths. Solutions were analyzed for product formation with a 6 ft \times 0.125 in. column containing 3% Carbowax 20 M on Chromosorb G or a J&W fused silica megabore column coated with DB-1 on a Varian 3700 or a Hewlett-Packard 5890A gas chromatograph equipped with flame ionization detector. Products were identified by comparison of their GC retention times and mass spectral fragmentation patterns with those of authentic samples. Mass spectra were recorded on a Hewlett-Packard 5958A gas chromatograph/mass spectrometer system with an ionizing voltage of 70 eV.

Electrochemistry. Oxidation and reduction potentials were obtained in acetonitrile solution by means of cyclic voltammetry with a BAS Model CV-27 voltammograph with platinum working and auxiliary electrodes, Ag/AgI reference electrode, and a scan rate of 100 mV/s. Ferrocene ($E_{1/2} = 0.875$ V) was used as a standard external reference. Measurements were performed in dry acetonitrile solution containing 3×10^{-3} M stilbene and 0.1 M tetraethylammonium tetrafluoroborate electrolyte. Reduction of DCA and TCA is reversible, and half-wave potentials are

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reported. Oxidation of most of the stilbenes is irreversible, and peak potentials are reported.

Transient Spectroscopy. Acetonitrile solutions of DCA or TCA (10^{-5} M) were excited at 410 nm in the presence of various electron donors with an excimer-pumped (Questek 2000) Lumonics Model EPD-330 dye laser (DPS dye, ca. 15-ns pulses, 2 mJ/pulse). Transient absorption spectra of the stilbene cation radicals are obtained either directly, via electron-transfer quenching by stilbene (0.1 M), or indirectly, via primary quenching by biphenyl (0.15 M) followed by secondary electron transfer from stilbene (5×10^{-4} M) to the biphenyl cation radical. The overlapping absorption of DCA^{•+} can be removed by means of irradiation in the presence of oxygen, which is reduced by DCA^{•+}, forming superoxide, which is transparent in the visible region. Extinction coefficients were determined with the cation radical of tritolyamine ($\lambda_{\text{max}} = 668$ nm, $\epsilon = 26\,200^{15}$), generated under identical secondary electron transfer conditions, as an actinometer. All spectra were recorded 0.5 μ s after the excitation pulse.

Relative quantum yields for the formation of free stilbene cation radicals were determined by means of electron-transfer quenching of singlet DCA or TCA by stilbene (0.05 M) followed by secondary electron transfer from the stilbene cation radical to *trans*-4,4'-dimethoxystilbene. Absolute quantum yields were obtained from the triplet state of benzophenone as an actinometer.

Singlet lifetimes were measured by time-correlated single photon counting in argon-purged acetonitrile solutions. Lifetimes were independent of cyanoanthracene concentration (10^{-5} – 10^{-6} M).

Note Added in Proof. Subsequent to the completion of this paper, the formation of low yields of stilbene dimers has been observed from both the chemical oxidation (N. L. Bauld, University of Texas, Austin, private communication) and the photochemical oxidation of *trans*-stilbene (B. A. Winset, Northwestern University, unpublished results). These observations lend credence to the proposed formation of the stilbene dimer cation radical (eq 3).

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forming us of his electrochemical results. Work performed at Northwestern University is supported by the National Science Foundation (Grant CHE-8618994).

Appendix I

Thermochemical Estimates. The enthalpy of reaction for addition of *t*-S^{•+} and *c*-S to form an acyclic cation radical is estimated from the thermochemical cycle shown in Scheme VI (energies in kilocalories per mole). The oxidation potential of *t*-S is from Table III, and that of the diyl is assumed to be the same as for the 1-phenylethyl radical.⁴⁶ The diyl bond dissociation energy can be estimated either by consideration of the energies of the bonds being broken (C–C: 65 kcal/mol) and formed (C=C: *t*-S = 39, *c*-S = 35 kcal/mol) or by means of Benson group additivity calculations.^{47,48} The resultant value of $\Delta H^\circ = -18$ kcal/mol can be corrected for the loss of translational energy in a typical dimerization reaction ($\Delta S^\circ \sim -35$ eu or +10 kcal/mol)⁴⁹ to provide a value of $\Delta G^\circ = -8$ kcal/mol.

The enthalpy of reaction for ring opening of TPCB^{•+} can be estimated from the thermochemical cycle shown in Scheme VII (energies in kilocalories per mole). The oxidation potential of TPCB was determined in the present investigation while that of the diyl is assumed to be the same as for the 1-phenylethyl radical.⁴⁶ The TPCB bond dissociation energy is assumed to be the same as that of several other 1,2-diarylcyclobutanes.⁵⁰ The resultant value of ΔH° is -7 kcal/mol.

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Synthesis and Photoproperties of Diamagnetic Octabutoxyphthalocyanines with Deep Red Optical Absorbance

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Abstract: The synthesis and photoproperties of six new metal 1,4,8,11,15,18,22,25-octabutoxyphthalocyanines and photoproperties of the known, analogous Zn and metal-free phthalocyanines are described. The new compounds are AlPc(OBu)₈OSiEt₃, GaPc(OBu)₈OSiEt₃, GePc(OBu)₈(OSiEt₃)₂, SnPc(OBu)₈(OSiEt₃)₂, RuPc(OBu)₈(py)₂, and PdPc(OBu)₈ (where Pc(OBu)₈ represents the octabutoxyphthalocyanine ligand). Benzene-*d*₆ solutions of all eight of the compounds give NMR spectra showing large ring-current effects. Benzene solutions of the compounds give visible spectra with absorption maxima in the 688–779-nm range having extinction coefficients between 1.0×10^5 and 2.2×10^5 M⁻¹ cm⁻¹. The triplet-state properties of the phthalocyanines in benzene solutions have been measured by laser flash photolysis. The triplet states have absorption maxima in the 550–640-nm range, quantum yields in the 0.1–0.9 range, and lifetimes when the solutions are deaerated in the 0.5–150- μ s range. The rate constants for energy transfer from the triplet states of the compounds to O₂ are between 1.3×10^8 and 2.8×10^9 M⁻¹ s⁻¹. Analysis of kinetic data pertaining to the photogeneration of O₂ (¹Δ_g) by the main-group compounds shows that the energy gap between their singlet (S₁) and triplet (T₁) states is 14.9 ± 0.3 kcal/mol. Relationships between the photoproperties of the metal complexes and the position in the periodic chart of the metals they contain are apparent.

Introduction

The 1,4,8,11,15,18,22,25-octaalkoxyphthalocyanines (Figure 1) generally are stable compounds that have intense absorptions

in the red to deep red region.¹ This suggests that some of them have potential for use in optical data storage² and in photodynamic therapy, PDT.³

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