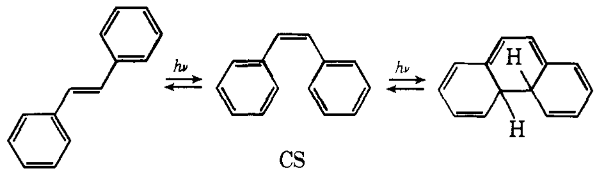
1,2-Diarylethylene-Diene Exciplexes. Solvent-Induced Changes in Chemical and Physical Processes[1]

Frederick D. Lewis*[2a] and Charles E. Hoyle[2b]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received November 1, 1976*

Abstract: The fluorescence of several 1,2-diarylethylenes can be quenched by conjugated dienes. Quenching of *trans*-stilbene and diphenylvinylene carbonate results in the formation of cycloadducts and the appearance of weak red-shifted fluorescence. Both cycloaddition and fluorescence are shown to occur from a singlet exciplex intermediate. The temperature dependence of 1,2-diarylethylene fluorescence quenching rate constants indicates that the exciplex intermediates are formed reversibly, more stable exciplexes being formed less reversibly. The effect of solvent on diphenylvinylene carbonate-2,5-dimethyl-2,4-hexadiene exciplex lifetime, radiative decay, and cycloaddition has been investigated. In moderately polar solvents cycloaddition reactivity decreases rapidly with increasing solvent polarity leading to an increase in exciplex lifetime and fluorescence quantum yield. This decrease in cycloaddition reactivity is attributed to greater solvent stabilization of the polar exciplex intermediate than the transition state leading to nonpolar cycloadducts. In highly polar solvents, both exciplex cycloaddition and fluorescence rate constants decrease. A solvated ion pair may be of lower energy than the exciplex in highly polar solvents. The chemical consequences of exciplex-solvent interactions are discussed.

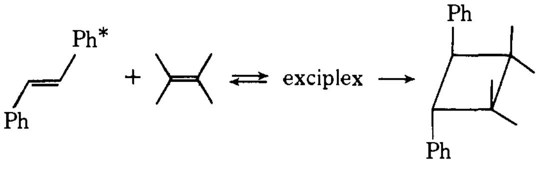
The stilbenes have played an important role in the development of organic photochemistry. Two reversible unimolecular reactions, cis,trans isomerization[3,4] and *cis*-stilbene $\rightleftarrows$ dihydrophenanthrene interconversion (eq 1),[5,6] have been the



(1)

TS CS

subject of extensive investigation and some controversy. Recently, attention has been drawn to the bimolecular photochemical addition reactions of *trans*-stilbene and other 1,2-diarylethylenes.[7-12] Chapman's[7a,b] observation of a negative temperature dependence of the rate constant for cycloaddition of singlet *trans*-stilbene and 2,3-dimethyl-2-butene provided the first evidence for a reversibly formed exciplex intermediate in this class of reactions (eq 2).



(2)

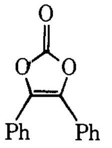
We have been interested in the photocycloaddition reactions of 1,2-diarylethylenes, principally *trans*-stilbene (TS)[8] and diphenylvinylene carbonate (DPVC),[9] with conjugated dienes for several years. Investigations of these reactions have provided a wealth of stereochemical information about both the singlet and triplet cycloaddition process. This information along with photochemical kinetics[13] suggested the presence of exciplex intermediates in these reactions. Conclusive evidence for exciplex intermediates based on observations of exciplex fluorescence is presented in the present report. We also wish to report the first systematic investigation of solvent-induced changes in both the chemical and physical behavior of an exciplex.[14]

1,2-Diarylethylene Spectroscopic Properties. Absorption data for the stilbenes and several diarylethylenes are given in Table I. The three cyclic diarylethylenes, DPVC, di(*p*-methoxyphenyl)vinylene carbonate (DMVC), and diphenylcyclobutene (DPCB), all have more intense and longer wavelength absorption maxima than *cis*-stilbene, indicative of more nearly planar structures.[15a] The only unusual feature of the absorption spectra is the bathochromic effect of benzene on the TS and DPVC absorption. The red shift of TS absorption in benzene is the result of ground state complex formation.[15b,c] The absorption maxima of TS and DPVC in all solvents employed in the present investigation other than benzene are at 295 ± 1 and 292 ± 2 nm, respectively. Absorption spectra in solvents other than benzene are unaffected by the addition of high concentrations (2 M) of conjugated dienes.

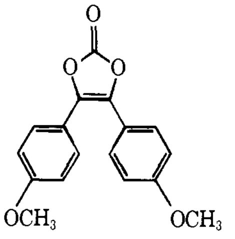
Table I. Absorption Spectra of 1,2-Diarylethylenes

	Solvent	λ_{max}, nm	$\epsilon \times 10^4$
trans-Stilbene[a]	Heptane	294	2.80
	Benzene	299	2.53
	Ethanol	295	2.79
Diphenylvinylene carbonate	Hexane	294	1.45
	Benzene	299	1.35
	Ethanol	291	1.33
Di(*p*-methoxyphenyl)vinylene carbonate	Hexane	295	1.8
Diphenylcyclobutene	Hexane	297	1.8
cis-Stilbene[a]	Ethanol	277	1.04

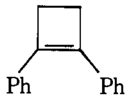
[a] Data from ref 15.



DPVC



DMVC



DPCB

Fluorescence data for several 1,2-diarylethylenes are given in Table II. The fluorescence maxima of TS and DPVC show an even larger special bathochromic effect of benzene than the absorption spectra. Emission maxima for TS and DPVC in the other solvents used are at 350 ± 2 and 368 ± 2 nm, respectively. The fluorescence quantum yield (Φ_f) of DPVC is larger in benzene than in several other solvents (0.10 ± 0.05 in ether, ethyl acetate, several alcohols, and acetonitrile). In hexane-benzene mixtures, intermediate values of Φ_f and λ_{max} are obtained. Values for the singlet lifetime (τ) and fluorescence

Table II. 1,2-Diarylethylene Singlet State Photophysical Properties

	Solvent	λ_{max}, nm	Φ_f	τ, ns	$10^8 k_f$, s^{-1}
trans-Stilbene	Alkane	350 ± 2	0.044[a]	0.07[a]	4.6[a]
	Benzene	357			
Diphenylvinylene carbonate	Hexane	368	0.10 ± 0.05[b]	0.3[c]	3.3[d]
	Benzene	373	0.26 ± 0.05[b]	0.8[c]	3.1[d]
Di(*p*-methoxyphenyl)-vinylene carbonate	Hexane	370	0.16[b]	0.7[c]	3.2[d]
Diphenylcyclobutene	Hexane	385	1.0[e]	4.0[f]	2.5

[a] Data from ref 16. [b] Substrate concentration 1×10^{-5} M, λ_{ex} 320 nm. [c] Estimated from $\tau = \Phi_f k_f^{-1}$. [d] Estimated from Birks-Dyson relation.[17b] [e] Value from C. D. DeBoer and R. H. Schlessinger, *J. Am. Chem. Soc.*, **90**, 803 (1968). [f] Measured by single photon counting.

Table III. Singlet State Electron Affinities

	$E_{A^-/A}$, V[a]	E_s, eV[b]	EA*, eV
trans-Stilbene	2.26	3.53	1.27
Diphenylvinylene carbonate	2.06	3.48	1.42
Diphenylcyclobutene	2.35	3.50	1.15

[a] Half-wave reduction potential in acetonitrile. [b] Onset of fluorescence.

quantum yield and rate constant (k_f) were provided by Charlton and Saltiel.[16] These values are considered the most reliable for the planar (^{1}B) singlet state of *trans*-stilbene. The longer lived fluorescence observed by Birch and Birks[4b] (τ = 1.5 ns at 25 °C) apparently is delayed fluorescence resulting from thermal repopulation of the ^{1}B state from the twisted ^{1}A state. The delayed fluorescence is a minor component (≈23%) of the total emission at 25 °C.[16] The singlet lifetimes of DPVC and DMVC in Table II are obtained from measured values of Φ_f and values of k_f estimated from the Birks-Dyson relation.[17] The smaller value of τ for DPVC in hexane vs. benzene is confirmed by direct measurement using the single photon counting technique. The measured lifetime in benzene solution is 0.5 ± 0.3 ns, near the lower limit attainable with our apparatus using deconvolution by the method of moments. The singlet lifetime of DPVC in hexane and other solvents is too short to allow direct measurement (<0.5 ns). Values of k_f for DPVC, DMVC, and DPCB are similar to the value for the planar (^{1}B) state of TS, in accord with the inability of the former molecules to undergo rapid twisting about the central double bond.

The electron affinity (EA) of an organic molecule is greater in the excited singlet state than in the ground state by an amount equal to the singlet energy (E_s, eq 3).[18]

$$EA^* = EA^0 + E_s = -E_{A^-/A} + E_s \qquad (3)$$

Ground state electron affinities (Table III) are provided by the half-wave reduction potentials measured by ac polarography in acetonitrile solution at 23 ± 1 °C.[19] Singlet energies are estimated from the onset of fluorescence in hexane and acetonitrile solution. Since the singlet energies of TS, DPVC, and DPCB are similar, the differences in excited state electron affinities result primarily from differences in reduction potential.

Fluorescence Quenching by Dienes. Structure-Reactivity Relationships. Previous investigations have demonstrated that the fluorescence of diarylethylenes is quenched by conjugated dienes and that quenching leads to efficient stereospecific $[{}_\pi 2_s + {}_\pi 2_s]$ cycloaddition.[8,9] The usual Stern-Volmer analysis of the variation in fluorescence intensity (I_f) with diene concentration provides the values of $k_q\tau$ (eq 4) given in Table IV.

$$I_f^0/I_f = 1 + k_q\tau[Q] \qquad (4)$$

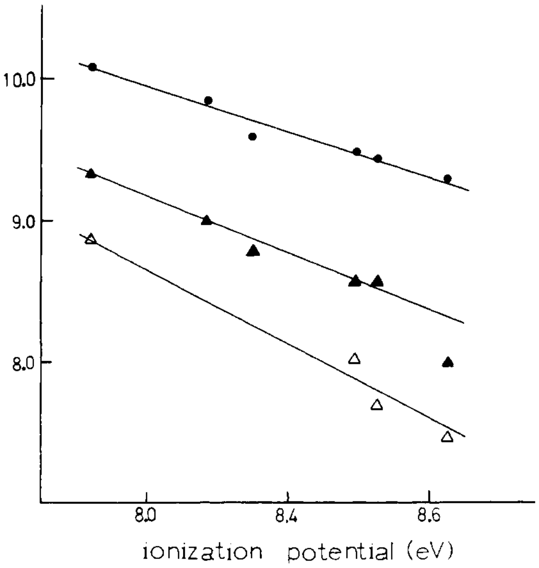


Figure 1. Correlation of fluorescence quenching rate constants with diene vertical ionization potential: (●) diphenylvinylene carbonate, (▲) diphenylcyclobutene, (△) di(*p*-methoxyphenyl)vinylene carbonate.

Values of k_q can be obtained from the lifetime data in Table II for DPVC, DMVC, and DPCB. The possibility of quenching both prompt and delayed fluorescence complicates the calculation of k_q for TS.[4b,16] Exclusive quenching of the prompt fluorescence (τ = 0.07 ns)[16] gives unreasonably high k_q values (6.4×10^{10} M^{-1} s^{-1} for 2,5-dimethyl-2,4-hexadiene). Thus quenching of either the delayed component or some combination of the prompt and delayed components of TS fluorescence must occur. In the absence of additional information on TS fluorescence quenching mechanisms, literature k_q values[7-10] must be regarded with reservation.

Plots of log k_q vs. diene vertical ionization potential (Figure 1) are approximately linear. For a given diene, values of k_q increase with increased excited state electron affinity (Table III). Such correlations of fluorescence quenching rate constants with ground state electron-donating and excited state electron-accepting abilities are commonly taken as prima facie evidence for a quenching mechanism which involves formation of a singlet exciplex stabilized by partial charge transfer from a ground state donor to an excited state acceptor (eq 5).[20-25]

$$A^* + D \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} \underbrace{(A^*D \longleftrightarrow A^- \cdot D^+ \cdot)}_{\text{exciplex}} \xrightarrow{k_d} \text{decay processes} \qquad (5)$$

The slopes of the log k_q vs. diene ionization potential plots in Figure 1 are substantially less than the slope expected for a process involving essentially complete electron transfer (1

Table IV. Stern-Volmer Constants for Fluorescence Quenching in Hexane Solution[a]

Sensitizer Diene (IP)[f]		TS[b]	DPVC[c]	DMVC[d]	DPCB[e]
2,5-Dimethyl-2,4-hexadiene	(7.84)	4.5	5.0	0.33	9.2
trans,trans-2,4-Hexadiene	(8.17)	3.0	2.9		4.0
1,3-Cyclohexadiene	(8.30)	1.5	1.5		3.2
trans-1,3-Pentadiene	(8.59)	1.2	1.2	0.048	1.4
cis-1,3-Pentadiene	(8.65)	1.2	0.9	0.024	1.5
2-Methyl-1,3-butadiene	(8.85)	0.8	0.8	0.01	0.42

[a] Least-squares slopes obtained from five or more quencher concentrations. Diene concentrations adjusted to give maximum I_f^0/I_f values of 1.5–2.5. [b] 1.5×10^{-4} M TS, λ_{ex} = 320 nm. [c] 1.1×10^{-4} M DPVC, λ_{ex} = 320 nm. [d] 1.2×10^{-4} M DMVC, λ_{ex} = 340 nm. [e] 2.1×10^{-4} M DPCB, λ_{ex} = 322 nm. [f] Vertical ionization potentials from ref 20.

Table V. Solvent Effects on Quenching of Diphenylvinylene Carbonate Fluorescence by Dienes[a]

	Diene			
	2,5-Dimethyl-2,4-hexadiene[c]		*cis*-1,3-Pentadiene[d]	
Solvent (τ, ns)[b]	$k_q\tau$, M^{-1}	$10^9 k_q$, M^{-1} s^{-1}	$k_q\tau$, M^{-1}	$10^9 k_q$, M^{-1} s^{-1}
Hexane (0.3)	5.0	16.7	0.91	3.0
Benzene (0.8)	4.1	5.1	0.80	1.0
tert-Butyl alcohol (0.3)			0.21	0.70
n-Propyl alcohol (0.3)	1.2	4.0	0.27	0.90
Methanol (0.3)	2.6	8.7	0.23	0.77
Acetonitrile (0.3)	2.7	9.0	0.28	0.93

[a] 1.1×10^{-4} M DPVC, λ_{ex} = 320 nm, 23 °C. [b] Lifetime data from Table II. [c] Diene concentrations 0.05–0.3 M. [d] Diene concentrations 0.1–1.2 M.

Table VI. Temperature Dependence of Fluorescence Quenching Kinetics

Temp, °C	DPVC[a]	DPVC Dimethylhexadiene		DPVC *cis*-1,3-Pentadiene		TS *cis*-1,3-Pentadiene
	τ, ns	$k_q\tau$, M^{-1}	$10^9 k_q$, M^{-1} s^{-1}	$k_q\tau$, M^{-1}	$10^9 k_q$, M^{-1} s^{-1}	$k_q\tau$, M^{-1}
6.0 ± 1	1.2	5.1	4.3	1.2	1.0	0.47
16	0.98	4.4	4.5	1.0	1.0	0.44
23	0.80	4.1	5.1	0.80	1.0	0.42
37	0.60	3.4	5.7			0.39
41	0.54			0.46	0.85	
50	0.44	2.8	6.4	0.36	0.82	0.37
63	0.30			0.30	1.0	0.37
66	0.26	1.8	6.9			0.37

[a] Lifetimes estimated from Φ_f values assuming k_f is independent of temperature.

eV^{-1} vs. 17 eV^{-1}).[26] The free-energy change for full electron transfer calculated according to eq 6[26]

$$\Delta G_{ET} = -E_{A^-/A} + E_s + E_{D/D^+} + \text{constant} \qquad (6)$$

is slightly endothermic ($\Delta G \approx +0.1$ eV) even in the most favorable case, DPVC-2,5-dimethyl-2,4-hexadiene.[27] Small slopes, such as those in Figure 1, have been interpreted as reflecting a minor charge-transfer contribution to exciplex stabilization (eq 5).[23-25] This interpretation rests on the assumption that exciplex formation is the rate-determining step for fluorescence quenching ($k_q = k_e$, eq 5).

The effect of solvent upon fluorescence quenching of DPVC by two dienes is given in Table V. Similar small variations in $k_q\tau$ values with solvent are observed for other diarylethylenes. The absence of rate enhancement by polar solvents has also been attributed to a small degree of charge transfer in the quenching process.[23-25] This interpretation again rests on the assumption that $k_q = k_e$.

Temperature Dependence of Fluorescence Quenching. Stern-Volmer constants for quenching of DPVC and TS fluorescence by 2,5-dimethyl-2,4-hexadiene and *cis*-1,3-pentadiene were determined at several temperatures between 6 and 66 °C. Representative data are given in Table VI. The temperature dependence of the DPVC singlet lifetime was determined from the fluorescence quantum yields, assuming that singlet lifetimes are proportional to quantum yields over the limited temperature range of interest.[28,29] Arrhenius activation energies for quenching of DPVC by 2,5-dimethyl-2,4-hexadiene and *cis*-1,3-pentadiene in benzene solution are 1.3 and 0.0 kcal/mol, respectively. Both of these values are less than the temperature coefficient for viscous flow in benzene (2.7 kcal/mol[30]), thus requiring that the quenching process proceed via a reversibly formed intermediate.[13] The simplified mechanism given in eq 5 yields the following expression for the fluorescence quenching rate constant:

$$k_q = k_e[k_d/(k_d + k_{-e})] \qquad (7)$$

Thus the values of k_q in Tables IV and V are lower limits for the rate constant of exciplex formation. Comparison of the Arrhenius temperature coefficients for DPVC quenching by 2,5-dimethyl-2,4-hexadiene and *cis*-1,3-pentadiene shows that the quenching process is more reversible with the diene of higher ionization potential. Thus the increase of k_q with decreased diene ionization potential (Figure 1) is due to a de-

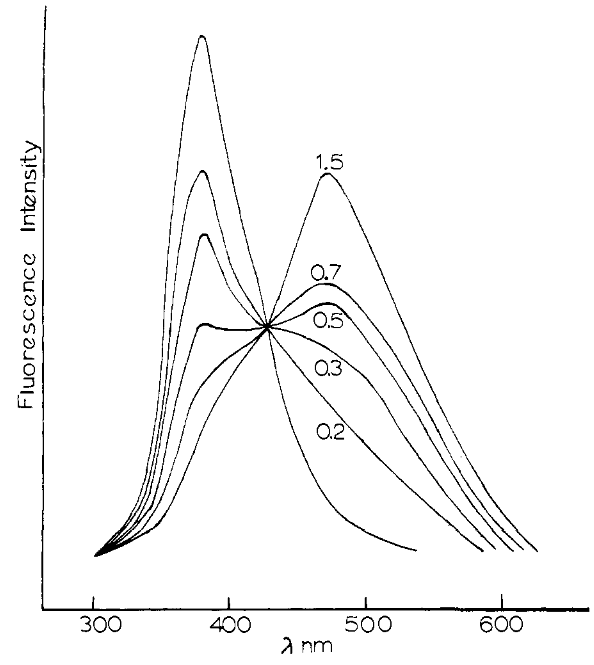


Figure 2. Diphenylvinylene carbonate fluorescence in degassed *n*-propyl alcohol quenched by 2,5-dimethyl-2,4-hexadiene (concentrations indicated).

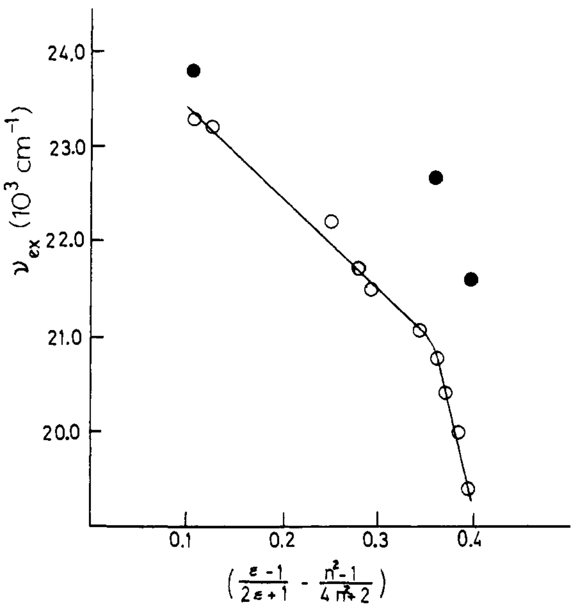


Figure 3. Frequency of exciplex fluorescence maxima vs. solvent polarizability (eq 8) for diphenylvinylene carbonate (○) and *trans*-stilbene (●) with 2,5-dimethyl-2,4-hexadiene.

crease in k_{-e} rather than an increase in k_c. A similar conclusion based on more extensive data has been reached by Ware and co-workers[31] for several α-cyanonaphthalene–alkene exciplexes. Evaluation of the TS fluorescence quenching data is again complicated by the possibility of quenching both prompt and delayed fluorescence[16,17a] and by the effect of temperature on the interconversion of planar and twisted TS singlet states.

The reversible nature of exciplex formation must be considered when interpreting fluorescence quenching data. The slopes of Figure 1 and similar correlations[23-25] are not directly related to the rate of exciplex formation (k_c) and hence cannot provide information about the extent of charge transfer in the exciplex. Similarly, the absence of polar solvent rate enhancement (Table V) cannot be readily interpreted since all of the rate constants in eq 7 may be subject to solvent effects. The recent results of Ware,[31] Caldwell et al.,[32a] and Saltiel et al.[32b] along with our results for quenching of aromatic hydrocarbons by dienes[13a] and dialkyl ketones by vinyl ethers and amines[13b] indicate that reversible exciplex formation is a pervasive phenomenon.

Exciplex Fluorescence. Polarity of the Exciplex. Quenching of 1,2-diarylethylene fluorescence by conjugated dienes is accompanied in several instances by the appearance of a new structureless emission at longer wavelength than the diarylethylene fluorescence. The emission from the DPVC–2,5-dimethyl-2,4-hexadiene (DMHD) system in *n*-propyl alcohol solution is shown in Figure 2. The isoemissive point at 420 nm and the linearity of plots of either 368 nm or 480 nm emission vs. diene concentration indicate that a 1:1 DPVC–DMHD exciplex is the emitting species.[33] The intensity and wavelength of exciplex emission are dependent upon the choice of diarylethylene, diene, and solvent. The strongest donor–acceptor pairs (Table IV) display the most intense and red-shifted exciplex emission. For example, the emission from DPVC–DMHD is more intense and red-shifted than that from DPVC-*cis*-1,3-pentadiene (λ_{max} 23.2 vs. 24.4 × 10^3 cm^{-1} in benzene) or than from TS–DMHD (λ_{max} 23.3 vs. 23.8 × 10^3 cm^{-1} in hexane). No exciplex emission was detected for weaker donor–acceptor pairs.

The emission maxima for diarylethylene–diene exciplexes shifts to lower energy with increasing solvent polarity (Tables VII–IX). Ground state solute–solvent interactions are negligible except in the special case of benzene (Table I). Thus the frequency shifts observed for exciplex fluorescence result primarily from stabilization of the polar exciplex by polar solvents. The exciplex emission maximum ($\tilde{\nu}_x$) is related to the solvent dielectric constant (ϵ) and index of refraction (n) by

$$\tilde{\nu}_s = \tilde{\nu}_0 - \frac{2\mu^2}{\hbar c a^3}\left[\frac{\epsilon-1}{2\epsilon+1} + \frac{n^2-1}{4n^2+2}\right] \qquad (8)$$

where $\tilde{\nu}_0$ is the gas phase emission frequency (ϵ = 0), μ is the dipole moment of the exciplex, a is the solvent cavity radius, $\hbar$ is Planck's constant, and c is the velocity of light.[34] Figure 3 shows plots of the data for DPVC–DMHD (Table VII) and TS–DMHD (Table VIII). Rather than the usual linear plots,[33] distinct curvature is observed with the slope increasing in the most polar solvents. Previous observations of curvature in such plots have been attributed to a change in the structure of the excited state complex in more polar solvents.[14,35,36] In mixed diethyl ether–acetonitrile solutions, the frequency of the exciplex emission maximum is not a linear function of mole fraction of acetonitrile (Table IX and Figure 4). The initial curvature in Figure 4 indicates that the exciplex is preferentially solvated by acetonitrile.[37]

A further indication that a change in DPVC–DMHD exciplex solvation or structure occurs in highly polar solvents is provided by the temperature dependence of the monomer vs. exciplex fluorescence intensity (Table X). In *n*-propyl alcohol and other nonpolar and moderately polar solvents the intensity of exciplex emission (I_{ex}) decreases with increasing temperature, but the residual DPVC emission (I_m) remains constant. The decrease in I_{ex}/I_m with increasing temperature is indicative of reversible exciplex formation,[33] in accord with the Arrhenius parameters for DPVC–DMHD exciplex formation in benzene and *n*-propyl alcohol solution (Table VI). In acetonitrile solution both exciplex and residual DPVC emission intensity decrease with increasing temperature. Thus exciplex formation is less reversible in the more polar solvent.[33]

Exciplex dipole moments can be estimated from the dependence of the exciplex emission maxima upon solvent polarizability (eq 8). Assuming a value of 4.5 Å for the solvent cavity radius, a, a dipole moment of 9.1 ± 0.2 D for the DPVC–DMHD exciplex is obtained from the initial slope of

Table VII. Diphenylvinylene Carbonate-2,5-Dimethyl-2,4-hexadiene Exciplex Fluorescence and Cycloadduct Formation

Solvent	ϵ[a]	ν_{max}, cm^{-1} [b]	τ_{ex}, ns[c]	$\Phi_{f_{ex}}$[d]	$10^7 k_{f_{ex}}$, s^{-1} [f]	Φ_a[g]	$10^8 k_a$, s^{-1} [h]
Hexane	2.0	23 300	<0.5	0.006 (0.006)[e]	>1.5	0.50	>17
Benzene	2.3	23 200	<0.5	0.008	>1.9	0.59 (0.93)[e]	>19 (19)[e]
Diethyl ether	3.9	22 200	≈0.5	0.015	3.7	0.50	17
Ethyl acetate	5.3	21 700	3.5	0.046	1.6	0.39	1.9
Dimethoxyethane	5.9	21 500	5.7	0.071	1.5	0.22	0.66
tert-Butyl alcohol	10.5	21 100	4.6	0.059	2.2	0.28	1.5
n-Propyl alcohol	16.7	20 800	4.7	0.070 (0.12)[e]	2.4 (2.6)[e]	0.17 (0.88)[e]	1.0 (1.9)[e]
Ethanol	19.6	20 400	5.0	0.044	1.1	0.12	0.41
Methanol	26.7	20 000	2.6	0.019	0.92	0.014	0.10
Acetonitrile	31.5	19 400	1.5	0.004 (0.006)[e]	0.25 (0.4)[e]	<0.001	<0.01

[a] Dielectric constant of 1.45 M diene solutions calculated assuming $\epsilon = \Sigma_i \epsilon_i V_i$, where V_i is the volume fraction of component i. [b] Maximum of exciplex fluorescence spectrum corrected for spectrometer response, accuracy ±500 cm^{-1}. [c] Exciplex fluorescence lifetime in 1.45 M diene solutions, accuracy ±0.5 ns. [d] Corrected quantum yield for exciplex fluorescence in 1.45 M diene solutions, relative accuracy ±20%, absolute accuracy ±50%. [e] Value extrapolated to infinite diene concentration. [f] Calculated using eq 9. [g] Quantum yield for cycloadduct formation in 0.46 M diene solution, accuracy ±10%. [h] Calculated using an equation analogous to eq 9.

Table VIII. *trans*-Stilbene-2,5-Dimethyl-2,4-hexadiene Exciplex Fluorescence and Cycloadduct Formation

Solvent	ν_{max}, cm^{-1} [a]	$\Phi_{f_{ex}}$ (rel)[b]	Φ_a[c]
Hexane	23 800	1.0	
Benzene			0.36 (0.83)[d]
Ethyl acetate			0.39
n-Propyl alcohol	22 700	3.0	0.42
Methanol			0.40
Acetonitrile	21 600	3.8	0.49

[a] See Table VII, footnote *b*. [b] Corrected exciplex fluorescence intensity relative to value in hexane. [c] Quantum yield for cycloadduct formation in 1.0 M diene solution, accuracy ±10%. [d] Value extrapolated to infinite diene concentration from ref 8c.

Table IX. Diphenylvinylene Carbonate-2,5-Dimethyl-2,4-hexadiene Exciplex Fluorescence in Diethyl Ether-Acetonitrile Mixed Solvents

Mole fraction CH_3CN	ϵ[a]	ν_{max}, cm^{-1} [b]	Φ_{rel}[c]
0	3.9	22 700	1.0
0.047	4.8	22 200	1.6
0.13	6.4	21 700	2.7
0.26	9.3	21 300	4.4
0.39	12.5	20 800	4.6
0.51	16.0	20 400	3.8
0.62	19.7	20 200	2.2
0.72	23.8	19 800	1.5
1.0	31.5	19 400	0.4

[a] See Table VII, footnote *a*. [b] See Table VII, footnote *b*. [c] Corrected fluorescence intensity relative to the value in diethyl ether.

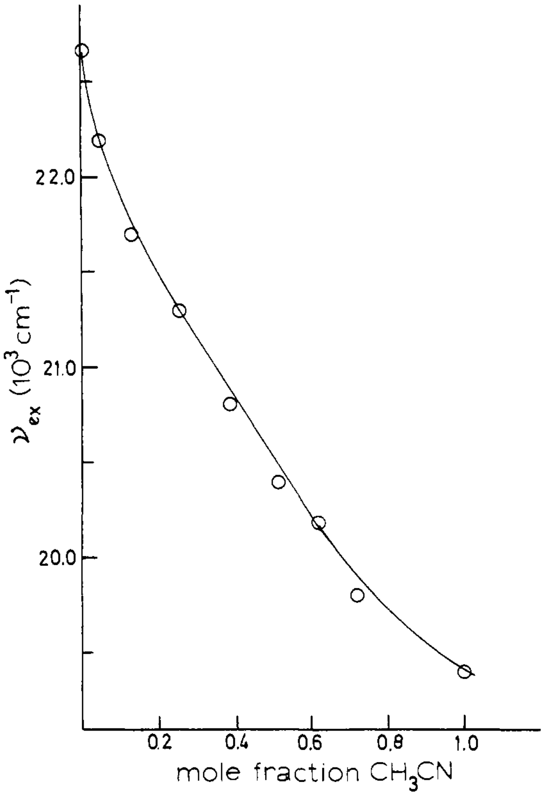


Figure 4. Frequency of diphenylvinylene carbonate-2,5-dimethyl-2,4-hexadiene exciplex fluorescence in diethyl ether-acetonitrile mixed solvent.

Figure 3. The limited data for the TS-DMHD exciplex are indicative of a lower dipole moment. The dipole moment of the DPVC-DMHD exciplex is similar to that reported by Taylor[22] for the α-cyanonaphthalene-DMHD exciplex, but is lower than the dipole moments of a number of aromatic hydrocarbon-amine exciplexes ($\mu \approx$ 11-13 D).[38,39] Thus the DPVC-DMHD exciplex can be viewed as a moderately polar exciplex.

Exciplex Fluorescence Yields and Lifetimes. Quantum yields for exciplex fluorescence normally decrease with increasing solvent polarity.[35,40,41] Mataga[41] has demonstrated that the decrease in fluorescence intensity for the pyrene-*N*,*N*-dimethylaniline exciplex is accompanied by an increase in radical ion formation. Either rapid exciplex dissociation to radical ions or direct electron transfer from ground state donor to excited state acceptor may be responsible for the normal decrease in exciplex fluorescence intensity.

The quantum yield for DPVC-DMHD exciplex fluorescence displays unusual solvent dependence, first increasing, then decreasing with increasing solvent polarity.[42,43] The same effect is observed both in pure solvents (Table VII) and in ether-acetonitrile mixed solvents (Table IX). Thus it appears unlikely that solvent-induced changes in exciplex fluorescence intensity result from specific exciplex-solvent interactions.[44a] Limited data for the TS-DMHD exciplex (Table VIII) indicate that the exciplex fluorescence intensity increases continuously with increasing solvent polarity.

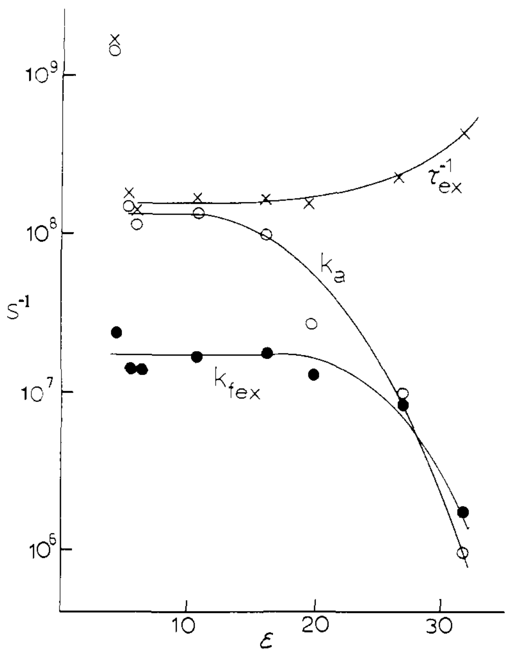


Figure 5. Solvent dependence of the diphenylvinylene carbonate 2,5-dimethyl-2,4-hexadiene exciplex decay (τ_{ex}^{-1}), fluorescence ($k_{f_{ex}}$), and cycloaddition (k_a) rate constants.

The lifetime of the DPVC-DMHD exciplex in hexane or benzene solution is too short to allow measurement by single photon counting. In more polar solvents, exciplex fluorescence decay was observed. At high diene concentrations (1.45 M) the exciplex fluorescence displayed single exponential decay in the time interval 20-50 ns following excitation. The decay constants obtained provide approximate values for the exciplex lifetimes (Table VII).[44b] The exciplex lifetimes show the same unusual[40,41] solvent dependence as the exciplex fluorescence quantum yields, first increasing, then decreasing with increasing solvent polarity.

Rate constants for DPVC-DMHD exciplex fluorescence can be calculated from the quantum yield and lifetime data in Table VII using

$$k_f = \frac{\Phi_{f_{ex}}}{\tau_{ex}}\left(1 + \frac{1}{K_{sv}[D_f]}\right) \qquad (9)$$

where K_{sv} is the Stern-Volmer constant, $k_q\tau$ from Table V, and $[D_f]$ is the concentration of diene used for exciplex fluorescence quantum yield measurements (1.45 M). Values of k_f obtained using eq 9 are in fair agreement with those using limiting fluorescence quantum yields measured in *n*-propyl alcohol and acetonitrile (Table VII). Values of $k_{f_{ex}}$ are independent of solvent in moderately polar solvents, but decrease in more polar solvents. This decrease could reflect either a change in the structure of the exciplex, as suggested by the change of slope in Figure 3,[14,35,36] or simply a decrease in the quantum yield for exciplex formation resulting from competing electron transfer.[40] Values of $k_{f_{ex}}$ observed in moderately polar solvents ($\approx 1 \times 10^7$ s^{-1}) are somewhat larger than previously reported values for exciplex radiative decay.[32,33] The high $k_{f_{ex}}$ for the DPVC-DMHD exciplex could be related to the unusually high k_f value for the DPVC monomer (Table II).

Exciplex Cycloaddition. We have previously reported that the photochemical [2 + 2] cycloaddition of singlet TS and DPVC with conjugated dienes in nonpolar solvents is an efficient process.[8,9] Cycloaddition quantum yields (Φ_a) for cycloaddition of TS and DPVC with DMHD extrapolated to infinite diene concentration in benzene solution are 0.83 ± 0.1 and 0.93 ± 0.1, respectively. The effect of solvent on cycloaddition of DPVC with 0.46 M DMHD and TS with 1.0 M DMHD is given in Tables VII and VIII. Values of Φ_a in Tables VII and VIII are lower than the extrapolated values owing to incomplete quenching by the concentrations of dienes used. When corrections are made for incomplete quenching, cycloaddition is found to be the predominant pathway for nonradiative decay of TS in all solvents and for DPVC in all solvents less polar than ethanol.

Table X. Temperature Dependence of Monomer and Exciplex Fluorescence Intensity[a]

n-Propyl alcohol			Acetonitrile		
Temp, °C	I_{cx}	I_m	Temp, °C	I_{cx}	I_m
7	1.0	0.28	7	1.0	1.9
28	0.85	0.27	27	0.65	1.4
45	0.69	0.26	47	0.53	1.3
81	0.56	0.25	75	0.42	0.9

[a] Corrected fluorescence intensity relative to I_{ex} at 7 °C.

Cycloaddition was demonstrated to occur via a singlet exciplex using the exciplex quenching technique of Creed and Caldwell.[45] Fumaronitrile was found to quench the DPVC-DMHD exciplex more efficiently than the DPVC singlet in *n*-propyl alcohol solution. The longer lifetime for the exciplex (4.7 ns) vs. DPVC (<1 ns) is responsible for most of the difference in quenching constants. Addition of 1.2×10^{-3} M fumaronitrile to a propanol solution of DPVC containing 0.45 M DMHD results in a 25% reduction in both the cycloaddition and exciplex and residual monomer fluorescence quantum yields. In the absence of diene, DPVC fluorescence is not measurably quenched by 1.2×10^{-3} M fumaronitrile.

Rate constants for DPVC-DMHD exciplex cycloaddition (k_a) can be calculated from the observed exciplex lifetimes and cycloaddition quantum yields using an equation equivalent to eq 9. The values of k_a given in Table VII display a complex and unprecedented solvent dependence. Decreases in k_a are observed in solvents of low polarity ($\epsilon < 6$) and high polarity ($\epsilon > 20$). The second decrease occurs in the same region as the previously discussed decrease in the fluorescence rate constant; however, the decrease in k_a is larger than that in k_f.

Solvent-Induced Changes. Interpretation. The variations in DPVC-DMHD exciplex lifetime and rate constants for fluorescence and cycloaddition with solvent dielectric constant are summarized in Figure 5. The significant features of these results are (a) a large decrease in both k_a and τ_{ex}^{-1} in solvents of low polarity, (b) relatively constant values of k_a, k_f, and τ_{ex}^{-1} in solvents of intermediate polarity, and (c) a large decrease in k_a, a moderate decrease in k_f, and an increase in τ_{ex}^{-1} in highly polar solvents. Solvent-induced changes in exciplex behavior (Scheme I) can be interpreted using the model of exciplex structure and photophysical processes which has evolved principally from the work of Weller[18,26,40] and Mataga[34-36,41] along with Michl's[46] theory of exciplex cycloaddition.

Encounter of an excited acceptor A* and ground state donor D in nonpolar solvents leads exclusively to the formation of a moderately polar exciplex, which is considered to be a resonance hybrid of locally excited and charge transfer configurations ($A^*D \leftrightarrow A^-{\cdot}D^+{\cdot}$). With increasing solvent polarity, the energy of the solvated ion pair state ($A^-{\cdots}D^+{\cdot}$) will at some point drop below that of the exciplex. At this point the solvated ion pair formation may occur either directly or via the exciplex. In highly polar solvents the solvated ion pair may exist in equilibrium with free radical ions ($A^-{\cdot} + D^+{\cdot}$).

The relative energies of the isolated molecules (A* + D), exciplex, solvated ion pair, and free radical ions for DPVC-DMHD are shown schematically in Figure 6. Crossing points

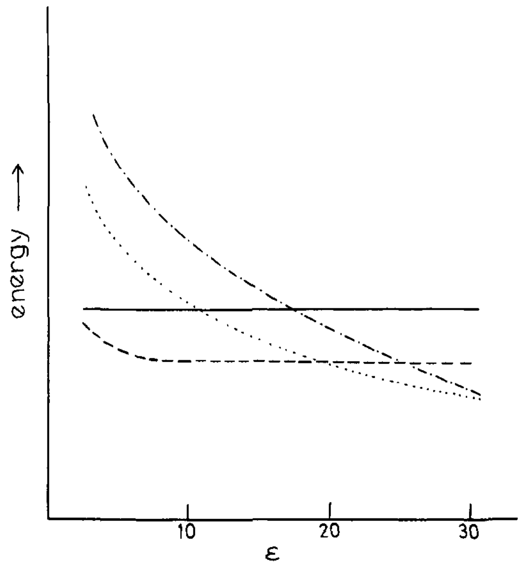
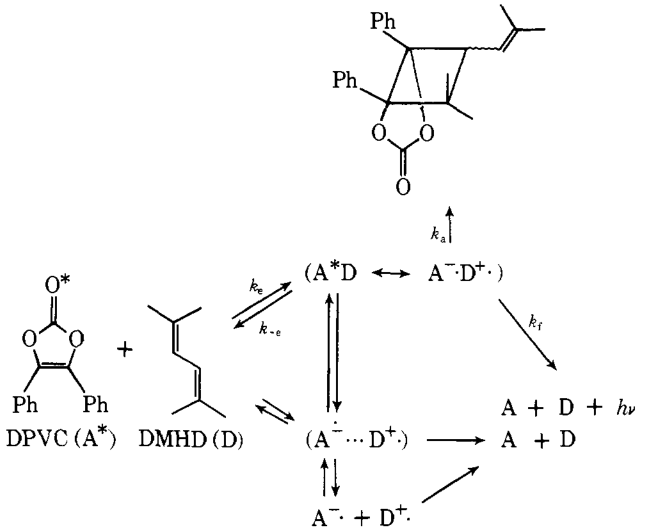


Figure 6. Schematic representation of the solvent dependence of the energy of the isolated molecules $A^* + D$ (—), the exciplex $A^*D \leftrightarrow A^{-}\cdot D^{+}\cdot$ (- - - -), the solvated ion pair $A^{-}\cdots D^{+}\cdot$ (·····), and the solvent separated radical ions $A^{-}\cdot + D^{+}\cdot$ (·-·-·-); after Mataga.[41]

Scheme I



for the various states cannot be calculated owing to the lack of reliable thermodynamic data for the DPVC-DMHD exciplex. The transition from exciplex to solvated ion pair is assumed to occur when the solvent dielectric constant exceeds 20. This assumption is consistent with the observed changes in the exciplex fluorescence maxima (Figure 3) and rate constants for fluorescence and cycloaddition (Figure 5). It also seems reasonable that ion pair formation from DPVC-DMHD should require higher solvent polarity than is the case for more polar aromatic hydrocarbon-amine exciplexes.[40,41] The TS-DMHD exciplex is even less polar than the DPVC-DMHD exciplex (Figure 3). The absence of large solvent-induced changes in TS-DMHD exciplex fluorescence intensity or cycloaddition quantum yield (Table VIII) indicates that the exciplex is more stable than the solvated ion pair even in acetonitrile solution.

According to Mataga,[41] the energy of an exciplex decreases rapidly in nonpolar solvents ($\epsilon < 10$), but decreases only slightly in more polar solvents (Figure 6). The decrease in the rate constant for exciplex cycloaddition in nonpolar solvents (Figure 5) thus parallels the increase in exciplex stability. The exciplex cycloaddition process has recently been described by Michl[46] as involving a rate-determining surface crossing from an exciplex to a pericyclic minimum followed by vertical deactivation to ground state products (Figure 7). The pericyclic minimum correlates with a doubly excited state of the isolated molecules and is thus expected to be nonpolar. Stabilization of the exciplex via solvation should therefore increase the activation energy for surface crossing to the pericyclic minimum. The observed increase in the exciplex lifetime and fluorescence quantum yield in nonpolar solvents (Table VII) is a consequence of exciplex solvation leading to decreased cycloaddition reactivity. Cycloaddition from a solvated ion pair state would involve an even greater change in solvent stabilization than exciplex cycloaddition. Thus it is not surprising that a large decrease in k_a accompanies the change in exciplex structure observed in polar solvents ($\epsilon > 20$). The decrease in exciplex lifetime in very polar solvents indicates the presence of nonradiative decay pathways not present in less polar solvents. Attempts to identify these pathways have thus far been unsuccessful.

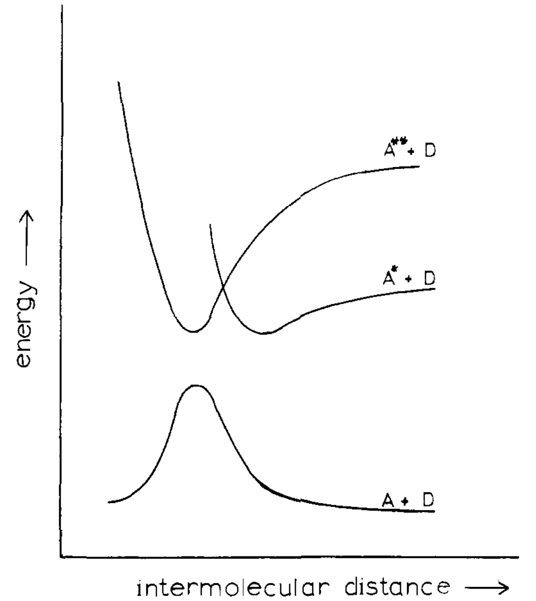


Figure 7. Schematic representation of the energy surfaces involved in exciplex cycloaddition; after Michl.[46]

We have previously reported that exciplex cycloaddition of DPVC with a series of conjugated dienes or vinyl ethers is most efficient for the most stable exciplex in the series.[9c,d] This conclusion may at first seem to contradict the observation that exciplex stabilization via solvation can decrease cycloaddition reactivity. However, whereas solvation stabilizes the exciplex far more than the nonpolar transition state leading to cycloadducts, a change in the structure of either the excited acceptor or ground state donor may affect all of the energy surfaces involved in exciplex cycloaddition (Figure 7).

Chemical Consequences. The photophysical processes of exciplexes have been extensively investigated during the past decade.[47] The solvent-induced changes in diarylethylene-diene exciplex fluorescence can readily be understood in the context of existing theories.[14,33-41] The novel aspect of our results is the further elucidation of the exciplex photochemical cycloaddition pathway. These results along with those of other workers[7,32,43,45] present incontrovertible evidence for exciplex intermediates in the photochemical cycloaddition process. As evidence accumulates that exciplexes are commonly intermediates in photochemical reactions, a thorough understanding of exciplex chemical and physical behavior becomes increasingly important. For example, stereospecific singlet cycloaddition reactions may not be the simple continuous processes depicted by Woodward-Hoffmann correlation diagrams. Conservation of orbital symmetry is not sufficient to ensure that surface crossing from a polar exciplex to a nonpolar pericyclic intermediate will be the preferred pathway for exciplex decay.

An important practical consequence of the imposition of exciplex intermediates in photochemical cycloaddition reactions is that the orientation of cycloaddition is determined by the orientation of a polar exciplex.[9b,48] The formation of unusual and counterthermodynamic regio- and stereoisomers in photochemical cycloaddition reactions can be rationalized in terms of Mulliken's[49] overlap and orientation principle for charge-transfer interactions. Our observations on the solvent dependence of exciplex cycloaddition reactivity have important consequences for preparative photochemistry. Cycloaddition reactions which proceed via relatively nonpolar exciplexes such as TS–DMHD may show little solvent dependence. For more polar exciplexes such as DPVC–DMHD, polar solvents may favor formation of solvated ion pairs with a resulting decrease in cycloaddition. We have encountered several examples of pronounced decreases in cycloaddition quantum yields simply upon changing the solvent from hexane to ethyl acetate ($\epsilon = 6.02$).[9c,50] Thus the traditional use of hexane and benzene as solvents for photochemical cycloaddition reactions has a definite scientific basis. In those cases where exciplex products are formed via a solvated or solvent-separated radical ion pair, efficient product formation requires the use of polar solvents.[51] Thus the choice of solvent can be an important factor in determining the outcome of a bimolecular photochemical reaction.

Experimental Section

Materials. *trans*-Stilbene (Aldrich) was recrystallized several times from benzene prior to use and contained <0.5% *cis*-stilbene by GC analysis. Diphenylvinylene carbonate and di(*p*-methoxyphenyl)vinylene carbonate were prepared by the method of Lewis and Hirsch.[9d] 1,2-Diphenylcyclobutene was prepared by the method of Dodson and Zielske.[52] Dienes were obtained from Aldrich or Chemical Samples Co. and distilled prior to use. Fumaronitrile (Aldrich) was recrystallized several times from benzene, then vacuum sublimed. Spectrograde solvents (Fischer, Baker, or Burdick and Jackson) were dried and distilled by standard methods prior to use.

Procedures. Absorption spectra were recorded on a Cary 14 or GCA McPherson EU 707 spectrophotometer. Fluorescence spectra were recorded using a Perkin-Elmer MPF-2A spectrophotometer. Spectra were corrected for photomultiplier response and fluorescence quantum yields determined using quinine bisulfate as a primary standard.[53] Fluorescence lifetimes were measured using the single photon counting apparatus of Professor R. P. VanDuyne. Cycloaddition quantum yields were determined as previously described.[9d] All fluorescence and cycloaddition data were obtained using degassed solutions contained in sealed Pyrex ampules constructed of either 15 mm o.d. round or 14 mm o.d. square truebore tubing.

Acknowledgment. Support of this work by the National Science Foundation (MPS 75-07181) is gratefully acknowledged. The authors thank J. Michl, J. Saltiel, and R. A. Caldwell for helpful suggestions and sharing unpublished results. We also thank R. P. VanDuyne for access to the single photon counting apparatus and D. Rushforth and M. R. Suchanski for experimental assistance.

References and Notes

(1) Presented in part at the Xth Great Lakes American Chemical Society Regional Meeting Photochemistry Symposium, Evanston, Ill., June 1976, and the VIth IUPAC Photochemistry Symposium, Aix-en-Provence, France, July 1976.
(2) (a) Camille and Henry Dreyfus Teacher Scholar, 1973–1978, and Alfred P. Sloan Fellow, 1975–1977. (b) Northwestern University Fellow, 1974–1976.
(3) J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, **3**, 1 (1973).
(4) (a) J. Birks, *Chem. Phys. Lett.*, **38**, 437 (1976); (b) D. J. S. Birch and J. B. Birks, *ibid.*, **38**, 432 (1976).
(5) K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 662 (1967).
(6) P. Sammes, *Synthesis*, 636 (1970).
(7) (a) O. L. Chapman and R. D. Lura, *J. Am. Chem. Soc.*, **92**, 6352 (1970); (b) J. Saltiel, J. T. D'Agostino, O. L. Chapman, and R. D. Lura, *ibid.*, **93**, 2804 (1971); (c) O. L. Chapman, R. D. Lura, R. M. Owens, E. D. Plank, S. C. Shim, D. R. Arnold, and L. B. Gillies, *Can. J. Chem.*, **50**, 1984 (1972).
(8) (a) F. D. Lewis and R. H. Hirsch, *Tetrahedron Lett.*, 4947 (1973); (b) F. D. Lewis, C. E. Hoyle, and D. E. Johnson, *J. Am. Chem. Soc.*, **97**, 3267 (1975); (c) R. H. Hirsch, Ph.D. Thesis, Northwestern University, 1974.
(9) (a) F. D. Lewis and R. H. Hirsch, *Tetrahedron Lett.*, 2651 (1975); (b) *J. Am. Chem. Soc.*, **97**, 5914 (1976); (c) F. D. Lewis, R. H. Hirsch, P. M. Roach, and D. E. Johnson, *ibid.*, **98**, 8438 (1976); (d) F. D. Lewis and C. E. Hoyle, *ibid.*, **98**, 4338 (1976).
(10) (a) H. M. Rosenberg, R. Rondeau, and M. P. Servé, *J. Org. Chem.*, **34**, 471 (1969); (b) H. M. Rosenberg and P. Servé, *ibid.*, **36**, 3015 (1971); (c) M. P. Servé, *Can. J. Chem.*, **50**, 3744 (1972).
(11) (a) T. Kubota and H. Sakurai, *Chem. Lett.*, 923 (1972); (b) T. Kubota and H. Sakurai, *ibid.*, 1249 (1972); (c) M. Kawanisi and K. Matsunaga, *J. Chem. Soc., Chem. Commun.*, 313 (1972).
(12) B. S. Green and M. Rejto, *J. Org. Chem.*, **39**, 3284 (1974).
(13) (a) F. D. Lewis and C. E. Hoyle, *J. Am. Chem. Soc.*, **97**, 5950 (1975); (b) C. E. Hoyle, unpublished results.
(14) For a review of solvent effects on the photophysical processes of excited state complexes see J. Prochorow and E. Bernard, *J. Lumin.*, **8**, 471 (1974).
(15) (a) H. Suzuki, *Bull. Chem. Soc. Jpn.*, **33**, 379, 410 (1960); (b) L. Jannelli, V. Lamanna, and O. Sciacovelli, *Gazz. Chim. Ital.*, **93**, 1231 (1963); (c) L. Jannelli, M. Della Monica, and O. Sciacovelli, *ibid.*, **93**, 1316 (1963).
(16) J. L. Charlton and J. Saltiel, *J. Phys. Chem.*, submitted.
(17) J. B. Birks and D. J. Dyson, *Proc. R. Soc. London, Ser. A*, **275**, 135 (1963).
(18) H. Knibbe, D. Rehm, and A. Weller, *Z. Phys. Chem. (Frankfurt am Main)*, **56**, 95 (1967).
(19) We thank R. J. Schwall for performing the polarographic experiments.
(20) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Am. Chem. Soc.*, **94**, 3679 (1972).
(21) T. R. Evans, *J. Am. Chem. Soc.*, **93**, 2081 (1971).
(22) G. N. Taylor, *Chem. Phys. Lett.*, **10**, 355 (1971).
(23) (a) J. B. Guttenplan and S. G. Cohen, *J. Am. Chem. Soc.*, **94**, 4040 (1972); (b) J. B. Guttenplan and S. G. Cohen, *Tetrahedron Lett.*, 2163 (1972).
(24) P. J. Wagner and R. A. Leavitt, *J. Am. Chem. Soc.*, **95**, 3669 (1973).
(25) N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, **97**, 2482 (1975).
(26) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).
(27) Diene oxidation potential calculated assuming $E_{D/D^+} = \mathrm{IP} - 6.5$.[23]
(28) J. C. Dalton and N. J. Turro, *J. Am. Chem. Soc.*, **93**, 3569 (1971).
(29) H. E. Zimmerman, D. P. Werthmmann and K. S. Kamm, *J. Am. Chem. Soc.*, **96**, 439 (1974).
(30) N. Janz and P. T. Tompkins, "Nonaqueous Electrolytes Handbook", Vol. I, Academic Press, New York, N.Y., 1972.
(31) W. R. Ware, D. Watt, and J. D. Holmes, *J. Am. Chem. Soc.*, **96**, 7853 (1974).
(32) (a) D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *J. Am. Chem. Soc.*, **98**, 621 (1976); (b) J. Saltiel, D. E. Townsend, B. D. Watson, and P. Shannon, *ibid.*, **97**, 5688 (1975).
(33) B. Stevens, *Adv. Photochem.*, **8**, 161 (1971).
(34) N. Mataga, Y. Torihashi, and K. Ezumi, *Theor. Chim. Acta*, **2**, 158 (1964).
(35) S. Masaki, T. Okada, N. Mataga, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **49**, 1277 (1976).
(36) N. Mataga, T. Okada, H. Masuhara, N. Nakashima, Y. Sakata, and S. Misumi, *J. Lumin.*, **12**, 159 (1976).
(37) T. Yoshino, *J. Chem. Phys.*, **24**, 76 (1956).
(38) H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967).
(39) D. Gupta and S. Basu, *J. Photochem.*, **4**, 307 (1975).
(40) H. Knibbe, K. Röllig, F. P. Schäfer, and A. Weller, *J. Chem. Phys.*, **47**, 1184 (1967).
(41) N. Mataga, Y. Taniguchi, and Y. Nishina, *Bull. Chem. Soc. Jpn.*, **45**, 764 (1972).
(42) Similar behavior has been reported without explanation for an intramolecular anthracene-*N,N*-dimethylaniline exciplex: T. Okada, T. Fujuta, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **14**, 563 (1972).
(43) Due to incomplete quenching of DPVC fluorescence by 1.45 M DMHD, the exciplex fluorescence quantum yields are 20–40% less than limiting values at infinite diene concentration.
(44) (a) E. A. Chandros and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 397 (1971); (b) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1970, p 307.
(45) D. Creed and R. A. Caldwell, *J. Am. Chem. Soc.*, **96**, 7369 (1974).
(46) J. Michl, *Pure Appl. Chem.*, **41**, 507 (1975).
(47) M. Gordon and W. R. Ware, Ed., "The Exciplex", Academic Press, New York, N.Y., 1975.
(48) N. C. Yang, K. Srinivasachar, B. Kim, and J. Libman, *J. Am. Chem. Soc.*, **97**, 5006 (1975).
(49) W. B. Person and R. S. Mulliken, "Molecular Complexes", Wiley, New York, N.Y., 1969.
(50) F. D. Lewis and B. Holman, manuscript in preparation.
(51) R. M. Bowman, T. R. Chamberlain, C.-W. Huang, and J. J. McCullough, *J. Am. Chem. Soc.*, **96**, 692 (1974).
(52) R. M. Dodson and A. G. Zielske, *J. Org. Chem.*, **28**, 28 (1967).
(53) J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, **75**, 991 (1971).