then the triplex energies will be lower than the *trans*-stilbene triplet energy (Figure 7).

Concluding Remarks. The results of this investigation demonstrate that the photophysical behavior of stilbene–amine exciplexes in nonpolar solvent is highly dependent upon amine structure and concentration due to varying degrees of interaction between positively charged and neutral nitrogen. For the sterically hindered amine EDA there is no evidence for nitrogen–nitrogen interaction. For the 1,2-diaminoalkanes Dabco and tetramethyl-1,2-diaminoethane, weak thru-bond interactions[1] result in enhanced exciplex intersystem crossing without diminishing the efficiency of triplet *trans*-stilbene formation. For the less hindered monoamines TEA, TMA, and Abco and the 1,3- and 1,4-diaminoalkanes, formation of a triplex in which the two amine nitrogens form a strong three-electron σ bond accounts for exciplex quenching and the concomitant quenching of triplet *trans*-stilbene formation. In the accompanying paper our investigations of the interactions of singlet stilbene with monoamines and diaminoalkanes in polar solvent are described.

Experimental Section

Materials. *trans*-Stilbene (Aldrich) was recrystallized once from benzene and twice from absolute ethanol. Diisopropylethylamine, triethylamine, *N,N,N′,N′*-tetramethyl-1,4-butanediamine, *N,N,N′,N′*-tetramethyl-1,3-propanediamine, and *N,N,N′,N′*-tetramethylethanediamine (all Aldrich) were distilled under reduced pressure. 1,4-Diazabicyclo[2.2.2]octane (Aldrich) and 1-azabicyclo[2.2.2]octane (Aldrich) were sublimed. Spectroquality benzene (Aldrich) was refluxed over sodium and distilled.

Stilbene Isomerization. Oxygen-free samples were prepared by purging with prepurified nitrogen. Samples were irradiated on a merry-go-round apparatus immersed in a water bath. Monochromatic 313-nm light was provided by a potassium chromate filter solution. Light intensities were measured by stilbene actinometry.[21] The extent of *trans*-stilbene isomerization was determined with a Varian 3700 dual flame ionization gas chromatograph with a 6 ft × $^1/_8$ in. column containing 5% SF-96 on Chromasorb G.

Spectroscopic Studies. Fluorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrofluorimeter. Oxygen quenching of fluorescence was investigated by first purging the samples with nitrogen, followed by extended oxygenation (1 atm). Nanosecond exciplex lifetimes were determined via single photon counting techniques with excitation wavelength at 315 nm and observation at $\lambda > 455$ nm.[38] Subnanosecond fluorescence decay kinetics were studied by means of a "Synchroscan" streak camera, in conjunction with UV picosecond pulses (2 ps) for excitation ($\lambda = 300$ nm; frequency doubled output of a rhodamine 6G dye laser synchronously pumped by an acoustooptically mode-locked Ar$^+$ laser). The streak image was monitored by an optical multichannel analyzer and the decay curve stored in a minicomputer.[39] Due to abnormal electronic jitter in the oscillator of the streak camera, the time resolution was limited to about 60 ps. The deconvolution of the decay curve with the exciting laser pulse (half-width 60 ps) profile still allowed determination of lifetimes of the order of 20 ± 5 ps. Fluorescence lifetimes and amplitude ratios were derived by a least-square fit procedure.[40] To distinguish between *trans*-stilbene and exciplex fluorescence Kodak wratten filters have been applied in the detection channel.

Acknowledgment. Financial support of the Deutsche Forschungsgemeinschaft and the National Science Foundation (CHE80-26020) and compensation of travel expenses by NATO Research Grant No. 1911 are gratefully acknowledged. We thank Dr. G. Woolfe and P. Geiselhart for their assistance in the picosecond measurements and Professor A. Weller for illuminating discussions and correspondence.

Registry No. EDA, 7087-68-5; TEA, 121-44-8; TMA, 75-50-3; Abco, 100-76-5; Dabco, 280-57-9; tetramethyl-1,2-ethanediamine, 110-18-9; tetramethyl-1,3-propanediamine, 110-95-2; tetramethyl-1,4-butanediamine, 111-51-3; *trans*-stilbene, 103-30-0.

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trans-Stilbene–Amine Exciplexes. Behavior of the Exciplex, Solvent-Separated Radical Ion Pair, and Free Radical Ions

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Abstract: The interaction of singlet *trans*-stilbene with several trialkylamines and diamines in acetonitrile solution has been investigated by a combination of steady-state measurements and time-resolved resonance Raman spectroscopy. Adduct formation between *trans*-stilbene and acyclic monoamines is proposed to occur via a short-lived exciplex (contact radical ion pair) intermediate, which is not quenched by ground-state amine. A solvent-separated radical ion pair is formed either directly from an encounter complex or via the exciplex and decays by intersystem crossing to yield triplet *trans*-stilbene, dissociation to yield free radical ions, or quenching by ground-state amine. Intersystem crossing is more rapid for the diamines vs. monoamines, resulting in a lower yield of free radical ions. Quenching of the solvent-separated radical ion pair by ground-state amine is subject to the same stereoelectronic effect as observed for exciplex quenching in nonpolar solvent. Free *trans*-stilbene anion radical decay is by recombination with amine cation radical and is independent of amine structure or concentration.

Photoinduced electron transfer between neutron electron donor (D) and acceptor (A) molecules leads to the formation of a pair of radical ions, A^{-}· and D^{+}·.[1,2] As is the case for classical ion pairs,[3] it is possible to distinguish spectroscopically between contact radical ion pairs (exciplexes), solvent-separated ion pairs, and separated free radical ions. Time-resolved spectroscopic investigations have established that diffusive encounter of an excited singlet state acceptor and ground-state donor in polar solvent can result in initial formation of either an exciplex ^{1}(A^{-}·D^{+}·)* or solvent-separated ^{1}(A^{-}· + D^{+}·)* ion pair (Scheme I).[1,2] Long-

Scheme I. Formation of Radical Ion Pairs and Free Radical Ions

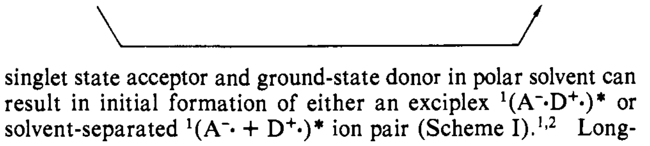

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Table I. Fluorescence Quenching and *trans*-Stilbene Isomerization Data

amine	$k_{qs}\tau_s$,[a] M^{-1}	$10^{-10}k_{qs}$,[b] $M^{-1}\ s^{-1}$	$\phi_{cs}'(^1/_2)$[c]	$\phi^0_{cs}{}'$[d]	$k_{qip}\tau_{ip}$[e]
ethyldiisopropylamine (EDA)	4.9	6.8	0.36	0.45	1.3
triethylamine (TEA)	2.3	3.2	0.27	0.50	3.7
trimethylamine (TMA)	1.0	1.4	0.07		
1-azabicyclo[2.2.2]octane (Abco)	3.8	5.3	0.28		
tetraethyl-1,2-ethanediamine (TEED)	6.2	8.6	0.30		
1,4-diazabicyclo[2.2.2]octane (Dabco)	8.0	11	0.26	0.45	12

[a] Least-squares slope of Stern-Volmer plot. Limits of error ±5%. [b] Calculated from Stern-Volmer slope and measured *trans*-stilbene singlet lifetime. Limits of error ±10%. [c] Quantum yield for *cis*-stilbene formation from the radical ion pair at the half-quencher concentration, calculated using eq 2. Limits of error ±20%. [d] Quantum yield for *cis*-stilbene formation from the radical ion pair in the limit of low amine concentration, from the intercept of Figure 7. [e] Slope/intercept ratios from Figure 7, plotted according to eq 3.

range electron transfer has also been observed; however, the rates for such processes are substantially slower than for diffusive processes. As is the case of ion pairs, the equilibrium between exciplex and solvent-separated ion pair is highly solvent dependent, the former being favored in solvents of low polarity and the latter in solvents of high polarity. Furthermore, the electronic structure of the exciplex (eq 1) may be dependent upon solvent polarity,

$$\psi_{ex} = a\psi(A^{-}\cdot D^{+}\cdot) + b\psi(A^{*}D) + c\psi(AD^{*}) \qquad (1)$$

the contribution of locally excited configurations (A*D, AD*) being more important in nonpolar solvents. Only in the case of a "pure charge-transfer exciplex" ($a >> b + c$) can the exciplex be described as a contact radical ion pair in both nonpolar and polar solvents.

The role of exciplexes, solvent-separated radical ion pairs, and free radical ion pairs as intermediates in photochemical reactions is a topic of active investigation.[4-6] Pronounced solvent effects on photochemical reactions have been attributed to the formation and reaction of exciplexes in nonpolar solvents and radical ion pairs in polar solvents.[4,7] Evidence has been recently presented for divergent chemical behavior for the exciplex, solvent-separated radical ion pair, and free ions of a single donor-acceptor system in polar solvent. For example, Simon and Peters[8] observed by picosecond absorption spectroscopy that proton transfer from tertiary amines to triplet benzophenone occurs via the exciplex (contact radical ion pair) but not via the solvent-separated radical ion pair. Mattes and Farid[9] have reported different chemical behavior for radical ion pair vs. free radical ion intermediates in the electron-transfer sensitized reactions of phenylacetylene and 1,1-diphenylethylene. One of us has suggested that the complex photochemical behavior of the 9-phenanthrenecarbonitrile-2,3-dimethyl-2-butene system in methanol solution can be attributed to cycloaddition via an exciplex, nucleophilic attack by solvent on the solvent-separated radical ion pair, and deprotonation of the free alkene cation radical by solvent.[10]

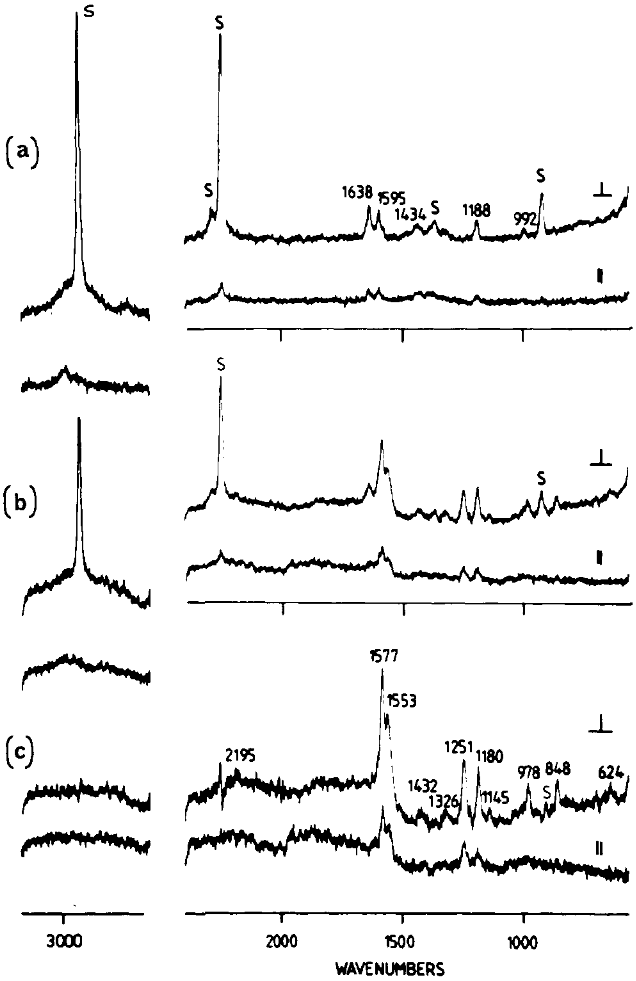

Figure 1. Raman spectra of *trans*-stilbene (0.03 M) and ethyldiisopropylamine (0.75 M) in acetonitrile solution: (a) normal Raman spectrum; (b) 60 ns after pulsed laser excitation; (c) difference spectrum.

We report here the results of our investigations of the interaction of singlet *trans*-stilbene with several tertiary amines and diamines in acetonitrile solution. The combination of steady-state measurements (fluorescence quenching, stilbene-amine adduct formation, stilbene trans → cis isomerization) and time-resolved resonance Raman spectroscopy permits characterization of the singlet exciplex, the solvent-separated radical ion pair, and the free *trans*-stilbene anion radical.[11]

Results

Fluorescence Quenching and Exciplex Fluorescence. The short-lived fluorescence of singlet *trans*-stilbene (TS) is quenched

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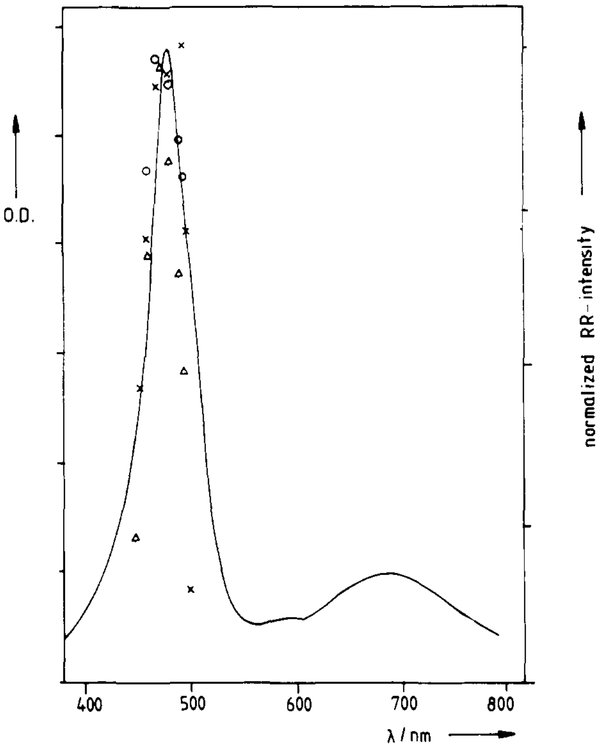

Figure 2. Excitation profiles of the *trans*-stilbene anion radical transient Raman signal from singlet *trans*-stilbene and ethyldiisopropylamine: (X) 1577/1553 cm^{-1}, (○) 1251 cm^{-1}, (△) 1180 cm^{-1}. Solid line is the absorption spectrum from ref 16.

by the tertiary monoamines ethyldiisopropylamine (EDA), triethylamine (TEA), trimethylamine (TMA), and 1-azabicyclo[2.2.2]octane (Abco) and the diamines 1,4-diazabicyclo[2.2.2]octane (Dabco) and *N,N,N′,N′*-tetraethyl-1,2-ethanediamine (TEED) in acetonitrile solution. The least-squares slopes of linear Stern–Volmer plots for fluorescence quenching by 0.05–0.5 M amine are given in Table I ($k_{qs}\tau_s$ values) along with the fluorescence quenching constants (k_{qs}) calculated using the singlet lifetime of TS in acetonitrile solution (τ = 72 ps) measured with a synchroscan streak camera using 300 nm picosecond excitation. Values of k_{qs} approach or exceed the calculated rate of diffusion in acetonitrile solution (2.9 × 10^{10} M^{-1} s^{-1}).[12] No exciplex fluorescence can be detected with any of the quenchers in acetonitrile solution at room temperature.

Time-Resolved Resonance Raman (TR^3) Spectroscopy. The normal Raman spectrum of a deaerated acetonitrile solution of TS (0.03 M) and EDA (0.75 M) excited at 480 nm with an excimer laser pumped dye laser is shown in Figure 1a. Peaks attributed to the solvent are labeled S. The other labeled peaks are of the same frequency and relative intensity as those previously reported by Takahashi and Maeda[13] for TS. No prominent peaks can be attributed to EDA. The TR^3 spectrum of the same solution measured at a delay time δt = 60 ns following irradiation at 337 nm with a pulsed nitrogen laser at 298 °K is shown in Figure 1b. The difference spectrum (Figure 1c) is obtained by subtracting the normal Raman spectrum (Figure 1a) from the TR^3 spectrum (Figure 1b), using the solvent peak at 1372 cm^{-1} for normalization. The frequencies and relative intensities of the prominent peaks in the difference spectrum correlate well with those previously reported by Takahashi and Maeda[13] and by Dosser[14] et al. for the anion radical of *trans*-stilbene (TS$^-$·). Identical spectra were obtained upon laser irradiation of *trans*-stilbene with the monoamine TEA and Abco and the diamines Dabco and TEED. No prominent peaks in the TR^3 difference spectra can be attributed to amine cation radicals, even in the case of Dabco. The cation radical of Dabco is known to absorb at λ_{max} = 465 nm with ϵ_{max} = 2.1 × 10^3.[15] All of the prominent bands of the anion radical are polarized (Figure 1c); the depolarization ratios are 0.24 (1577/1553 cm^{-1}), 0.31 (1251 cm^{-1}), 0.43 (1180 cm^{-1}), 0.09 (978 cm^{-1}), and 0.25 (848 cm^{-1}).

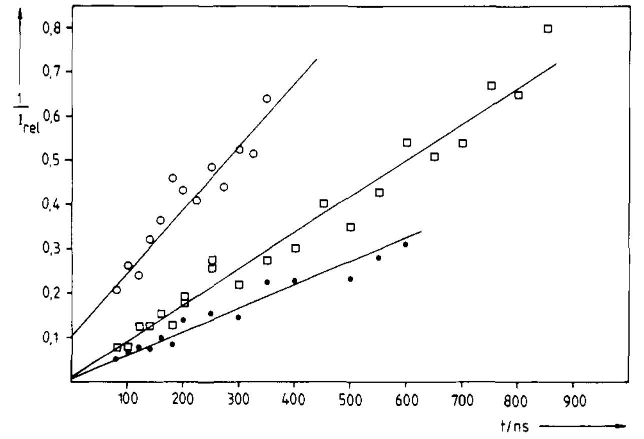

Figure 3. Second-order decay of the *trans*-stilbene anion radical transient Raman signal from singlet *trans*-stilbene and ethyldiisopropylamine: (●) 0.75 M, (□) 0.2 M, (○) 0.02 M.

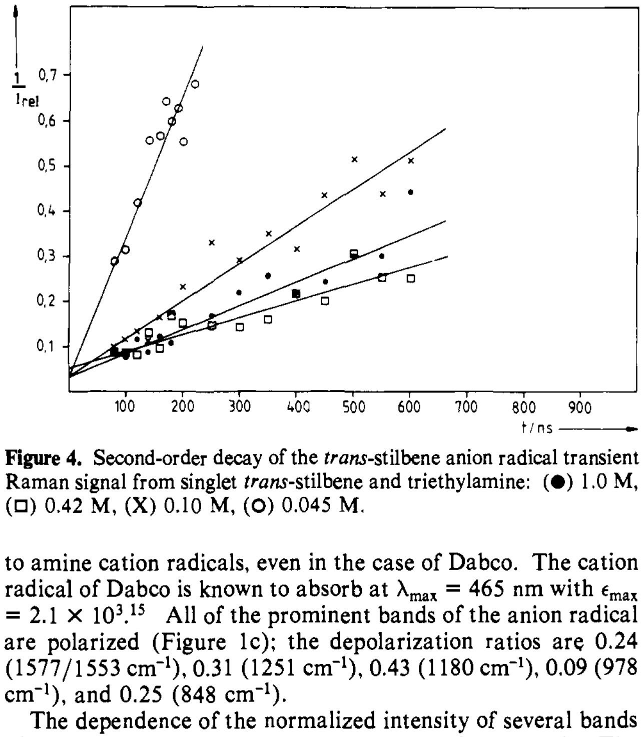

Figure 4. Second-order decay of the *trans*-stilbene anion radical transient Raman signal from singlet *trans*-stilbene and triethylamine: (●) 1.0 M, (□) 0.42 M, (X) 0.10 M, (○) 0.045 M.

The dependence of the normalized intensity of several bands of TS$^-$· upon excitation wavelength is shown in Figure 2. The experimental data display a single maximum which nearly coincides with the published absorption spectrum of the sodium salt of TS$^-$·.[16] Since the absorption maximum is dependent upon the counterion, exact correspondence of the TR^3 and absorption maxima is not expected.[17]

The time dependence of the stilbene anion radical signal intensity was determined by comparing the intensity of the 1577/1553 cm^{-1} peaks in the difference spectra with the intensity of the solvent bands at 1372 cm^{-1} at various delay times. This procedure normalizes the transient intensity for each measurement in the series to equal probe laser intensity and corrects for the time-dependent absorption of the solution.[18,19] The data obtained

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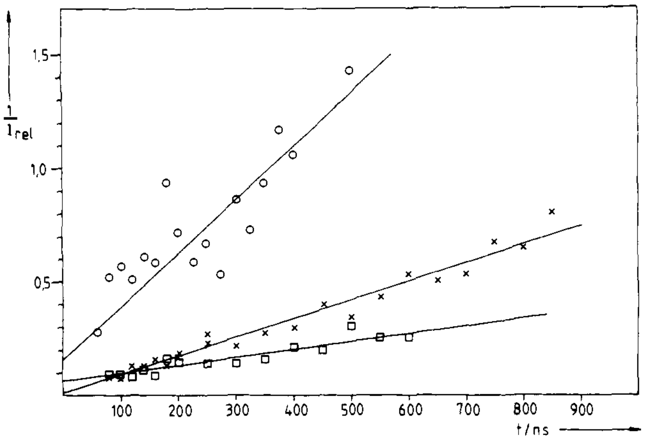

Figure 5. Second order decay of the *trans*-stilbene anion radical transient Raman signal from singlet *trans*-stilbene and 0.20 M ethyldiisopropylamine (X), 0.42 M triethylamine (□), and 0.12 M Dabco (○).

Table II. Formation and Decay of *trans*-Stilbene Anion Radical

amine[a]	M^{-1}	% quenching[b]	$\phi^0_{TS^-\cdot}$ (rel)[c]	k_2 (rel)[d]
EDA	0.75	79	(1.0)	(1.0)
	0.2	50	0.64	1.5
	0.1	33	0.26	1.2
	0.02	9	0.07	
TEA	1.0	70	0.23	0.97
	0.42	50	0.15	0.75
	0.1	19	0.22	1.5
	0.045	9	0.25	
Abco	0.26	50		
Dabco	0.12	50	0.05	
TEED	0.16	50	<0.05	

[a] See Table I for names of the amines. [b] Calculated from Stern–Volmer quenching data (Table I) and amine concentration. [c] Values from intercepts of Figures 3–5. Limits of error ±20%. [d] Second-order slopes from Figures 3–5. Limits of error ±20%.

obey a second-order rate law of the A + A → B type (linear plot of I^{-1} vs. t). Results obtained for EDA and TEA at several amine concentrations are shown in Figures 3 and 4. Figure 5 compares the data obtained for EDA, TEA, and Dabco using amine concentration sufficient to quench half of the TS fluorescence. Intercepts of Figures 3–5 provide relative quantum yields for the formation of $TS^-\cdot$ and the second-order slopes provide the relative rate constants for the disappearance of $TS^-\cdot$. These data are summarized in Table II. The TR^3 spectrum obtained for TEED at the half-quencher concentration is too weak to permit kinetic analysis. Data for Abco were obtained under different conditions than those used to obtain the data in Table II and are thus not strictly comparable. However, the second-order slope is similar to those for EDA and TEA. The absolute quantum yields for the formation of $TS^-\cdot$ have not been measured but can be estimated to be ≤0.1 on the basis of the equally good compensation of the bands from TS and the solvent in the TR^3 spectra. All of the peaks in the TR^3 difference spectra decay with the same rate constant; there are no persistent Raman-active species.

The effect of solvent polarity on the TR^3 signal intensity for the TS/EDA system was briefly investigated. The $TS^-\cdot$ signal was readily detected in acetone solution ($\epsilon = 21$) but not in ethyl acetate solution ($\epsilon = 6$), where relative strong exciplex fluorescence was observed instead.

Formation of *cis*-Stilbene and Stilbene Amine Adducts. Quenching of stilbene trans → cis isomerization is less efficient than quenching of TS fluorescence, as previously observed in nonpolar solvents.[20-22] The observed quantum yield for *cis*-stilbene

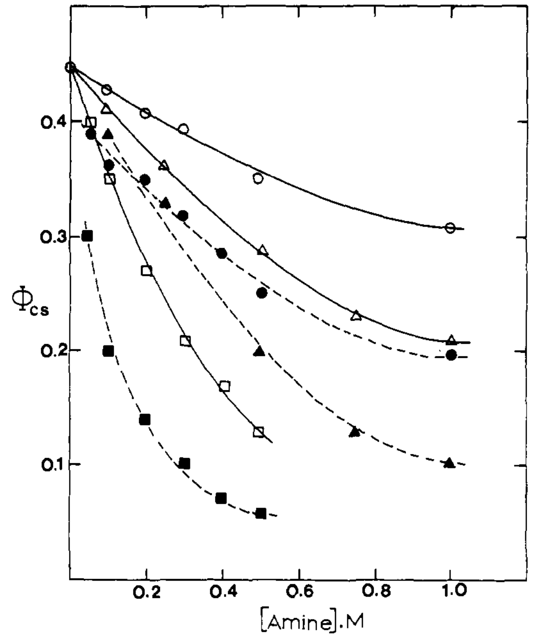

Figure 6. Amine concentration dependence of the quantum yields for *cis*-stilbene formation. Empty symbols are total quantum yields (ϕ_{obsd}) and filled symbols are values for quenched *trans*-stilbene ($\phi_{cs'}$, eq 2): (○) ethyldiisopropylamine; (△) triethylamine; (□) Dabco.

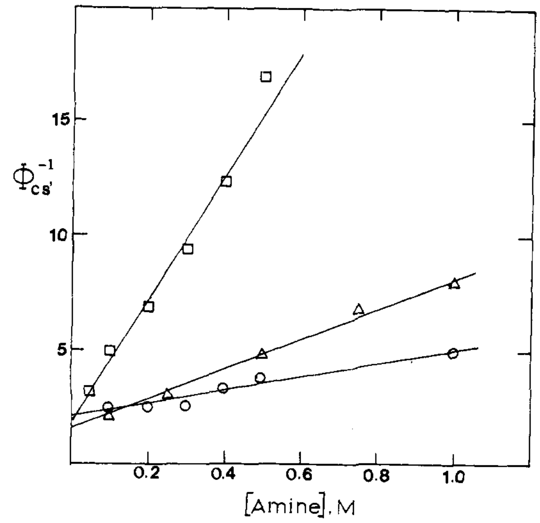

Figure 7. Amine concentration dependence of the quantum yield for *cis*-stilbene formation from *trans*-stilbene-amine radical ion pairs: (○) ethyldiisopropylamine; (△) triethylamine; (□) Dabco.

formation can be separated into components arising from unquenched TS ($\phi_{cs} = 0.45^{23}$) and quenched TS ($\Phi_{cs'}$) using eq 2,

$$\phi_{obsd} = (1 - a)\phi_{cs} + a\phi_{cs'} \qquad (2)$$

where a is the fraction of singlet quenched, calculated from the fluorescence quenching data in Table I and the amine concentration. Plots of ϕ_{obsd} and $\phi_{cs'}$ vs. [amine] are shown in Figure 6. Values of $\phi_{cs'}$ measured at the amine half-quencher concentration are given in Table I and range from 0.07 for TMA to 0.36 for EDA. Values of $\phi_{cs'}$ decrease with increasing amine concentration, indicating that a precursor of *cis*-stilbene (presumably an ion pair) is quenched by ground-state amine. Assumption of simple quenching kinetics provides eq 3, where k_{qip} is the rate

$$(\phi_{cs'})^{-1} = (\phi^0{}_{cs'})^{-1}(1 + k_{qip}\tau_{ip}[\text{amine}]) \qquad (3)$$

constant for amine quenching and τ_{ip} is the lifetime of the species

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Table III. Quantum Yield and Kinetic Data for *trans*-Stilbene–Monoamine Product Formation

amine[a]	ϕ_{add}- (1.0 M)[b]	ϕ^0_{add}[c]	ϕ_{tot} (1.0 M)[b]	ϕ^0_{tot}[d]	$k_{qs}\tau_s$[e]
EDA	0.11	0.16	0.25	0.30	3.2
TEA	0.059	0.11	0.12	0.17	1.0
TMA	0.014		0.033	0.07	

[a] See Table I for names of the amines. Limits of error for quantum yield data ±20%. [b] Data from ref 20b. [c] Values from intercepts of Figure 8. [d] Calculated from measured values for 1.0 M amine and fluorescence quenching data. [e] Intercept/slope ratios from Figure 8, plotted according to eq 4.

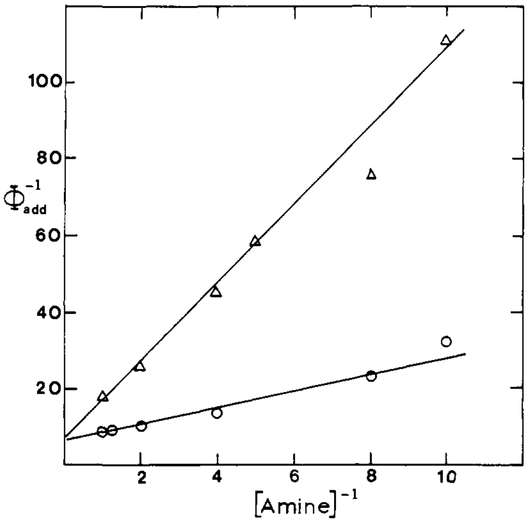

Figure 8. Amine concentration dependence of the quantum yield for formation of stilbene–amine adducts: (O) ethyldiisopropylamine; (△) triethylamine.

which is quenched. Plots of $(\phi_{cs'})^{-1}$ vs. [amine] are shown in Figure 7. Values of $\phi^0_{cs'}$ and $k_{qip}\tau_{ip}$ obtained from the intercepts and slope/intercept ratios of these plots are given in Table I.

Irradiation of TS and the monoamines EDA, TEA, and TMA in acetonitrile solution results in moderately efficient formation of stilbene–amine adducts and reduced stilbene (eq 4).[20] Quantum

$$\begin{aligned} PhCH{=}CHPh + Me_3N \xrightarrow{h\nu} {} & PhCH_2CH(Ph)CH_2NMe_2 + \\ & PhCH_2CH_2Ph + PhCH_2CH(Ph)CH(Ph)CH_2Ph \end{aligned} \quad (4)$$

yields for adduct formation (ϕ_{add}) and total stilbene containing products (ϕ_{tot}) from 0.01 M TS and 1.0 M amine have been reported and are summarized in Table III.[20] Quantum yields for adduct and 1,2-diphenylethane formation increase with increasing amine concentration. Plots of ϕ_{add}^{-1} vs. $[\text{amine}]^{-1}$ are linear (Figure 8), in accord with standard singlet quenching kinetics (eq 5). Values of the limiting quantum yield for adduct

$$\phi_{add}^{-1} = (\phi^0_{add})^{-1}(1 + k_{qs}\tau_s[\text{amine}])^{-1} \quad (5)$$

formation at infinite amine concentration (ϕ^0_{add}) and $k_{qs}\tau_s$ for EDA and TEA are given in Table III. Limiting total quantum yields (ϕ^0_{tot}) are estimated from the measured values at 1.0 M amine and fluorescence quenching kinetic data (Table I). The Stern–Volmer quenching constants ($k_{qs}\tau_s$) obtained from Figure 8 are somewhat smaller than those obtained from fluorescence quenching (Table I).

Discussion

The initial investigation of the interaction of singlet *trans*-stilbene with trialkylamines by Lewis and Ho[20a] established that exciplex fluorescence can be observed in nonpolar but not in polar solvents and that stilbene–amine adducts and stilbene reduction products (eq 4) are formed in polar but not in nonpolar solvents. On the basis of the solvent dependence of exciplex fluorescence and adduct formation, it was hypothesized that the interaction of singlet TS with tertiary amines yields a fluorescent exciplex in nonpolar solvents and a chemically reactive radical ion pair in polar solvents. Using Weller's equation (eq 6),[1] formation of

$$\Delta G_{ip} = -E_a^* - E_a^{red} + E_D^{ox} - 0.06 \text{ eV} \quad (6)$$

a solvent-separated radical ion pair from singlet TS ($E_A^* = 3.53$ V, $E_a^{red} = -2.26$ V) and TEA ($E_D^{ox} = 0.78$ V) is exothermic by ca. 0.55 eV. As expected for a highly exothermic electron-transfer process, the rate constants for quenching of TS fluorescence (k_{qs}) by amines (Table I) equal or exceed the calculated rate of diffusion in acetonitrile solution. The dependence of k_{qs} values on amine structure is similar to that observed for benzene solution and is discussed in the preceding manuscript.[22]

Incontrovertible evidence for the occurrence of photostimulated electron transfer upon reaction of singlet TS and amines in acetonitrile solution is provided by the direct observation of free $TS^{-}\cdot$ by TR[3] spectroscopy (Figures 1 and 2). The yields of both stilbene–amine adduct[18] and free $TS^{-}\cdot$ increase with increasing solvent polarity and amine substitution (EDA > TEA > TMA) suggesting that the two processes are related. However, the yield of adduct increases with increasing amine concentration (Figure 8) while the yield of free $TS^{-}\cdot$ from EDA does not (Table II). *Thus free $TS^{-}\cdot$ is not a precursor of stilbene–amine adduct and cannot be formed from the same intermediate.*

Since neither stilbene–amine adducts nor free $TS^{-}\cdot$ are formed with high quantum yields, other decay pathways must compete effectively with these processes. As is the case for fluorescent TS–amine exciplexes in benzene solution,[21,22] the predominant decay pathway of the singlet radical ion pair at low amine concentration in polar solvent is intersystem crossing to yield the low energy triplet state of *trans*-stilbene (2.12 eV), which isomerizes to yield *cis*-stilbene with a quantum yield of 0.55.[24] The quantum yield for *cis*-stilbene formation, like that for free $TS^{-}\cdot$, decreases with increasing amine concentration (Figure 6 and 7), indicating that intersystem crossing and formation of $TS^{-}\cdot$ may occur from the same intermediate.

The results of transient and steady state investigations of the interaction of singlet *trans*-stilbene with tertiary mono- and diamines can be accommodated by the mechanism shown in Scheme II. The encircled parameters are those which have been measured as functions of amine structure and concentration. The salient features of this Scheme are (a) the formation of a short-lived exciplex (contact radical ion pair) which undergoes proton transfer to yield a 1,2-diphenylethyl-α-aminoalkyl radical pair or dissociates to form a solvent-separated radical ion pair, (b) the formation of triplet *trans*-stilbene and free *trans*-stilbene anion radical from a longer-lived solvent-separated radical ion pair, and (c) the quenching of the solvent-separated ion pair by ground-state amine. Each of these processes is dependent upon amine structure and concentration.

Exciplex Proton Transfer. The postulated formation of stilbene–amine adducts from an exciplex, but not from a solvent-separated ion pair, finds analogy in the recent results of Simon and Peters[8] for triplet benzophenone–amine systems. Proton transfer fails to occur for Abco and the diamines Dabco and TEED. The TS–amine exciplexes formed in acetonitrile solution differ from the fluorescent exciplexes formed in nonpolar solvents both in chemical reactivity and susceptibility to quenching by ground-state amine. The lifetime of the TS–TEA exciplex in benzene solution is 12 ns.[22] While the lifetime of the contact radical ion pair in acetonitrile solution has not been measured, a value of ≤2 ns can be estimated from the rate constant for dissociation of exciplexes to solvent-separated radical ion pairs (typically 5×10^8 s^{-1}).[1d,e] Thus the short lifetime of the contact ion pair may preclude the observation of the relatively slow decay processes observed for the TS–TEA exciplex in benzene solution: fluorescence (2×10^6 s^{-1}), intersystem crossing (5×10^7 s^{-1}), or quenching by ground-state amine (3×10^8 M^{-1} s^{-1}).[22] The ob-

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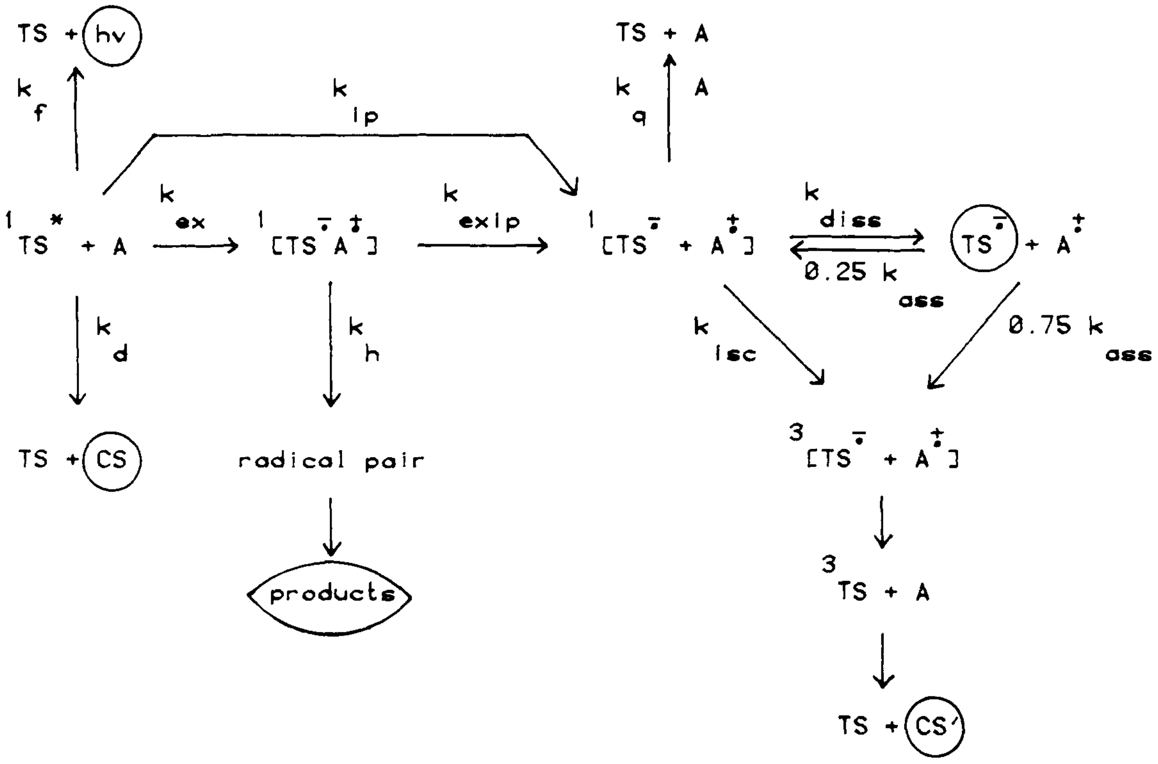
[24] Saltiel, J.; Chang, D. W. L.; Megarity, E. D.; Rousseau, A. D.; Shannon, P. T.; Thomas, B.; Uriarte, A. K. *Pure Appl. Chem.* **1975**, *41*, 559–579.

Scheme II. Mechanism of Reaction of Singlet *trans*-Stilbene with Tertiary Amines in Acetonitrile Solution



servation of proton transfer in polar but not in nonpolar solvents plausibly reflects a solvent-induced change in structure for the exciplex. *trans*-Stilbene–amine exciplex emission in benzene solution occurs at lower energy than expected for a "pure charge-transfer exciplex," indicative of the interaction of charge-transfer and locally excited states (eq 1). Stabilization of the charge-transfer state in polar solvents leads to formation of a "pure charge-transfer" exciplex or contact radical ion pair.[1e]

The marked dependence of TS–amine adduct formation upon amine structure could reflect either differences in the partitioning of an encounter complex between exciplex vs. solvent-separated radical ion pair or in rates of proton transfer vs. diffusion within the contact radical ion pair (Scheme II). Thus the decrease in yield of adduct formation in the series EDA > TEA > TMA may reflect faster solvent reorganization about the smaller TMA cation radical in either the encounter complex (k_{ip} vs. k_{ex}) or the exciplex (k_{exip} vs. k_h). The lower yield of adduct for TMA vs. EDA probably does not reflect a slower rate of proton transfer (k_h), as independent investigation of the reactions of singlet TS with nonsymmetrically substituted amines (R_2NR') have established that aminomethyl groups react as fast or faster than ethyl or isopropyl groups in intramolecular competitive reactions.[20b] The absence of adduct formation or stilbene reduction products with Abco may well reflect a slower rate of proton transfer for Abco vs. the acyclic monoamines as a consequence of stereoelectronic control of amine cation radical deprotonation.[20b,25] That is, the rigid bicyclic structure of Abco prevents overlap of the α-C–H bonds with the half-vacant nitrogen p orbital. The same argument can be applied to Dabco, but not to the acyclic diamine TEED, which also fails to yield an adduct or stilbene reduction products. The more stable, delocalized diamine cation radicals may either form the solvent-separated radical ion pair directly ($k_{ip} >> k_{ex}$) or form an unreactive contact ion pair ($k_{exip} >> k_h$). The available data do not unequivocally distinguish between branching vs. consecutive pathways for the formation of TS–amine exciplexes and solvent-separated radical ion pairs (Schemes I and II). The observation of smaller $k_{qs}\tau_s$ values for stilbene–amine adduct formation (Table III) vs. fluorescence quenching (Table I) is consistent with a branching mechanism for which k_{qs} (fluorescence) = $k_{ip} + k_{ex}$ (product).

Reactions of the Solvent-Separated Radical Ion Pair. Once formed, the solvent-separated radical ion pair can undergo intersystem crossing to yield triplet TS, dissociate to yield free ions, or undergo quenching by ground-state amines (Scheme II). The high quantum yields for *cis*-stilbene formation (Table I) and the low yields for free TS$^{-}\cdot$ formation indicate that intersystem crossing is the predominant decay pathway for the singlet solvent-separated ion pair at low amine concentrations, for both chemically reactive (EDA, TEA, TMA) and unreactive (Abco, Dabco, TEED) amines. Values of $\phi_{cs'}$ decrease with increasing amine concentration (Figure 6), as is the case for exciplex intersystem crossing in nonpolar solvents.[22] Plots of $\phi_{cs'}^{-1}$ vs. [amine] are linear (Figure 7) in accord with quenching of a single intermediate, presumably the solvent-separated radical ion pair.

The $k_{qip}\tau_{ip}$ values given in Table I roughly parallel the $k_{qe}\tau_{ex}$ values obtained for *cis*-stilbene formation from TS–amine exciplexes in benzene solution.[22] Thus we conclude that the mechanisms of exciplex and solvent-separated radical ion pair quenching are the same; namely the interaction of a neutral amine with an amine cation radical to yield a triplex of TS$^{-}\cdot$ and a three-electron, σ-bonded amine dimer cation radical ($(R_3N)_2{}^{+}\cdot$). Since this triplex is of lower energy than triplet TS, quenching of *cis*-stilbene formation is observed.[22] The observation of quenching of *cis*-stilbene formation by ground-state amines for the TS–EDA radical ion pair in acetonitrile solution but not for the exciplex in benzene solution suggests that the former species may be the more reactive. Assuming a typical solvent-separated radical ion pair lifetime of ca. 2 ns (limited by the rate of dissociation, k_{diss}),[1c,d,9b] the rate constant for quenching of the TS–TEA radical ion pair by TEA is ca. 2×10^9 M^{-1} s^{-1}, substantially faster than the value for exciplex quenching in benzene solution (3×10^8 M^{-1} s^{-1}). Similarly, the rate constant for intersystem crossing of the TS–TEA radical ion pair is estimated to be $\geq 5 \times 10^8$ s^{-1} vs. 5×10^7 s^{-1} for the exciplex in benzene solution.

Free Radical Ions. The formation and decay of the free *trans*-stilbene anion radical (TS$^{-}\cdot$) can be monitored by TR^3 spectroscopy. This method yields vibrational information and thus allows structural assignment with far greater certainty than the more conventional transient absorption spectroscopy. For example,

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(25) Griller, D.; Howard, J. A.; Marriott, P. R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 619–623.

the absorption spectra of TS$^{-}\cdot$ and TS$^{+}\cdot$ are almost identical, whereas their RR spectra are significantly different.[19] Conclusive evidence for the formation of TS$^{-}\cdot$ upon irradiation of TS in the presence of tertiary amines is provided by the TR^3 spectrum (Figure 1) and excitation profile (Figure 2) which match literature Raman[13,14] and absorption[16,17] spectra of TS$^{-}\cdot$ generated under steady-state conditions. While TR^3 spectroscopy has been widely used to characterize transient intermediates in photochemical reactions on the basis of the RR frequencies observed,[26,27] little use has been made of the quantitative kinetic information which is provided by the time dependence of the RR band intensities in pump-probe experiments.[19] The present work provides the first application of TR^3 spectroscopy to the investigation of ionic photodissociation and also demonstrates the importance of the kinetic information for the identification of the transient species in reactions where the transient could appear in different molecular complexes (e.g., solvent separated radical ion pair or free radical ions). In such cases the nature of the transient species cannot be determined from vibrational frequencies alone.

The decay of the TS$^{-}\cdot$ TR^3 spectrum obeys a second-order rate law (Figures 3–5). The second-order slopes are similar for EDA and TEA and are independent of amine concentration. While neither the second-order rate constant nor the concentration of TS$^{-}\cdot$ can be determined independently from the TR^3 data,[19] the initial concentration of TS$^{-}\cdot$, measured as the normalized intensity of the 1577/1553-cm^{-1} band, is reduced to 50% within 20 to 200 ns. Since solvent-separated singlet radical ion pairs are known to react or diffuse apart within several nanoseconds of their formation,[1c,d] the stilbene anion radicals observed in the present investigation must arise from diffusion of the initially formed radical ion pair. Both the observed lifetime and second-order decay of the stilbene anion radical are indicative of homogeneous (out of cage) recombination with an amine cation radical as the exclusive decay pathway for TS$^{-}\cdot$. Recombination is expected to yield triplet and singlet solvent-separated ion pairs in a spin-statistical 3:1 ratio.[1] The triplet radical ion pair thereby produced should rapidly decay to the low energy triplet of TS (Scheme II).

The intercepts of Figures 3–5 provide the ratio of initial concentrations of TS$^{-}\cdot$ (Table II). Values are dependent both upon amine structure and concentration. For amine concentrations sufficient to quench half of the TS monomer fluorescence, the relative yields of TS$^{-}\cdot$ from EDA, TEA, and Dabco are 1.0:0.2:0.05. The initial yield of TS$^{-}\cdot$ from EDA increases with increasing amine concentration, in accord with the increased efficiency of TS singlet quenching by amine. In contrast the initial yield of TS$^{-}\cdot$ from TEA appears to be independent of the amine concentration (Table II). These results are consistent with free TS$^{-}\cdot$ formation from the same intermediate as triplet TS formation, the solvent-separated radical ion pair. The yields of free TS$^{-}\cdot$ from EDA and TEA roughly parallel the extent of solvent-separated radical ion pair quenching by ground-state amine at the amine concentrations employed. Thus these solvent-separated radical ion pairs have approximately the same lifetimes and rate constants for intersystem crossing. The lower yields of free TS$^{-}\cdot$ from Dabco and TEED reflect faster radical ion pair intersystem crossing for the diamines vs. monoamines, as is the case in nonpolar solvent.[22]

It is of interest to note that increasing amine concentration decreases the initial yield but not the lifetime of free TS$^{-}\cdot$. Free amine cation radicals would be expected to react with neutral amine molecules to yield diamine cation radicals, as observed for exciplex and solvent-separated radical ion pair quenching by amines. However, since decay of free TS$^{-}\cdot$ by homogeneous radical ion pair recombination is a diffusive process, the nature of the cation radical ($R_3N^{+}\cdot$ vs. $(R_3N)_2{}^{+}\cdot$) should not affect its rate. Since the yield of free TS$^{-}\cdot$ is low, the expected decrease in the yield of triplet *trans*-stilbene formation from homogeneous radical ion pair recombination at high amine concentrations cannot be detected experimentally.

Concluding Remarks. The exciplex (contact radical ion pair), solvent-separated radical ion pair, and free radical ions formed upon the interaction of singlet TS with tertiary amines and diamines display remarkably different chemical behavior. Proton transfer leading to stilbene–amine adduct formation occurs exclusively via the exciplex intermediate. Evidently, exciplex solvation to form the solvent-separated radical ion pair or free radical ions renders the tertiary amine cation radical unreactive. The increase in exciplex chemical reactivity with increasing solvent polarity can be attributed to a change in the electronic structure of the exciplex from that of a heteroexcimer in nonpolar solvent to that of a pure charge-transfer exciplex in acetonitrile.

It is interesting to compare the chemical behavior of the exciplexes of secondary vs. tertiary amines in light of the conclusion that α-C–H proton transfer of tertiary amines occurs only via a pure charge-tranfer exciplex. Secondary amines undergo N–H addition to singlet TS,[20] anthracene,[28] and 9-phenanthrenecarbonitrile[29] (inter alia) with higher quantum yield in nonpolar vs. polar solvent. Hydrogen atom or proton transfer of the arene–secondary amine heteroexcimer reflects the greater kinetic acidity of the N–H vs. α-C–H bond, which may result from N–H–arene hydrogen bonding.[30] Increased solvent polarity may decrease the lifetime of the heteroexcimer (enhanced internal conversion or ionic dissociation) without increasing the rate of N–H transfer. It remains to be established whether or not all photoreduction and addition reactions of amines involve exciplex (contact radical ion pair) intermediates.

The predominant decay pathway of the TS–trialkylamine solvent-separated radical ion pairs at low amine concentrations is intersystem crossing to yield the low energy triplet of *trans*-stilbene. As is the case for the exciplexes formed in nonpolar solvents,[20] intersystem crossing is more rapid for the diamines Dabco and TEED than for the monoamines. This observation is in accord with an energy gap dependence for the intersystem crossing process.[1c,31] Dissociation of the solvent-separated radical ion pair yields small amounts of free radical ions, which have been detected by TR^3 spectroscopy. At higher amine concentration, the solvent-separated radical ion pair is quenched by ground-state amine, thereby decreasing the yields of triplet TS and free TS$^{-}\cdot$. On the basis of the observed stereoelectronic effect for quenching by ground-state amine, quenching is proposed to occur upon interaction of an amine cation radical and neutral to form an amine dimer cation radical.[22]

While formation of free radical ions is a relatively minor process for the TS–amine system, the direct detection of TS$^{-}\cdot$ by TR^3 spectroscopy provided the cornerstone upon which Scheme II was erected. The characterization of TS$^{-}\cdot$ provided the first direct evidence for electron-transfer quenching of singlet TS by amines. Moreover, the observation of higher initial yields of TS$^{-}\cdot$ for the chemically reactive monoamines vs. unreactive diamines ruled out the possibility that the more stable diamine cation radicals efficiently dissociate to yield free ions. This in turn led to a quantitative investigation of the dependence of intersystem crossing and free radical ion formation upon amine structure and concentration.

Experimental Section

Materials. *trans*-Stilbene and the various amines (Aldrich) were purified as described in the preceding paper.[22]

Quantum Yields. Quantum yields for *cis*-stilbene formation were measured by the procedures described in the preceding paper.[22] Quantum yields for stilbene–amine adduct and stilbene reduction product formation were determined by published procedures.[20] Light intensities were measured by stilbene actinometry.[23]

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Spectroscopic Studies. Fluorescence spectra of nitrogen-purged samples were recorded on a Perkin-Elmer MPF-44A spectrofluorimeter. The TR^3 measurements were carried out with the apparatus described in ref 32. The beams of a pulsed nitrogen laser and of an excimer laser pumped dye laser (3 mJ at 480 nm, 20 ns) were focused into the cell through quartz windows. The scattered light was collected under 90° and spectrally dispersed in a double grating spectrograph (5-cm^{-1} resolution; bandpass 550 cm^{-1} at 480 nm). After amplification in a gated image intensifier the Raman spectra were recorded by an optical multichannel analyzer and stored in a minicomputer for further data handling. Improvement in signal to noise ratio is achieved by sampling over 500 excite-probe cycles. Complete RR spectra (400–2500 cm^{-1}) were composed of four spectrally overlapping sequences with a fixed number of pump-probe cycles and subsequent computer calculation. The excitation spectrum was measured with a fixed delay time between photolysis and probe laser pulse as the dependence of TR^3 band intensities upon the excitation wavelength. The TR^3 band intensities were normalized to the simultaneously measured solvent band intensities of the same spectral window. This procedure cancels the variation of the probe laser intensity with different laser dyes and also the wavelength dependent absorption of the excitation laser intensity in the sample.[19] The measurements of the kinetic behavior of the transient species were carried out with fixed probe laser wavelength by observing the normalized TR^3 band intensities as a function of the delay time between the photolysis and the probe laser pulse.

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Registry No. *trans*-Stilbene•ethyldiisopropylamine, 88131-18-4; *trans*-stilbene•triethylamine, 88131-19-5; *trans*-stilbene•1,4-diazabicyclo[2.2.2]octane, 88131-20-8; ethyldiisopropylamine, 7087-68-5; triethylamine, 121-44-8; trimethylamine, 75-50-3; 1-azabicyclo[2.2.2]octane, 100-76-5; tetraethyl-1,2-ethanediamine, 150-77-6; 1,4-diazabicyclo[2.2.2]octane, 280-57-9; *trans*-stilbene, 103-30-0; *trans*-stilbene radical anion, 34473-61-5; ethyldiisopropylamine radical cation, 88131-21-9; triethylamine radical cation, 36752-99-5; 1,4-diazabicyclo[2.2.2]octane radical cation, 54159-20-5.

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Photoinitiated Autocatalytic Chain Decomposition of Phenyl Azide

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Abstract: Quantum yields of disappearance of phenyl azide (ϕ-PhN$_3$) were determined for 10^{-5}–10^{-1} M acetonitrile solutions at room temperature by monitoring changes in its electronic absorption spectra. For dilute solutions, ϕ-PhN$_3$ = 0.5; however, at higher concentrations ϕ-PhN$_3$ values *greatly exceed unit efficiency* and indicate a chain decomposition mechanism. At ca. 2×10^{-1} M, ϕ-PhN$_3$ $\simeq$ 3000! A plot of [ϕ-PhN$_3$] vs. log [PhN$_3$] appears exponential and since a plot of the chain length, n, vs. [PhN$_3$] is linear ($r^2 = 0.972$), when n is calculated from an exponential function, the experimental results provide evidence for a branching chain reaction also known as an autocatalytic (spontaneously explosive) reaction. The branching chain mechanism is thought to result from reaction of a phenyl nitrene intermediate with a ground-state phenyl azide molecule to form *two* phenyl nitrenes. A 1,4-tetraazadiene or triaza species may also participate in the chain reaction.

The use of organic azides as photoaffinity labels, as photopolymerization initiators, as starting materials in the synthesis of nitrogen heterocycles, and in the preparation of photoresists has prompted considerable interest in their photochemical properties.[1] The chemistry of phenyl azide (PhN$_3$) is particularly interesting. Upon irradiation in organic matrices at 77 K, molecular nitrogen is lost and phenyl nitrene is formed[2-5] with a temperature-independent quantum yield, determined by monitoring the production of molecular nitrogen (ϕ-N$_2$), somewhat higher in nonpolar (ϕ-N$_2$ = 0.52)[6] than in polar solvents (ϕ-N$_2$ = 0.43).[4,7] ESR studies have shown that the triplet state is the ground state of phenyl nitrene.[8-10]

In neutral solvents, azobenzene[11] and an intractable polymeric material[12,13] are the major photoproducts. Azobenzene is formed exclusively as the *E* isomer in deaerated solvents;[14] however, in oxygen-saturated solutions nitrosobenzene is the primary photoproduct.[14] Azepines and anilines are produced upon irradiation of PhN$_3$ in solutions containing ammonia, organic amines, or other nucleophilic reagents.[12,15] The pathway by which azepines are formed is a subject of controversy since phenyl nitrene is thought to undergo intramolecular rearrangement to form 7-azabicyclo[4.1.0]hepta-2,4,6-triene[12,16,17] or 1-aza-1,2,4,6-cycloheptatetraene.[18,19]

Our investigation[20] of the photochemical properties of PhN$_3$ has led to discovery of a photoinitiated autocatalytic chain de-

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