ion intensity at *m/e* 30, and at pressures greater than 10^{-4} Torr the signal at *m/e* 32 from the $CH_3NH_3^+$ ion becomes evident.

At CH_3^+ kinetic energies in excess of 1 eV, an additional endothermic reaction channel becomes available in the condensation of CH_3^+ with CH_4.

$$CH_3^+ + CH_4 \longrightarrow C_2H_3^+ + 2H_2 - 24 \text{ kcal/mol} \qquad (48)$$

This reaction is successfully observed by heating the CH_3^+ primary ion to kinetic energies in excess of 1 eV using high-intensity double-resonance irradiating fields.[25,37] Attempts made to observe by double resonance, or to force by excessive double-resonance heating, the reaction

$$\underset{15}{CH_3^+} + NH_3 \not\twoheadrightarrow \underset{28}{H_2CN^+} + 2H_2 + 25 \text{ kcal/mol} \qquad (49)$$

have been unsuccessful. This result is somewhat surprising in view of the fact that the reaction is exothermic. Assuming that the collision of a methyl cation with either methane or ammonia involves the formation of strongly bound complexes $[C_2H_7^+]^*$ and $[CH_3NH_3^+]^*$, the excitation energies contained in the intermediates are ~30 and 101 kcal/mol, respectively. In the case of $[CH_3NH_3^+]^*$, more than sufficient energy is present for decomposition to H_2CN^+ and yet this reaction is not observed. The reason for this difference in behavior may be that a large portion of the excitation energy contained in the $[CH_3NH_3^+]^*$ intermediate is converted to internal excitation of the $CH_2NH_2^+$ product ion and that this energy is no longer available for further decomposition to H_2CN^+.

Some percentage of the excitation energy of the $[CH_3NH_3^+]^*$ intermediate must go into internal excitation of the product ion. Sjögren[38] has recently suggested that the first electronically excited state of the $CH_2{=}NH_2^+$ ion should be 2 eV above the ground state and should have the structure $^+CH_2{-}NH_2$. The exothermicity of the condensation reaction, 3.2 eV, is sufficient to reach this state, and localization of charge on carbon in the proposed structure for this state is interesting with respect to the origin of the proton transferred to ammonia in this state. The carbon site on the molecule is much less basic than the nitrogen site. Decomposition of the neutral product of the proton transfer reaction 20 to HCN and H_2 requires only 15 kcal/mol of excitation energy for the excited reactant ion, based on $\Delta H_f(CH_2NH_2^+)$ 175[30,34] and $\Delta H_f(CH_2NH)$ 17 kcal/mol.[34]

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Triplet–Singlet Energy Transfer in Fluid Solution[1]

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Abstract: The process of triplet–singlet energy transfer by a dipole–dipole interaction has been studied in fluid solution. The quenching rate constants for the donor–acceptor combinations of phenanthrene–Rhodamine B in ethanol and benzophenone–perylene in Freon are 3.9×10^7 and 7.1×10^9 M^{-1} sec^{-1}, respectively. The ratio of these experimental rate constants is in agreement with the ratio of the relative strengths of the dipole–dipole interactions in these systems. The efficiency of the energy transfer process is governed by the solution lifetime of the triplet state donor and its ability to diffuse to within the critical transfer distance during that lifetime.

Energy transfer from the triplet state of a donor molecule to a singlet state of an acceptor molecule by long-range dipole–dipole resonance interaction was first predicted by Förster (eq 1).[3–6] He stated that the

$$^3D + A_0 \longrightarrow D_0 + {}^1A \qquad (1)$$

forbidden nature of the donor transition will cause the strength of the donor–acceptor interaction to be small, as compared to the totally spin-allowed singlet–singlet process. However, the long lifetime of the spin-forbidden transition in the donor compensates for the weak interaction and consequently large transfer distances are predicted for this process.

By considering a long-range, weak intermolecular interaction between excited donor and ground state acceptor, Förster obtained an expression for the rate of energy transfer

$$k_{D \rightarrow A} = \frac{9000 \ln 10 k^2}{128 \pi^5 n^4 N \tau_0 R^6} \int f_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}_4} \qquad (2)$$

where N is Avogadro's number, k^2 is an orientation

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factor (equal to $^2/_3$ for randomly orientated solution), n is the refractive index of the supporting media, τ_0 is the intrinsic radiative lifetime of the donor, and R is the intermolecular distance between donor and acceptor. The integral in eq 2 is over the region of coincidence between the normalized emission spectrum of the donor, $f_D(\bar{\nu})$, and the absorption spectrum of the acceptor, $\epsilon_A(\bar{\nu})$, where ϵ_A is the molar decadic extinction coefficient on a wave-number scale, $\bar{\nu}$. He also defined a critical transfer distance, R_0 as being that distance at which the rate of energy transfer from the donor equals the sum of the other deactivation processes (eq 3) where ϕ is the

$$R_0^6 = \frac{9000 \ln 10 k^2}{128\pi^5 n^4 N}\phi \int f_D(\bar{\nu})\epsilon_A(\bar{\nu})\frac{d\bar{\nu}}{\bar{\nu}^4} \qquad (3)$$

quantum yield of donor emission.

Ermolaev and Sveshnikova[7] first observed the triplet–singlet energy transfer process in a number of biologically important compounds at 77°K. A large amount of overlap between the phosphorescence spectrum of the donor and the absorption spectrum of the acceptor was a necessary requirement for efficient transfer. In all cases, they found the experimental transfer distance to be in good agreement with that predicted from Förster's expressions. Transfer from the triplet level of phenanthrene-d_{10} to the singlet level of Rhodamine B was reported by Bennett, Schwenker, and Kellogg[8] at 77°K. They concluded that the transfer mechanism must be due to a dipole–dipole interaction. In a subsequent publication, Kellogg[9] analyzed the decay data for the phosphorescence emission of triphenylene in the presence of an energy acceptor, Rhodamine B, using the method of Inokuti and Hirayama.[10] He obtained a distance dependence of R^{-6}, thus confirming the dipole–dipole mechanism.

Between 1954 and 1962 various experimental and theoretical studies were made on the effects of solvent viscosity on the efficiency of the long-range dipole–dipole energy transfer mechanism.[11–16] During this period the experimental findings of the various workers seem to offer no definite conclusion, while the theoreticians argued that Förster's expressions represent the limit as the viscosity approaches infinity. The first experimentally sound study of the effect of solvent viscosity on the transfer of excitation energy was made by Melhuish.[17] Upon examining the donor–acceptor combination of 9-methylanthracene–perylene as a function of solvent viscosity at a constant temperature, he found that an increase in solvent fluidity brought about an increase in transfer efficiency.

An excellent treatment of the effect of solvent viscosity on the efficiency of dipole–dipole energy transfer can be found in the papers by Feitelson.[18,19] He discussed the influence of translational movement on the efficiency of the singlet–singlet energy transfer between 9-methylanthracene and perylene from a theoretical and experimental viewpoint. However, his experimental findings did not agree with his derived expressions; the results pointed to a larger viscosity dependence than Feitelson expected. In 1968, Feitelson, Katchalski, and Elkana[20] reported the systematic study of the energy transfer efficiency between naphthalene and anthranilic acid as a function of solvent viscosity. Naphthalene was chosen as a donor because of its long singlet lifetime, 100 nsec. The results were analyzed in accordance with the method of Steinberg and Katchalski,[21] and the dependence of the transfer efficiency on the diffusion coefficient was clearly established by their findings.

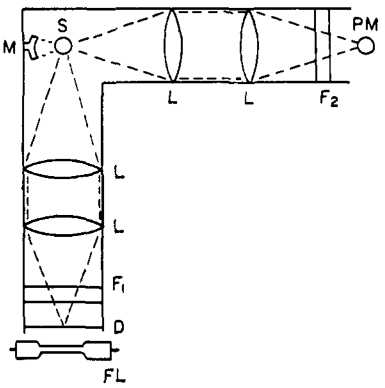

Figure 1. Phosphorescence lifetime apparatus: L, lenses; M, parabolic mirror; S, sample cell; D, diaphragm; F$_1$, excitation filter; F$_2$, emission filter; PM, photomultiplier; FL, flash lamp.

All of the previous work on triplet–singlet energy transfer has been done at low temperatures in solid media. In every case the critical transfer distance found experimentally agreed with the R_0 from Förster's expressions. Förster assumed in his derivation that the Brownian translational movement is slow enough so that each individual transfer process may be considered to occur at a constant distance. For solutions of moderate viscosity or solid solutions, this is a valid assumption. However, the average intermolecular distance for a donor–acceptor combination is not necessarily constant over the lifetime of the donor state in solutions of low to moderate viscosities. This is particularly true if the donor happens to be a triplet, where the solution lifetime can range from microseconds to tens of milliseconds. Therefore, even in dilute solutions, diffusion can turn the seemingly inefficient triplet–singlet transfer into a highly efficient process. Its application to photochemistry, photobiology, and chemiluminescence studies may find it to be an extremely productive photochemical tool.

Experimental Section

Chemicals. All compounds used in this study were obtained commercially and purified by recrystallization and/or vacuum sublimation. All solvents were of spectroquality and were used without further purification.

Apparatus. Spectra. Ultraviolet and visible absorption measurements were performed on a Cary 14 recording spectrophotom-

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eter. Fluorescence spectra were taken on a G. K. Turner Associates Model 210 Spectro absolute spectrofluorimeter.

Kinetics. The kinetics of the decay of the triplet state donor molecules were monitored by the techniques of flash photolysis and phosphorescence lifetime measurements. The flash photolysis apparatus used was a modified version of that described by Bailey, *et al.*[22] A Hilger-Engis f/5.2 monochromator-spectrograph was installed for use in both the kinetic and spectroscopic modes of operations. A Schmidt trigger meter system was installed to allow continuous voltage adjustments on the power supply for the main flash lamps.

The apparatus used to measure phosphorescence lifetimes is shown in Figure 1. Excitation was provided by a Suntron 6 flash lamp powered by a 2-μF, 10-kV power supply (Model B, Xenon Corp.) The time characteristics of this system are a 2-μsec rise time, a 4-μsec half-width, and a 12-μsec base width. Combinations of filters were used to ensure careful filtering of the unwanted regions of the spectrum. Corning filters No. 7-60 and 7-37 along with a 4850-Å broad pass filter and a Corion Corp. 4800-Å interference filter gave an absorption greater than five in all regions of the spectrum, except the 3200–3800- and the 4772–4825-Å regions used for the excitation and detection of the phosphorescence of benzophenone, respectively. Amplification of the phosphorescence signal was accomplished by placing a load resistor between the photomultiplier tube, an RCA 1P21, and the oscilloscope, taking care that the RC time constant of the network was smaller than the decay time of the phosphorescence. The oscilloscope was a Tektronix Model 556 with a Type 1A1 plug-in.

Procedure. Low-Temperature Phosphorescence. An Aminco–Bowman micro dewar and sample tube kept the solutions at liquid nitrogen temperatures, 77°K. No special degassing procedures were used in this work.

Fluorescence Enhancement. From stock solutions of donor and acceptor, solutions of varying concentrations of donor and fixed concentration of acceptor were prepared by transferring an aliquot of the stock to a volumetric flask. An absorption spectrum was taken on each of the solutions just prior to running the fluorescence spectra. The excitation band width of the Spectro 210 was set for 100 Å. Where possible all spectra were taken on the same sensitivity setting and the same emission band width. In no case was the emission band width changed during a set of solutions.

Triplet Quenching in Solution. The solutions used in the flash photolysis studies were degassed by freeze–pump–thaw at a residual pressure $<10^{-3}$ Torr. The ground state absorption of the donor in a 1-cm cell was kept below 0.7 to minimize the occurrence of concentration gradients upon flashing. The triplet–triplet absorption band in phenanthrene was centered at 4900 Å. The monochromator had a dispersion of 25 Å/mm at 5000 Å, with a slit width of 0.1 mm. Absorption spectra taken before and after flashing showed no decomposition in either the phenanthrene or the Rhodamine B. Ethanol was the solvent used in this study.

Careful degassing of the solvent was performed on the benzophenone solutions in Freon. An Ace Glass right-angle high-vacuum Teflon valve fitted with a Pyrex curvette was used in degassing by freeze–pump–thaw. The concentration of benzophenone was kept constant, while the acceptor concentration varied from 1.2×10^{-6} to 4.7×10^{-6} *M*. Absorption spectra of the solutions used served as a check on the concentration.

Results

Several types of experiments were performed on different donor–acceptor combinations to demonstrate the occurrence of triplet–singlet energy transfer in fluid solution. The donor–acceptor systems studied were benzophenone–perylene, phenanthrene–Rhodamine B, and diphenylamine–perylene.

Initial experiments on phosphorescence quenching at 77°K in EPA[23] demonstrated the dipole–dipole nature of this process. Each system showed a marked enhancement of acceptor fluorescence as a function of donor concentration in fluid solution at room temperature.

Additional fluid solution work was concerned with quenching of the triplet state lifetime of the donor molecule by the acceptor. By monitoring the decay of room-temperature phosphorescence emission[24–26] or the decay of the triplet–triplet absorption bands of the donor, the kinetics of the energy transfer process were followed.

None of the three systems proved to be ideal for each study. No room-temperature phosphorescence from either phenanthrene or diphenylamine was detectable and the interference of the triplet–triplet absorption bands of perylene with those of benzophenone prevented flash photolysis from being used in the benzophenone–perylene system. Therefore, independent quenching studies on the benzophenone–perylene system and the phenanthrene–Rhodamine B system were performed using the phosphorescence emission and the triplet–triplet absorption methods, respectively.

Low-Temperature Phosphorescence Quenching. Table I shows the effect of acceptor on the donor phosphorescence lifetimes in EPA at 77°K for the various donor–acceptor combinations. In all systems an increase in acceptor concentration resulted in a reduction of the donor lifetime. The concentrations of acceptors used in this study were sufficiently low that deviation from exponential decay caused by the dipole–dipole energy transfer was limited to the first one-third of the first lifetime of the donor triplet state. Measurements were made over three lifetimes. The straight-line portion of the decay curve that followed was used to calculate $k_t + k_{et}[A]$, which was then used in Stern–Volmer fashion to calculate k_{et}.

Table I. Phosphorescence Quenching at 77°K[a]

	Benzophenone[b]–perylene		Phenanthrene[c]–Rhodamine B		Diphenylamine[d]–perylene	
	[A],[e] *M*	k_p, sec^{-1}	[A],[e] *M*	k_p, sec^{-1}	[A],[e] *M*	k_p, sec^{-1}
	. . .	178	. . .	0.284	. . .	0.516
	1.5×10^{-4}	189	6.5×10^{-5}	0.290	1.5×10^{-4}	0.532
	3.0×10^{-4}	203	1.3×10^{-4}	0.297	3.0×10^{-4}	0.555
	4.5×10^{-4}	214.	2.0×10^{-4}	0.305	4.5×10^{-4}	0.568
	6.0×10^{-4}	223	2.6×10^{-4}	0.312	6.0×10^{-4}	0.609
k_{et}, M^{-1} sec^{-1}						
Obsd	7.4×10^4		1.1×10^2		1.1×10^2	
Calcd	2.4×10^4		0.4×10^2		0.5×10^2	
R_0, Å	55		53		45	

[a] Solvent is EPA. [b] [Benzophenone], 3.0×10^{-3} *M*. [c] [Phenanthrene], 3.4×10^{-3} *M*. [d] [Diphenylamine], 3.4×10^{-3} *M*. [e] Acceptor concentration.

Ware[27] has presented a procedure by which the second-order quenching constant can be calculated from Förster's expression and the experimentally obtained R_0. At R_0, the rate of deactivation of the donor triplet state by energy transfer is equal to the rate of deactivation of the donor in the absence of acceptor, as shown

$$k_{et}[A][D] = k_t[D] \qquad (4)$$

where [A] and [D] are the concentrations of the acceptor

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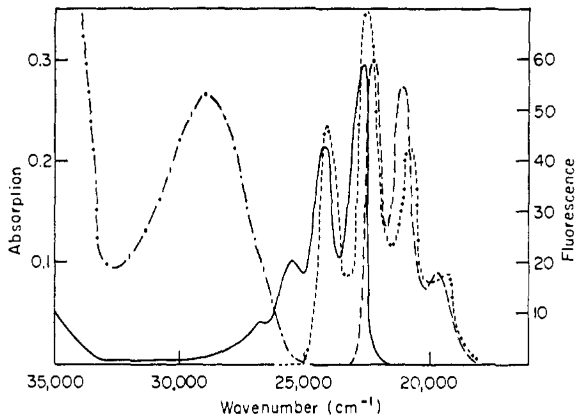

Figure 2. ------, phosphorescence spectrum of a 3.0 × 10^{-3} *M* solution of benzophenone in EPA at 77°K; —·—, absorption spectrum of a 2.2 × 10^{-3} *M* solution of benzophenone in benzene; ——, absorption spectrum of a 1.0 × 10^{-6} *M* solution of perylene in benzene; — —, fluorescence spectrum of perylene, given in relative units.

and donor, respectively, and k_t is the rate constant for triplet deactivation. The concentration of acceptor corresponding to an intermolecular distance of R_0 is given by

$$[A] = \frac{3000}{4\pi R_0^3} \tag{5}$$

By combining eq 2, 4, and 5 the expression for k_{et} is obtained.

$$k_{et} = 4.66 \times 10^{10} k_t \left[\phi \int f_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \right]^{1/2} \tag{6}$$

The values calculated for k_{et} by this method are k_{et} = 2.4 × 10^4, 0.5 × 10^2, and 0.4 × 10^2 l. mol^{-1} sec^{-1} for the benzophenone–perylene, diphenylamine–perylene, and the phenanthrene–Rhodamine B systems, respectively. In all cases, the experimental values were higher than the calculated values. However, it is worthwhile to note that the ratios of the experimental rate constants agree to within 10% with the ratios of the calculated rate constants. The higher values for the experimental rate constants are probably due to a nonuniform distribution of donor–acceptor pairs in the glass or possibly diffusion through the glass.

Work performed in our laboratory by Abbott[28] on the benzaldehyde–perylene, benzaldehyde–9,10-diphenylanthracene, and benzaldehyde–Rhodamine B systems gave similar results, *i.e.*, R_0 = 59, 46, and 38 Å and k_{et} = 2.4 × 10^4, 1.4 × 10^5, and 7.6 × 10^4 l. mol^{-1} sec^{-1}, respectively. Again the experimental values were higher than the calculated values. A critical transfer distance of approximately 45–55 Å has been found by most previous workers.[7–9]

Fluorescence Enhancement. The fluorescence intensity of an acceptor, $f_A^0(\lambda)$, is proportional to the percentage of incident light absorbed by the acceptor, $f_A^0(\lambda) = g(\lambda)\phi_f \alpha I_0$, where $g(\lambda)$ is an instrumental parameter dependent on the solid angle viewed by the detector and the sensitivity of the detector at the emission wavelength, ϕ_f is the quantum efficiency of fluorescence, α is the absorptivity of the acceptor at the exciting wavelength, and I_0 is the intensity of the exciting radiation. In the absence of an energy transfer process, the fluorescence intensity would decrease if the intensity of light available to the acceptor is reduced, *i.e.*, with the addition of another absorbing species. The expression for the fluorescence intensity of the acceptor would become $f_A(\lambda) = f_A^0(\lambda)(1 - \beta)$, where β is the fraction of the exciting radiation absorbed by the second species. Equation 7 expresses $f_A(\lambda)$ in terms of donor absorption

$$f_A(\lambda) = f_A^0(\lambda)/10^{A_D} \tag{7}$$

where A_D is the absorption of the donor at the exciting wavelength.

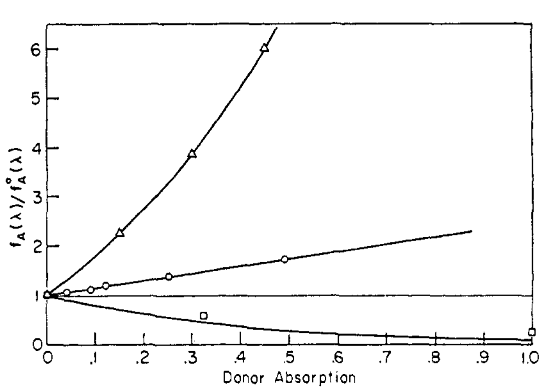

Figure 3. A plot of the ratio of the acceptor fluorescence intensity with and without donor *vs.* donor absorption. All measurements of perylene fluorescence were performed at 4750 Å: Δ, diphenylamine–perylene system, excitation at 3200 Å, [diphenylamine] 0.0, 2.0, 4.0, 6.0 × 10^{-4} *M*, [perylene] 3.75 × 10^{-5} *M*; ○, benzophenone–perylene system, excitation at 3300 Å, [benzophenone] 0.0, 4.0, 8.0, 10.0, 20.0, 40.0 × 10^{-4} *M*, [perylene] 1.0 × 10^{-6} *M*; □, benzil–perylene system, excitation at 3400 A, [benzil] 0.0, 1.7, 5.1 × 10^{-3} *M*; [perylene] 1.0 × 10^{-5} *M*; solid line, $f_A(\lambda)/f_A^0(\lambda)$ *vs.* 10^{+A_D}.

In all donor–acceptor combinations, the excitation wavelength was selected to minimize the acceptor absorption. Represented in Figure 2 are the absorption and phosphorescence spectra of benzophenone, along with the absorption and fluorescence spectra of perylene. By using 3300-Å radiation, the donor absorption can be maximized, while that of the acceptor will be minimized.

Figure 3 shows the plots of $f_A(\lambda)/f_A^0(\lambda)$ *vs.* the donor absorption for the diphenylamine–perylene and benzophenone–perylene systems along with a plot of eq 7. In both systems an enhancement of the acceptor fluorescence was noted with an increase in the donor concentration, thus indicating the transfer of excitation energy from the donor to the acceptor. In both cases the ratios of vibronic peaks in the perylene fluorescence spectrum did not vary with donor concentration, indicating a lack of interference from donor emission. When a donor molecule such as benzil was used along with perylene as the acceptor no fluorescence enhancement was observed; in fact the fluorescence intensity of the acceptor decreased with added donor.

The triplet energy levels of benzophenone (E_T = 69 kcal/mol) and diphenylamine (E_T = 72 kcal/mol) lie above the singlet level of perylene (E_S = 64 kcal/mol), while the triplet level of benzil lies 10 kcal/mol below the perylene singlet state. Therefore, while triplet–singlet energy transfer is energetically possible in the benzophenone–perylene and diphenylamine–perylene systems, it can be ruled out in the benzil–perylene case strictly on energy considerations.

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[28] S. R. Abbott and D. M. Hercules, MIT, unpublished results.

The addition of 5.7×10^{-4} M diphenylamine to a 1.0×10^{-6} M solution of perylene brought about a 60% increase in the fluorescence intensity of perylene. However, the area under the fluorescence spectrum of a 5.7×10^{-4} M diphenylamine solution remained constant to ±3% upon the addition of 1.0×10^{-6} M perylene. Therefore, while diphenylamine enhances the fluorescence of perylene, perylene does not affect the fluorescence intensity of diphenylamine. The overlap integral between the diphenylamine fluorescence spectrum and the perylene absorption spectrum is on the order of 10^{-16}–10^{-17}. This is three orders of magnitude smaller then the overlap integral found between a donor–acceptor pair for singlet–singlet energy transfer. Because of this poor overlap, the above results can not be attributed to energy transfer from the diphenylamine singlet. Therefore the energy transfer process must originate from a state other than the singlet state of diphenylamine.

In the benzophenone case, the intersystem crossing rate from the first singlet to the triplet manifold is known to be 10^{10} sec^{-1},[29] with a conversion efficiency greater than 99%. It is very unlikely that an intermolecular energy transfer process originating from the benzophenone singlet state can compete effectively with the intersystem crossing process.

Triplet Quenching in Fluid Solution. Both flash photolysis and direct measurement of phosphorescence decay have been employed in this study on the phenanthrene–Rhodamine B and the benzophenone–perylene systems, respectively. In the fluid solution lifetime studies, the time–base profile of the flash lamps used to excite the donor was sufficiently long to mask any early nonexponential decay of the donor in the presence of acceptor. As seen in Table II, the measured rate constant for the triplet decay of phenanthrene in an ethanol solution increased with added Rhodamine B. From a plot of these data, a quenching rate constant, $k_{et} = 3.9 \times 10^7$ l. mol^{-1} sec^{-1}, was obtained. The measured rate constant of the phosphorescence decay of benzophenone in Freon at 20° increased with added perylene. The quenching rate constant for this system was found to be $k_{et} = 7.1 \times 10^9$ l. mol^{-1} sec^{-1}.

Table II. Triplet Quenching in Fluid Solution

Phosphorescence quenching Benzophenone^a–perylene		Triplet–triplet absorption studies Phenanthrene^b–Rhodamine B	
[A],^{c} M	k_t, sec^{-1}	[A], M	k_t, sec^{-1}
. . .	2.73×10^4	. . .	3.12×10^3
1.2×10^{-6}	3.45×10^4	1.4×10^{-5}	3.59×10^3
2.3×10^{-6}	4.28×10^4	2.8×10^{-5}	4.10×10^3
3.4×10^{-6}	5.11×10^4	4.2×10^{-5}	4.90×10^3
4.7×10^{-6}	6.19×10^4	5.6×10^{-5}	5.21×10^3
		7.0×10^{-5}	5.95×10^3
k_{et}, M^{-1} sec^{-1}			
7.1×10^9		3.9×10^7	

[a] [Benzophenone], 1.0×10^{-3} M; solvent, Freon. [b] [Phenanthrene], 1.0×10^{-4} M; solvent, ethanol. [c] Acceptor concentration.

Solvent Viscosity. The effect of solvent viscosity on the efficiency of acceptor fluorescence enhancement is shown in Figure 4. This is a plot of the rate of change of acceptor fluorescence as a function of donor concentration, $d(f_A(\lambda)/f_A^0(\lambda))/d[D]$, plotted against the solvent viscosity. Phenanthrene and Rhodamine B were the donor and acceptor, respectively, in this study. The various solvents were ethanol, ethylene glycol, propylene glycol, and cyclohexanol, the viscosities of which were measured with an Ostwald viscometer and were found to be 1.2, 17, 43, and 61 cP at 20°, respectively.

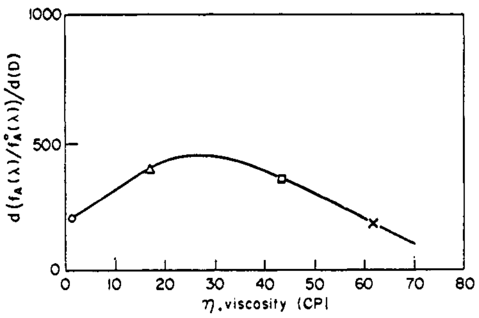

Figure 4. A plot of the change in the ratio of acceptor fluorescence with and without donor against donor concentration *vs.* solvent viscosity: ○, ethanol; △, ethylene glycol; □, propylene glycol; ×, cyclohexanol.

Discussion

Although triplet–singlet energy transfer by a dipole–dipole mechanism has been reported at low temperature, the observation of this process in fluid solution has not been reported to date. The fluorescence enhancement studies performed in fluid solution showed that the singlet state of the acceptor was sensitized by the donor. The spin-allowed process of singlet–singlet transfer or the trivial reabsorption mechanism, *i.e.*, reabsorption of donor fluorescence by acceptor, was shown not to occur in the diphenylamine–perylene system. If either of these processes were responsible for the sensitization of the acceptor singlet state, a corresponding decrease in donor emission intensity would have been observed. Since no decrease was found these processes were ruled out.

Alternately, one might argue that the results reported here can be explained by triplet–triplet (T–T) energy transfer, since this is a diffusion controlled process. If this were the case, fluorescence enhancement would require, first, T–T energy transfer to produce the acceptor triplet, and second, T–T annihilation to produce the acceptor singlet. That this combination could cause significant fluorescent enhancement for solutions 10^{-6} M in acceptor seems very unlikely.

Table III summarizes the quenching rate constants for the three systems studied at low temperature and in fluid solution at room temperature.

Table III. Quenching Rate Constants

Donor–acceptor	Low temperature	Fluid solution
Phenanthrene–Rhodamine B	1.1×10^2	3.9×10^7
Benzophenone–perylene	7.4×10^4	7.1×10^9
Diphenylamine–perylene	1.1×10^2	

In solutions of very high viscosity or in rigid media, such as low-temperature glass, diffusion of solute

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(29) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, and Co., New York, N. Y., 1965, p 78.

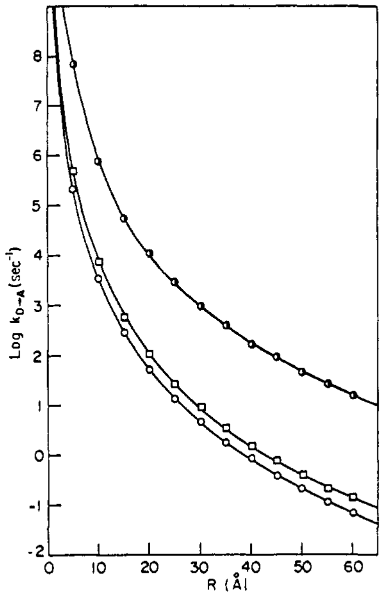

Figure 5. A plot of log K_{D-A} *vs.* R (Å): ◑, benzophenone–perylene (K = 7.9 × 10^{11}); □, phenanthrene–Rhodamine B (K = 7.7 × 10^9); ○, diphenylamine–perylene (K = 3.5 × 10^9).

molecules from one site to another is negligible. Thus, the average intermolecular distance is a fixed value and is governed by the concentrations of solute molecules present. However, in solutions of low to moderate viscosities the intermolecular distances are continuously changing. If an acceptor molecule is, on the average, at a distance R_0 from a donor during the lifetime of the excited state of the donor, energy transfer occurs at a rate equal to that of donor decay. Therefore, although the quantum yield of phosphorescence in fluid solution is usually many orders of magnitude lower than that in rigid media, the energy transfer efficiency may be higher for the same donor–acceptor systems. This was indeed found to be the case for the benzophenone–perylene and phenanthrene–Rhodamine B systems.

In accordance with Förster's theory of inductive dipole–dipole energy transfer, the strength of the donor–acceptor interaction must be equal to or greater than the strength of the transition moment in the excited donor molecule for energy transfer to occur. When the donor molecule is a triplet, the acceptor interaction need only compete with the relatively weak triplet–singlet transition of the donor. Therefore, each donor–acceptor combination will have a critical transfer distance at which the interaction strength can compete with phosphorescence. It has been observed that the critical transfer distance, R_0, found experimentally, and the R_0 predicted from Förster's theory (eq 2) are in good agreement for all systems studied at low temperature in rigid media.[7–9] However, for systems studied at room temperature in fluid solutions, the energy transfer process follows diffusion controlled kinetics, and large effects are observed at concentrations several orders of magnitude lower than that for rigid media.

The rate of energy transfer calculated from eq 2 depends strongly on the lifetime of the donor and the degree of overlap between the donor emission and the acceptor absorption spectra. Overlap integrals of 3.9 × 10^{-14}, 5.7 × 10^{-14}, and 2.2 × 10^{-13} were calculated for the benzophenone–perylene, the diphenylamine–perylene, and the phenanthrene–Rhodamine B systems, respectively, while the donor lifetimes are 6 × 10^{-3},[30] 1.9,[31] and 3.3[30] sec, respectively. In order to represent the rate of transfer graphically, eq 2 was expressed in the form $k_{D\rightarrow A} = K/R^6$, where K included all the parameters present in Förster's expressions. The values of K are given in Figure 5 for each donor–acceptor pair studied. The differences in the values of K are due primarily to the different lifetimes of the donor molecules and secondarily to the varying degree of overlap in these systems; therefore, K is a measure of the relative strength of the dipole–dipole interaction between the different donor–acceptor combinations.

The ratio of the viscosities of Freon and ethanol is 1.7. For bimolecular processes occurring at diffusion controlled rates in these solvents, the ratio of the diffusion controlled rate constants will also be 1.7. If the experimentally obtained quenching rate constant for the benzophenone–perylene and the phenanthrene–Rhodamine B systems are compared, one finds that the ratio of the two values is 1.8 × 10^2. Dividing this by the ratio of the diffusional rate constants, in order to correct for the differences in viscosities for the two experiments, a value of 1.05 × 10^2 is obtained. Referring back to Figure 5, a comparison of the relative strengths of the dipole–dipole interaction for the benzophenone–perylene and phenanthrene–Rhodamine B systems gave a value of 1.01 × 10^2. The agreement in the ratios for the relative strength of the dipole–dipole interaction and the experimental quenching rate constants indicates that the triplet–singlet energy transfer process occurring in fluid solution is indeed dipole–dipole in nature.

Referring to the results of Figure 4, it is probable that the initial rise in the energy transfer efficiency with increased viscosity was due to a lengthening of the triplet lifetime in solution. However, as the viscosity increased, the diffusion coefficient of the solutes became smaller, and consequently the donor and acceptor were not able to diffuse to within the critical transfer distance; hence a decrease in the transfer efficiency. It is interesting to note that the average distance a molecule can travel in 1 μsec in a solution with a viscosity of 1cP is approximately 500 Å. Therefore, even in a diluted solution of acceptor there exists a finite chance of a donor molecule approaching the critical transfer distance of 30–60 Å during the lifetime of the triplet donor.

The results presented here clearly indicated the occurrence of triplet–singlet energy transfer in fluid solution by a dipole–dipole interaction. The efficiency of this process is governed by the lifetime of the triplet state in solution and the viscosity of the solution, insofar as a long lifetime and low viscosity allows the donor–acceptor pair to diffuse to within the critical transfer distance. The importance of this process has not yet been realized in photochemistry, photobiology, and chemiluminescence. The triplet states of many large molecules behave as metastable "energy sinks" from which some very interesting chemistry can originate. In contrast to the well-known triplet–triplet energy transfer process, the sensitized state in the triplet–singlet process is an emissive state; therefore, it can be monitored with a simple fluorimeter. Also, the dipole–

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(30) J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966.

(31) Experimentally determined.

dipole nature of the triplet–singlet process allows for large intermolecular distances; and consequently, the efficiency of the triplet–singlet process may be orders of magnitude larger than the triplet–triplet process in solution, which proceeds *via* an exchange mechanism. The kinetics of the thermal decomposition of various aromatic peroxides have been stuided by Abbott and Hercules,[28] using triplet–singlet energy transfer as a mechanistic tool. Recently, White, *et al.*,[32] have postulated the occurrence of triplet–singlet energy transfer in the chemiluminescence of phthalic hydrazide derivatives. It will be interesting to look into the role of the triplet–singlet energy process in certain bioluminescence reactions.

Acknowledgment. This work was supported in part through funds provided by the United States Atomic Energy Commission under Contract No. AT(30-1)-905.

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Intermolecular Triplet Energy Transfer. II. From Benzene, Acetone, and Biacetyl to π-Bonded Molecules

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Abstract: The relative rates of the triplet electronic energy transfer from benzene to olefinic hydrocarbons (mono- and diolefins) and CS_2 have been measured in competition with *cis-trans* isomerization of *cis*-2-butene in the gas phase. In some cases, deuterated olefinic acceptor molecules have been used and varying degrees of deuterium isotope effects on rate have been observed. The rates of the triplet electronic energy transfer from acetone and and biacetyl to some π-bonded molecules have also been measured by the quenching of the direct phosphorescence emission. So far, CS_2 is found to be the most efficient quencher of the triplet benzene and acetone. These and other rate–energetics data will be discussed in reference to existing mechanistic models of triplet energy transfer processes.

The kinetics of the intermolecular triplet electronic energy transfer processes in the gas phase involving simple organic molecules of photochemical interest have been studied extensively in the recent years. These molecular energy transfer systems are expected to be simpler than those studied in the condensed media where the environmental effects are usually not negligible and therefore they can be used for a rigorous test of various mechanistic models in the laboratory.

Benzene in its lowest triplet state ($^3B_{1u}$) having an electronic excitation energy of 84.4 kcal/mol was first used by Ishikawa and Noyes to sensitize the phosphorescence emission from biacetyl.[1] Since then, the triplet benzene photosensitization method has been widely used for mechanistic diagnosis of primary photochemical processes,[2–6] and systematic studies of the triplet energy transfer rates involving various hydrocarbons, ketones, aldehydes and ethers as acceptors have been conducted.[2,7–9] Triplet energy transfer from acetone to biacetyl was studied by Heicklen and Noyes[10a] 10 years ago, and the relative rates of triplet energy transfer from acetone and biacetyl, having triplet excitation energies of 79–82 and 57 kcal/mol, respectively, to a variety of olefinic molecules were measured by Rebbert and Ausloos.[10b] The observation of substantial deuterium isotope rate effects for these systems as well as for the benzene–olefin systems studied in our laboratory has been recently reported.[8] Only recently an interesting study of the H atom scrambling and *cis–trans* isomerization of dideuterioethylene sensitized by triplet benzene and its derivatives has been reported.[11]

We have carried out additional measurements of the triplet energy transfer rates from the above-mentioned donors to a few more hydrocarbons and their deuterated analogs and CS_2, and we now wish to discuss in detail the experimental fit of the rate and energetics data to existing mechanistic models.

Experimental Section

Most of the chemicals used in this work are of the same grade as those used in the earlier study[7c] and they were handled similarly. Acetylene was generated from calcium carbide and purified on a vacuum line before use. A commercial grade 1,4-pentadiene was purified by gas chromatography before use. Acetone (Baker "Analyzed") was used directly. The following deuterated olefins were obtained from Merck Sharp and Dohme of Canada and used

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