

Figure 5 give $k_2/(k_1 + k_2) \cong 0.10$ and 0.073 , respectively. Although the agreement may be fortuitous, these values are in excellent accord with our previous estimates of this quantity for the pure SO_2 system. However, serious problems bar the acceptance of our simple mechanism involving a single $^3\text{SO}_2$ reactive species for the $3130\text{-}\text{\AA}$ excitation of the $\text{SO}_2\text{-CO}$ mixtures. Thus Cehelnik, *et al.*, found that only very incomplete quenching of the reaction resulted on addition of triplet quenchers. This result cannot be rationalized in terms of our simple mechanism. They also found that Φ_{CO_2} was independent of $[\text{SO}_2]$ at pressures above 60 Torr. This observation could be the accidental result of the experimental conditions employed by Cehelnik, *et al.* Light absorption must be very nonuniform in the runs at pressures greater than 60 Torr. The SO_3 product of reaction 8a would be concentrated in a small volume at a distance of only a few millimeters from the cell face. If the reaction $\text{SO}_3 + \text{CO} \rightarrow \text{SO}_2 + \text{CO}_2$ occurs significantly for these conditions, then Φ_{CO_2} may appear to be independent of $[\text{SO}_2]$.

In any case, it is obvious that the simple mechanism found to be adequate in this work for the $\text{SO}_2\text{-CO}$ mix-

ture photolyses within the "forbidden" absorption band cannot fit well the photochemistry found for these mixtures irradiated within the first allowed band of SO_2 . Further work will be necessary to define better this most interesting and complex system. We will await more definitive proof of the chemical involvement of the two nonemitting states of SO_2 invoked by Cehelnik, *et al.*,³ before accepting this explanation of their results.

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A Study of the Viscosity Dependence of Triplet-Singlet Energy Transfer in Solution^{1a}

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Abstract: A detailed study of the diffusion effects on triplet-singlet energy transfer in solution confirmed the dipole-dipole nature of this process. The probability of transfer was found to be proportional to $D^{3/4}$ as predicted for dipole-dipole energy transfer by Yokota and Tanimoto. The experimental and theoretical values of the strength of dipole-dipole coupling in the benzophenone-erylene system are compared.

The process of triplet-singlet energy transfer has recently been reported in fluid solution at room temperature by Vaudo and Hercules.^{2,3} Investigations into the decay kinetics of the donor-acceptor systems of benzophenone-erylene and phenanthrene-Rhodamine B in fluid solution have shown the ratio of the quenching rate constants for the two systems to be the same as the ratio predicted by the dipole-dipole interaction strength. The kinetic study provided qualitative evidence that triplet-singlet energy transfer in fluid solution proceeds *via* a dipole-dipole interaction mechanism. Quantitative confirmation of that conclusion was the aim of the present work.

The effects of diffusion on resonance energy transfer by a dipole-dipole mechanism have been the object of many studies in recent years. Weinreb and Cohen⁴

studied the efficiency of singlet-singlet transfer in the naphthalene-anthracene system as a function of the diffusion coefficient, D . These authors observed that as D approached zero, the energy transfer rate approached the value predicted by Förster's⁵ theory of dipole-dipole energy transfer. Similar observations have been reported by Kurskii and Selivanenko,⁶ Samson,⁷ and Melhuish.⁸

Feitelson and his coworkers⁹ in a series of articles from 1966 to 1968 discussed in detail the theoretical and experimental aspects of diffusion on dipole-dipole energy transfer. The observed increase in transfer yield in the naphthalene-anthranilic acid system with

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(1) (a) Taken in part from the Ph.D. thesis submitted by A. F. Vaudo to the Massachusetts Institute of Technology, Cambridge, Mass., June 1970; (b) National Institutes of Health Predoctoral Fellow, 1968-1970.

(2) A. F. Vaudo and D. M. Hercules, *J. Amer. Chem. Soc.*, **92**, 3573 (1970).

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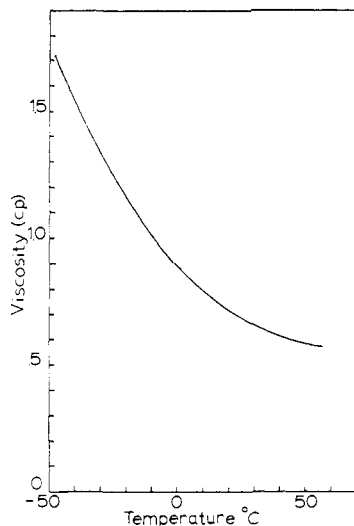


Figure 1. Viscosity of Freon 113 as a function of temperature.

increasing D matched that predicted by their theory. However, their derivation dealt with the effects of changing viscosity on the total luminescence yield of the energy-transfer process. The overlap requirements for the donor emission spectrum and the acceptor absorption spectrum in the dipole-dipole process are analogous to those in the trivial reabsorption process. Therefore, interference from that process could prove bothersome to the experimenter.

Recently, Yokota and Tanimoto¹⁰ presented a quantitative description for the reduction in the donor lifetime as a function of D where dipole-dipole energy transfer occurs. This procedure eliminates any possible interference from the trivial reabsorption process. For transfer by a collisional mechanism, the probability of transfer is proportional to D , a measure of the collision frequency. However, for a dipole-dipole mechanism, Yokota and Tanimoto's derivation predicts a $D^{3/4}$ dependence for the transfer probability.

The intent of this paper is to present experimental evidence that the probability of triplet-singlet energy transfer is proportional to $D^{3/4}$, confirming our previous qualitative conclusion that triplet-singlet energy transfer proceeds *via* a dipole-dipole mechanism.

Experimental Section

The benzophenone used was purchased from Aldrich Chemical Co., recrystallized three times from ethanol and hexane, and vacuum sublimed. Perylene also was purchased from Aldrich Chemical Co. and was vacuum sublimed three times. The solvent, trichlorofluoroethane (Freon 113), was spectroquality, purchased from Matheson Coleman and Bell, and was used without further purification.

Absorption spectroscopy was used to determine the change in concentrations of benzophenone and perylene at various temperatures. In this way no assumptions were needed regarding the change in density of the solvent with temperature. A Cary Model 14 spectrophotometer was used in this study.

The apparatus used to determine the phosphorescence lifetimes has been described.^{2,3} A specially designed dewar was used to vary the temperature of the solution over a wide range from -40 to $+50^\circ$. Measurement of the temperature was accomplished by positioning an alumel-chromel thermocouple adjacent to the cell. Thermal contact was made between the dewar and the cell by liberally applying a heat-conducting paste purchased from Air Products, Inc. During a run, the cell was cooled to its starting tem-

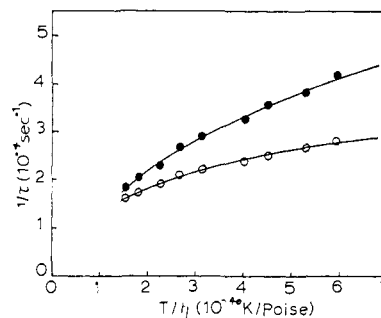


Figure 2. Dependence of the phosphorescence decay of benzophenone in Freon 113 on T/η : O, $1.0 \times 10^{-3} M$ benzophenone; ●, $1.0 \times 10^{-3} M$ benzophenone, $3.3 \times 10^{-6} M$ perylene.

perature (ca. -30°) and allowed to warm at a rate less than $1^\circ/\text{min}$. This slow warming rate ensured that the system was constantly in thermal equilibrium. Temperature measurements were $\pm 1^\circ$.

Viscosity measurements of Freon 113 were made on an Ostwald viscometer from -20 to 40° . Extrapolation was used to obtain viscosities in the higher and lower temperature regions. Changes in the density of Freon 113 as a function of temperature were measured by monitoring the absorbance change of a standard volume of a perylene solution as a function of temperature.

All donor and acceptor solutions were deoxygenated by the procedure of freeze-pump-thaw to a residual pressure of 2×10^{-3} Torr for a minimum of ten cycles. The cells were then flame sealed.

Kinetic Scheme

The decay of the phosphorescence of benzophenone in fluid solution, where impurity quenching is appreciable, can be given as

$$d(^3B)/dt = (k_T + k_Q(Q))(^3B) \quad (1)$$

Here k_T represents the first-order decay of the benzophenone triplet state, k_Q denotes the bimolecular quenching constant, and (Q) is the concentration of adventitious impurities. The second-order term also includes self-quenching of triplet states. The term $(k_T + k_Q(Q))$ will define the spontaneous lifetime $1/\tau_T$ of triplet benzophenone in solution at a particular temperature.

If acceptor perylene is added to the solution, subsequent reduction in triplet lifetime would result. This is represented in

$$d(^3B)/dt = (k_T + k_Q(Q) + k_{ET}(P))(^3B) \quad (2)$$

The measured phosphorescence lifetime will then be given as

$$1/\tau = 1/\tau_T + k_{ET}(P) \quad (3)$$

Therefore, the probability of energy transfer can be expressed by

$$P_{ET} = k_{ET}(P) = 1/\tau - 1/\tau_T \quad (4)$$

The relationship is expected to hold provided the decay kinetics of the donor can be adequately represented by eq 1 and 2.

Theory predicts that under the influence of dipole-dipole coupling the decay of the excited donor molecules will show a component of nonexponential decay. However, this deviation from a phenomenological relationship will be limited to the initial portion of the decay curve. In the present experiments, the long pulse width of the excitation source masked any observation of this nonexponential behavior, and the relations set forth in eq 1 and 2 were found to be valid.

(10) M. Yokota and Tanimoto, *J. Phys. Soc. Jap.*, **22**, 779 (1967).

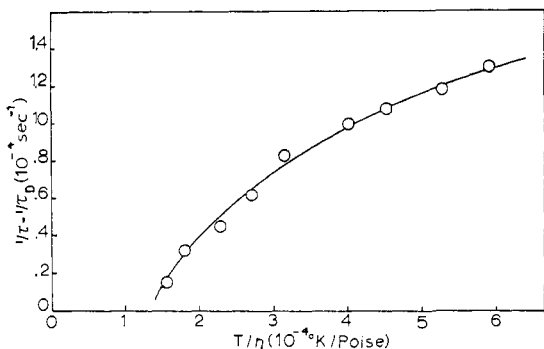


Figure 3. Plot of $1/\tau - 1/\tau_T$ vs. (T/η) .

Results

According to the Stokes–Einstein equation, the relative diffusion coefficient for a pair of unlike molecules in solution is directly related to temperature T and inversely related to viscosity, η , by

$$D = (k/6\pi)(T/\eta)[(1/r_A) + (1/r_D)] \quad (5)$$

where k is Boltzmann's constant and r_A and r_D represent the molecular radii of the donor and acceptor, respectively. Clearly, by varying the T/η ratio, large changes in D can be accomplished without changing the nature of the solvent. Figure 1 is a plot of the temperature dependence of the viscosity of Freon 113 from $+40$ to -40° . Over this range of temperature D will vary from 10^{-6} to 10^{-5} cm^2/sec for the benzophenone–perylene system.

For lifetime measurements at various temperatures, the following procedure was used. The sealed sample cell was placed in the dewar, making certain of good thermal contact. The dewar was then evacuated to 10^{-5} Torr. By adding chunks of Dry Ice to a methanol bath in the reservoir, the sample solution was cooled to below its freezing point. The solution was allowed to thaw slowly, then was refrozen, and thawed twice more to ensure uniformity of temperature. After the solution thawed the third time, lifetime measurements were taken at various temperatures as the solution warmed up to ambient temperature. For temperature above room temperature, hot methanol was added slowly to the reservoir until the desired temperature was reached. The entire procedure took 3 hr to perform.

Figure 2 shows the T/η dependence of the phosphorescence lifetime of benzophenone. The increase in lifetime with decreasing T/η stems from the impurity collisional quenching processes becoming more inefficient at higher viscosities. The energy-transfer process, also displayed in Figure 2, is similarly affected by the diminishing T/η . However, the T/η dependence of the measured phosphorescence lifetime is much more pronounced for the solution containing acceptor.

According to the derivations of Yokota and Tanimoto, the probability of energy transfer will be proportional to D or T/η for collisional quenching and $D^{3/4}$ or $(T/\eta)^{3/4}$ for quenching by a dipole–dipole mechanism. Figures 3 and 4 are plots of $1/\tau - 1/\tau_T$ as a function of T/η and $(T/\eta)^{3/4}$, respectively. The linear dependence of the energy-transfer process with $(T/\eta)^{3/4}$ supports a dipole–dipole mechanism for triplet–singlet energy transfer.

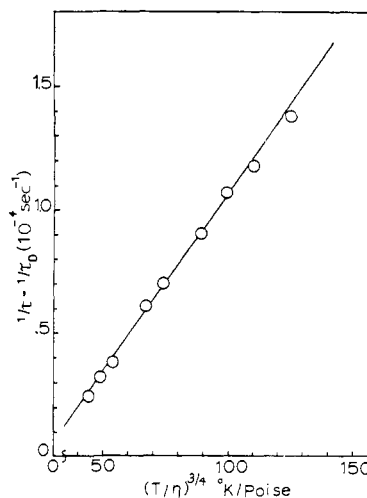


Figure 4. Plot of $1/\tau - 1/\tau_T$ vs. $(T/\eta)^{3/4}$.

Discussion

Yokota and Tanimoto approached the problem of diffusion in dipole–dipole energy transfer in solution as a problem in calculating the scattering length between an excited donor and a ground-state acceptor. The authors assumed as their boundary condition that at an intermolecular distance equal to or less than the collision diameters of both donor and acceptor, the excited donor must deactivate. This deactivation is accomplished by either thermal decay of the excitation energy or a transfer of energy to the acceptor by an exchange mechanism. For intermolecular distances greater than the collisional diameter the excited donor can transfer its energy only by a dipole–dipole mechanism.

The strength of the dipole–dipole interaction between donor and acceptor will be given as

$$V(|r - r_i|) = \alpha/|r - r_i|^6 \quad (6)$$

where α is a constant dependent upon the characteristics of the particular donor–acceptor pair. The term α can be calculated from a consideration of Förster's⁵ equation for dipole–dipole energy transfer

$$k_{D \rightarrow A} = \frac{9000 \ln 10 k^2}{128 \pi^3 n^4 N \tau_0} \frac{1}{R^6} \int f_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \quad (7)$$

Here k^2 is an orientation factor dependent upon the mutual orientation of the transition dipoles of the donor and acceptor (for randomly distributed solutions, $k^2 = 2/3$); n is the refractive index of the solvent; N is Avogadro's number; τ_0 is the intrinsic radiative lifetime of the donor; R is the intermolecular distance; and the integral represents the amount of coincidence between the donor's emission spectrum, $f_D(\bar{\nu})$, and the acceptor's absorption spectrum, $\epsilon_A(\bar{\nu})$, plotted on a wavenumber, $\bar{\nu}$, scale.

At a given distance, the strength of the dipole–dipole interaction for a particular donor and acceptor pair will depend on the magnitude of τ_0 and $\int f_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4}$. Therefore, the term α in eq 6 is a measure of the amount of spectral overlap in the donor–acceptor pair and the oscillator strength of the donor and acceptor transitions. Thus

$$\alpha = \frac{9000 \ln 10 k^2}{128 \pi^3 n^4 N \tau_0} \int f_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \quad (8)$$

Using eq 6 as the form of the interaction potential, Yokota and Tanimoto were able to solve the scattering length problem as a function of diffusion coefficient. The solution of this problem predicts a rather unique dependence on the rate of energy transfer by a dipole-dipole interaction. For quenching at collisional distances the rate of transfer is given by

$$P_{D \rightarrow A} = 4\pi N_A D \alpha \quad (9)$$

where α is the effective radius of collision and N_A is the concentration of the acceptor. For transfer by a dipole-dipole mechanism

$$P_{D \rightarrow A} = (0.676)(4\pi N_A \alpha^{1/4} D^{3/4}) \quad (10)$$

When D is large, both molecules migrate so rapidly that they collide before energy transfer by dipole-dipole interaction can occur, while in solutions with small D , the long-range energy transfer will occur before the donor and acceptor collide.

Verification of this treatment of the relationship between diffusion and dipole-dipole energy transfer was made by Mataga, *et al.*¹¹ In the S-S process between pyrene and perylene, the rate of transfer was proportional to D for values $>3.5 \times 10^{-5}$ cm²/sec and to $D^{3/4}$ for values $<3.5 \times 10^{-5}$ cm²/sec. These authors concluded that at large D , collisional deactivation occurs before dipole-dipole coupling becomes large enough to affect transfer, while at small D , the frequency of collisions is reduced and dipole-dipole energy transfer predominates as the quenching mechanism.

In the present work on T-S energy transfer, a linear dependence on the probability of triplet quenching as a function of $D^{3/4}$ was found. This is shown in Figure 4. The range of D used in this work was 10^{-6} – 10^{-5} cm²/sec.

From eq 10 the slope of the plot in Figure 4 is related to $\alpha^{1/4}$. For the benzophenone-peryene system in Freon 113, $\alpha^{1/4}$ was found experimentally to be 4.9×10^{-10} (cm⁶/sec)^{1/4}. From Förster's equation for dipole-dipole energy transfer $\alpha^{1/4}$ can be calculated from molecular parameters. Using eq 8, a value of 8.7×10^{-10} (cm⁶/sec)^{1/4} was calculated for the benzophenone-peryene system.

(11) M. Tomura, E. Ishiguro, and N. Mataga, *J. Phys. Soc. Jap.*, **25**, 1439 (1968).

Mataga, *et al.*,¹¹ suggested a value of 6.5 Å for r_A and r_D for the pyrene and perylene system. For the benzophenone-peryene system used in this work, a value of 6.5 Å was also assumed to calculate $\alpha^{1/4}$. However, it is interesting to note that if a value of r_D and $r_A = 5$ Å is used, $\alpha^{1/4}$ becomes smaller by a factor of $(5/6.5)^{1/4}$ and, correspondingly, $\alpha^{1/4}$ becomes larger by $(7.5/6.5)^{1/4}$ if 7.5 Å is used for r_A and r_D . The accuracy of the experimentally determined value of $\alpha^{1/4}$ will depend on the values of r_D and r_A chosen. Inaccuracies in the calculated value of $\alpha^{1/4}$ arise from determination of the overlap integrals in eq 8. A 10–20% error in $\int f_D(\bar{r})\epsilon_A(\bar{r})(d\bar{r}/\bar{r}^4)$ is to be expected. It is felt that the difference between $\alpha^{1/4}$ (exptl) and $\alpha^{1/4}$ (calcd) can easily be accounted for by the inaccuracies and approximations inherent in the methods of calculation used.

The linear dependence of $k_{D \rightarrow A}$ vs. $D^{3/4}$ conclusively proves that the T-S energy transfer process proceeds by a dipole-dipole mechanism in fluid solution. The curvature of the plot $k_{D \rightarrow A}$ vs. T/η in Figure 3 rules out the electron-exchange process as a possible mechanism for T-S energy transfer. The long-range nature of the dipole-dipole mechanism in T-S energy transfer allows it to compete successfully with the other triplet deactivation processes in fluid solution.

The solution decay constant of triplet benzophenone is ca. 2×10^4 sec⁻¹, which corresponds to a mean lifetime of $\tau_T = 50$ μsec. The relative diffusion coefficient for this D-A system at 20° is ca. 4×10^{-6} cm²/sec in Freon 113. The translational movement allowed by diffusion for such a solution of D-A is roughly 2000 Å. Therefore, over the lifetime of the triplet donor, the average intermolecular distance can approach collisional diameters. In so doing, the strength of dipole-dipole coupling between ³D and A₀ will increase as R^{-6} .

For the benzophenone-peryene system at a distance of 20 Å the rate of T-S energy transfer by dipole-dipole interaction will be greater than 2×10^4 sec⁻¹. The initial D-A distance for the benzophenone-peryene system in the phosphorescence lifetime studies in solution was on the order of 400 Å. Therefore, T-S energy transfer will become the preferred means of triplet deactivation as the intermolecular distance is reduced to less than 20 Å by diffusion of the D-A pair during the course of the triplet donor's lifetime.