

ENERGY TRANSFER PROCESSES

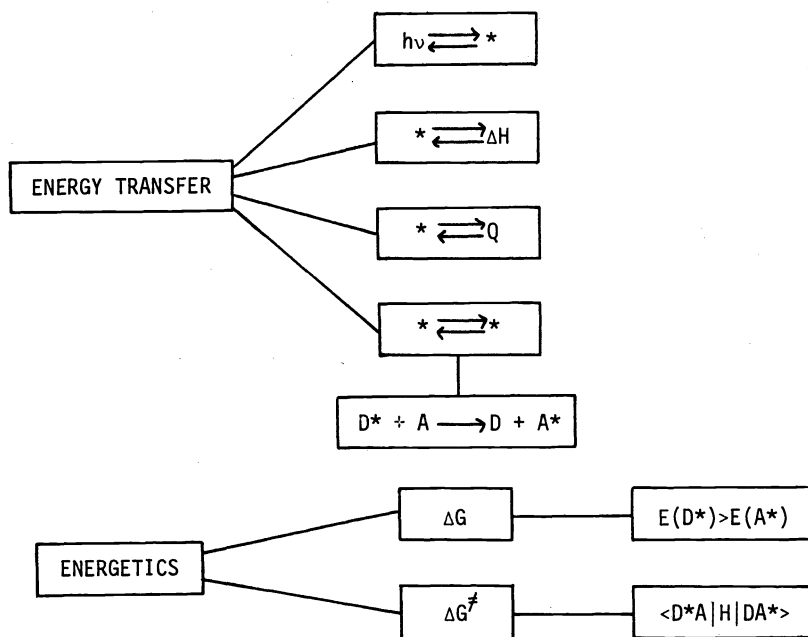
Nicholas J. Turro

Chemistry Department, Columbia University, New York, New York 10027

Abstract: A discussion of the major mechanisms for electronic energy transfer for organic molecules is presented. Application of the techniques and ideas of electronic energy transfer to study the properties of polymers is given.

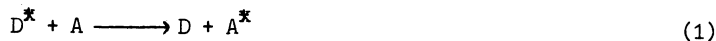
INTRODUCTION

Energy transfer processes are central to all dynamic processes of interest to chemists, e.g., the transfer and conversion of heat energy into chemical energy, of light energy into electronic excitation energy, of electronic excitation energy into chemical energy, etc. A common framework exists for the conceptualization and analysis of energy transfer processes. We consider that an ultimate goal of any such analysis is an understanding of the factors determining the rates and efficiencies of energy transfer events and a means of utilizing this understanding to control and manipulate the energy transfer processes. Scheme I displays, in a flow diagram, the procedures to be considered in analyzing energy transfer processes.



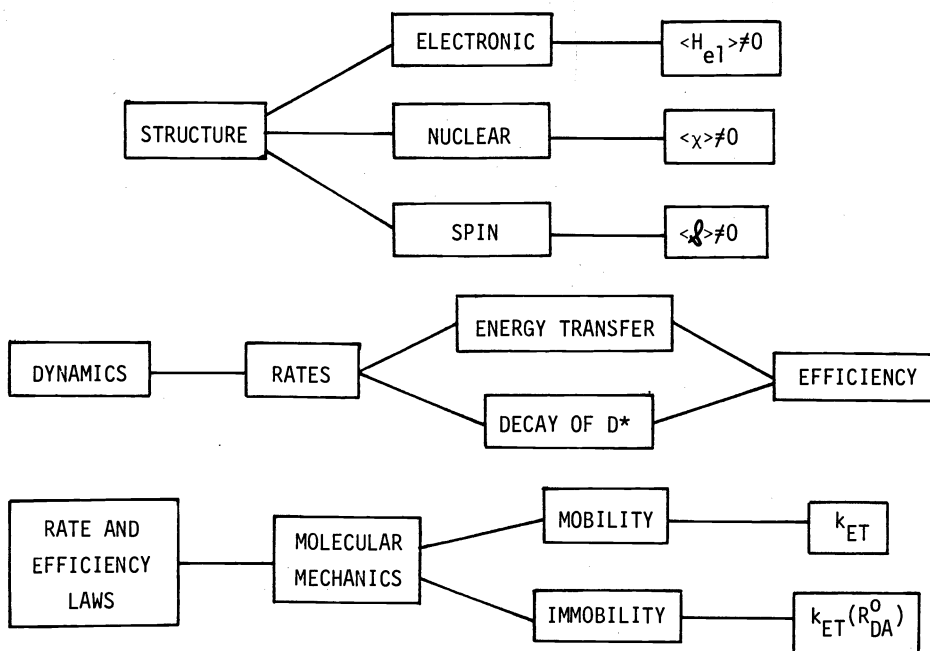
Scheme 1 : Flow diagram of energy transfer types and molecular energetics. Examples of energy transfer are light energy ($h\nu$) into electronic excitation energy ($*$); electronic excitation energy ($*$) into chemical energy (ΔH); electronic excitation energy ($*$) into heat (Q); electronic excitation energy transfer.

In this review, we shall be considered with electronic energy transfer processes,¹ by which we mean the overall events that may be identified as occurring as shown



where D represents a donor molecule, A represents an acceptor molecule and the asterisk represents electronic excitation. Conceptually, we suppose that at some initial time electronic excitation may be unambiguously associated with D and at some later time electronic excitation is unambiguously associated with A . As chemists we seek to visualize the manner in which reaction 1 occurs in terms of energetic and structure descriptions, and then to associate available

information on molecule energetics and structure with the rate and efficiency of reaction 1. We must consider molecular energetics and molecular structure in order to obtain an ultimate understanding of molecular dynamics that will reveal the factors controlling rates and efficiencies. The energetic considerations are classified in terms of overall reaction energetics (ΔG) and in terms of activation energy for reaction (ΔG^\ddagger). The former quantity is readily estimable from knowledge of $E(D^*)$ and $E(A^*)$ the electronic excitation energies of the initial donor excited state and the final acceptor excited state, respectively. The activation energy ΔG^\ddagger may be associated with theoretical quantities related to molecular structure. In particular, a quantum mechanical matrix element $\langle D^*A|H|DA^* \rangle$ may be formulated. The activation free energy is related magnitude of this matrix element. A large magnitude will indicate a fast rate of transfer and therefore a small value of ΔG^\ddagger . A small or zero value of $\langle D^*A|H|DA^* \rangle$ means a rate is slow or is precisely zero. As shown in Scheme 2, it is convenient to decompose $\langle D^*A|H|DA^* \rangle$ into terms that possess a direct relationship to molecular structure. For example, we may consider $\langle D^*A|H|DA^* \rangle$ to be the product of matrix elements of electronic, nuclear and magnetic (spin) factors; i.e., $H_{e1} \langle \chi \rangle \langle \mathcal{S} \rangle$. A set of selection rules related to structure immediately follow: The process is "allowed" only if $\langle D^*A|H|DA^* \rangle \neq 0$; therefore, a process is allowed only if each term in the product $\langle H_{e1} \rangle \langle \chi \rangle \langle \mathcal{S} \rangle$ is not equal to zero.



Scheme 2 : Flow diagram of structure, dynamics and kinetic laws. Molecular structure may be considered in terms of electronic, nuclear and spin structure. Chemical dynamics is concerned with the rates of chemical process. Knowledge of all rates allows evaluation of efficiencies. i.e., the rate of energy transfer in competition with the rate of decay of D^* . Rate and efficiency laws relate theoretical models to experimental quantities. If a rate or efficiency law is obeyed, parameters such as the rate constant for energy transfer (k_{ET}) and cross section efficiencies (R_{DA}^0) can be evaluated. The interpretation of these parameters must be made in view of the molecular mechanics available to the system (e.g., structural and molecular mobility or immobility).

The actual molecular dynamics of a real system will depend not only on the interactions between molecules but also the molecular and excitation mechanics which are possible for the system. By this we mean the mobility or immobility of groups or electronic excitation within a molecule and the intermolecular mobility or immobility of molecules and electronic excitation. Knowledge of the rate of energy transfer and the rate of decay of D^* allows evaluation of the efficiency of energy transfer. The rates and efficiencies in turn, are determined by both features of molecular structure and the available molecular mechanics. In order to compare the theoretical models relating rates and efficiencies to structure and molecular mechanics, we require quantitative formulations which allow us to relate experimental data to derive from these formulations energy transfer parameters which are useful in making comparisons between different systems and in evaluating mechanisms.

In the Coulombic interaction we view the electron cloud of D^* as oscillating back and forth along the molecular frame. To a nearby acceptor, D^* appears to be an oscillating electric dipole. The electronic interactions between D^* and A may, in fact, be treated in precisely the same fashion as the interaction of a light wave and A. The reason for this is that the electric field of a light wave may be approximated as an oscillating electric dipole. As a result of this analogy we expect that if electronic energy transfer occurs via Coulombic

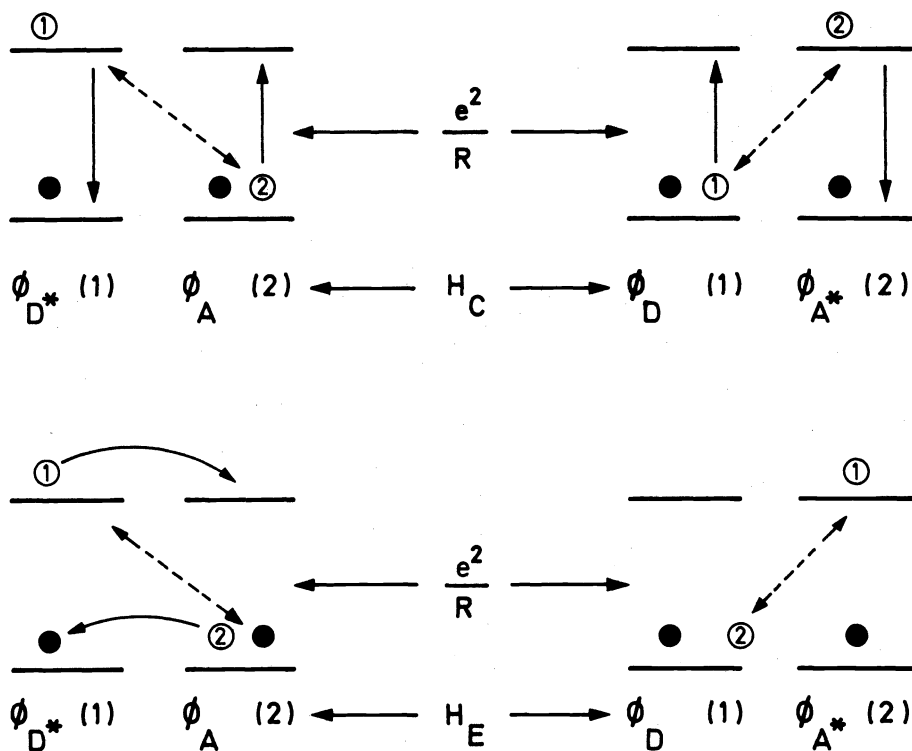


Figure 1 Schematic of the orbital interactions for energy transfer by the Coulombic (upper) and by the electron exchange (lower) mechanisms.

interactions between D^* and A, the following situations will obtain:

- (1) Electronic energy transfer will be possible through space, since the electronic interactions do not require direct overlap of electron clouds.
- (2) The rate of energy transfer will depend on the magnitude of the electric oscillations of D^* and the absorption coefficient of the transition $A \rightarrow A^*$

If we view electronic energy transfer by the electron exchange mechanism as being analogous to the electronic interactions which bring about bimolecular chemical reactions, we conclude:

- (1) Electronic energy transfer will require collisions of D^* and A and will not be possible over distances of separations of D^* and A which are large relative to molecular diameters;
- (2) The rate of energy transfer will depend on the magnitude of positive overlap and the nature of the orbital overlapping which induces the exchange interactions.

MOLECULAR ENERGETICS AND MECHANICS

We have sketched the general electronic interactions between D^* and A which can result, in general, in formation of D and A^* . The rate and efficiency of such an energy transfer process depends on factors such as the energetics of the process and the mechanical possibilities or restraints imposed upon the system by its molecular structure, environmental composition, etc. Clearly, in order for an energy transfer to occur, an isoenergetic resonance between D^* and A must be possible. Moreover, D^* and A must be separated by a distance which is not so large as to make electronic interactions negligible relative to the lifetime of D^* . If D^* and A are initially separated by a distance which is large relative to that required for significant interaction, then energy transfer can occur only if D^* and A are capable of undergoing molecular diffusion toward one another or if the electronic excitation can "leave" D^* and migrate through the environment.

The efficiency, rate and selectivity of electronic energy transfer is influenced by the following factors:

- (1) The electronic mechanisms by which electronic energy transfer occurs;
- (2) The ability or inability of donor and acceptor molecules to undergo relative diffusional motions;
- (3) The occurrence or non-occurrence of energy migration, which is independent of molecular diffusional motion.

ENERGETIC CONSIDERATIONS

The most general factors which influences the rate of an energy transfer process are the reaction energetics. Since energy conservation applies to eq. 1, any endothermic energy transfer requires an activation energy, E_a , at least equal to the endothermicity of the reaction. We imagine that since electronic energy transfer involves electronic transitions (which take

place in $\sim 10^{-15}$ sec), the event of energy transfer occurs isoenergetically, i.e., the transition energies $D^* \rightarrow D$ and $A \rightarrow A^*$ must match perfectly. In effect, we suppose that the electronic transitions occur so fast that thermal energy (which requires relatively slow nuclear motions) cannot be supplied or removed during the actual act of energy transfer. We may visualize the role of reaction exothermicity or endothermicity in terms of Figure 2.

Consider the following model of an electronically excited molecule D^* in a thermal bath capable of rapidly removing excess vibrational energy of any state. If the excited state formed by absorption of a photon has a higher vibrational energy than the surrounding medium (which is the solvent in a solution), thermal relaxation will occur, and the energy of the state will fall to lower vibration levels until thermal equilibrium is established, which usually takes

about 10^{-12} sec. The electronically excited molecule D^* now stays in its lowest vibrational level until it becomes deactivated by either emission or some nonradiative process.

If another molecule A with a low-lying state is in the neighborhood of the first one, excitation transfer may take place. If the energy difference for a deactivation process in D^* corresponds to that for a possible absorption transition in a nearby molecule of A, then with sufficient energetic coupling between these molecules, both processes may occur simultaneously, resulting in a transfer of excitation from sensitizer to acceptor by either a radiative or radiationless mechanism.

The broad spectra of polyatomic molecules in solution guarantees sufficient coincidence between D^* and A transitions if the absorption spectrum of A overlaps the emission spectrum of D^* . Indeed, the number of possible simultaneous isoenergetics which deactivate D^* and excite A may be deduced from knowledge of the electronic emission spectrum corresponding to the $D^* \rightarrow D$ transition and the absorption spectrum corresponding to the $A \rightarrow A^*$ transitions.

In Figure 2, emission of light from the $v = 0$ level of D^* to various vibrational levels of D results in the emission spectrum indicated at the bottom left of the drawing. Absorption of light from the $v = 0$ level of A to various vibrational levels of D^* results in the absorption spectrum shown at the bottom right of the drawing. We may conceive of a spectral overlap integral, J, which provides a measure of the overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor, and, therefore, the "density" of transitions which are energetically allowed. We may define J quantitatively by:

$$J = \int_0^{\infty} f_D f_A dv \quad (6)$$

where f_D is the spectral distribution of the donor emission and f_A is the spectral distribution of acceptor absorption, each expressed in quanta and appropriately normalized. In fig.2, the shaded areas correspond to J.

It is important to note that the magnitude of J, because it represents a normalized function, is independent of both the probability of donor emission and the probability of acceptor absorption. It is also important to note that the vibrational intensities employed to define J are a measure of the probability of transitions between different vibrational levels. Thus,

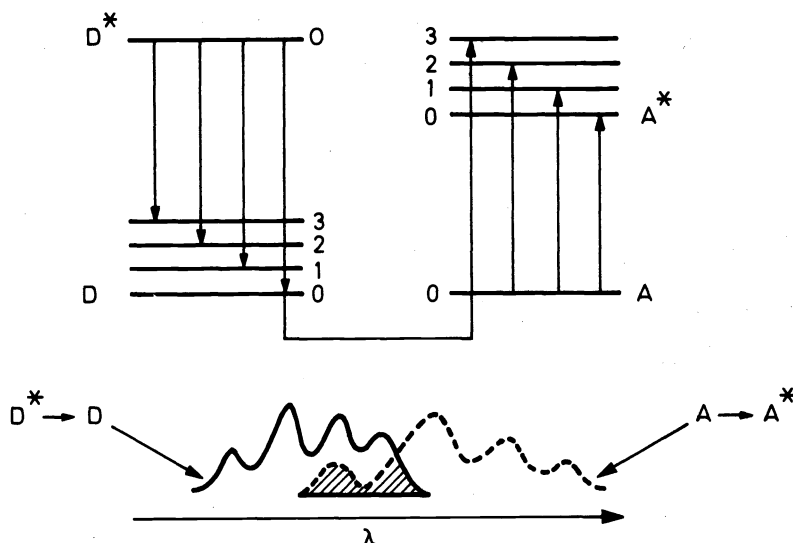


Fig. 2 Schematic of coupled transitions for an exothermic electronic energy transfer. The (0,0) and (0,1) $D^* \rightarrow D$ transitions overlap well with the (0,3) and part of the (0,2) $A \rightarrow A^*$ transitions. This spectral overlap determines the magnitude of J and is indicated by the shaded area in the fig.

J is also a measure of the "Franck-Condon Factors" or nuclear shape changes involved in donor emission and acceptor absorption processes.

In summary, any energy transfer process of the type represented in eq. 1 is subject to energetic restrictions. The rate of reaction 1 will always depend on the size of J , the overlap integral which is a measure of the density of states of D^* and A which may be "coupled" and undergo isoenergetic energy transfer. We might anticipate that J will be a useful experimental parameter in all cases of energy transfer except those for which strong chemical interactions between D^* and A occur. In the latter situation, the donor emission and acceptor absorption spectrum may no longer serve as a reliable guide to the reaction energetics. With this exception in mind we formulate the following selection rule for all electronic energy transfer processes which occur via direct interaction between D^* and A : The rate constant for electronic energy transfer is zero if $J = 0$. If $J \neq 0$, the rate constant for energy transfer is finite and its magnitude will depend on the specific mechanism by which energy transfer occurs.

STRUCTURAL CONSIDERATIONS

Even if the energetic restrictions ($J \neq 0$) discussed above are met, the magnitude of the rate of energy transfer will depend on structural considerations. We shall consider the two major molecular structural features which determine the rate of energy transfer to be electronic structure and nuclear structure. We shall assume that the electronic structures of D^* and A will be dominant in determining the magnitude of the direct interaction which determines the rate of energy transfer. However, the ability of the nuclei (of a molecule as a whole) to move in space (molecular diffusion) may influence which of the specific possible electronic interactions are most probable.

To a good approximation, the important interactions between the electronic systems of D^* and A may be viewed as electrostatic in nature. From the general quantum mechanical description of electrostatic interactions, the magnitude latter may be expressed as a sum of "coulomb" and "exchange" terms, as we have noted earlier (eq. 5).

Coulomb Interactions. The Dipole-Dipole Approximation

The electrostatic interactions in the coulomb term may be replaced to a good approximation by a dipole-dipole interaction. From theory the magnitude of the dipole-dipole interaction (between the electronic systems of D^* and A) may be directly related to the probabilities of

the radiative transitions $D^* \rightarrow D$ and $A \rightarrow A^*$. In terms of a qualitative orbital scheme (Fig. 1), the $D^* \rightarrow D$ transitions generally involves a jump of an electron from an antibonding orbital, ϕ_{D^*} , to a previously half-occupied bonding or non-bonding orbital ϕ_D and the $A \rightarrow A^*$ transition involves excitation from a filled bonding or non-bonding orbital ϕ_A to a previously unfilled antibonding orbital ϕ_{A^*} .

It can be shown from the theory of light absorption and emission that the probability of the $D^* \rightarrow D$ and $A \rightarrow A^*$ radiative transitions may be related to the orbital transitions $\phi_{D^*} \rightarrow \phi_D$ $\phi_A \rightarrow \phi_{A^*}$. The experimental quantities related to the probability of emission and the probability of absorption are the radiative rate constant $k_{D^*}^0$ and the extinction coefficient ϵ_A . At this point let us review the factors relevant to Coulombic interactions between D^* and A and see how we may relate the expected rate of energy transfer to experimental quantities. The classical interaction between a dipole μ_D and a second dipole μ_A is given by:

$$\text{dipole-dipole interaction} = \frac{\mu_D \mu_A}{R_{DA}^3} \quad (7)$$

where R_{DA} is the distance separating the centers of the dipoles. It is usually assumed that if the distance of separation R_{DA} is large relative to the dipole length, the dipoles may be approximated as points (i.e., orientation of the dipoles relative to one another is ignored). The energy of interaction between the dipoles is given by the square of eq. 7.

$$\left. \begin{array}{l} \text{energy of dipole-dipole} \\ \text{interactions} \end{array} \right\} = \left[\frac{\mu_D \mu_A}{R_{DA}^3} \right]^2 \quad (8)$$

The rate of energy transfer k_{ET} by dipole-dipole interaction is related directly to the energy of the dipole-dipole interaction. Thus, we have:

$$k_{ET} \text{ (dipole-dipole)} \propto \frac{\mu_D^2 \mu_A^2}{R_{DA}^6} \quad (9)$$

Forster² pointed out that if μ_D and μ_A are identified as the transition dipoles for the $D^* \rightarrow D$ and $A \rightarrow A^*$ radiative transitions, then:

$$k_D^0 \propto \mu_D^2 \quad (10)$$

$$\text{and } \epsilon_A \propto \mu_A^2 \quad (11)$$

Substitution of eqs. 10 and 11 into eq. 9 yields

$$k_{ET} \text{ (dipole-dipole)} \propto \frac{k_D^0 \epsilon_A}{R_{DA}^6} \quad (12)$$

We have seen earlier that any energy transfer mechanism will require overlap of the $D^* \rightarrow D$ and $A \rightarrow A^*$ transitions in order to satisfy the Law of Conservation of Energy. In effect, this means that k_{ET} will be directly related to J the spectral overlap integral. Thus, eq. 12 must be multiplied by J and we obtain the useful expression:

$$k_{ET} \text{ (dipole-dipole)} \propto \frac{k_D^0 \epsilon_A}{R_{DA}^6} J \quad (13)$$

Inspection of eq 13 reveals the molecular properties which will be of major importance in determining the rate of energy transfer by a dipole-dipole interaction:

- (1) k_D^0 the rate constant for emission from D^* to D (k_D^0 is the rate constant for the limiting situation that all D^* molecules emit);
- (2) ϵ_A the extinction coefficient for absorption from $A \rightarrow A^*$ (we shall identify ϵ_A with ϵ_A^{\max} since for our purposes only a qualitative appreciation of the effect of ϵ on k_{ET} is desired).

- (3) R_{DA}^{-6} , the inverse sixth power of the separation of D and A.
 (4) J , the spectral overlap integral.

It should be noted that the Coulombic interaction (which has been approximated as a dipole-dipole interaction) operates without the requirement of molecular "contact", i.e., overlap of the electron clouds of D^* and A. We now consider the second important general electrostatic interaction between D^* and A, the electron exchange interaction.

ELECTRON EXCHANGE

We normally view bimolecular chemical interactions as occurring via collisions between the reacting partners. By collision we mean that the electron clouds of the reaction species overlap significantly in space. In the region of overlap, electron exchange may occur. The situation is shown qualitatively in Figure 3.

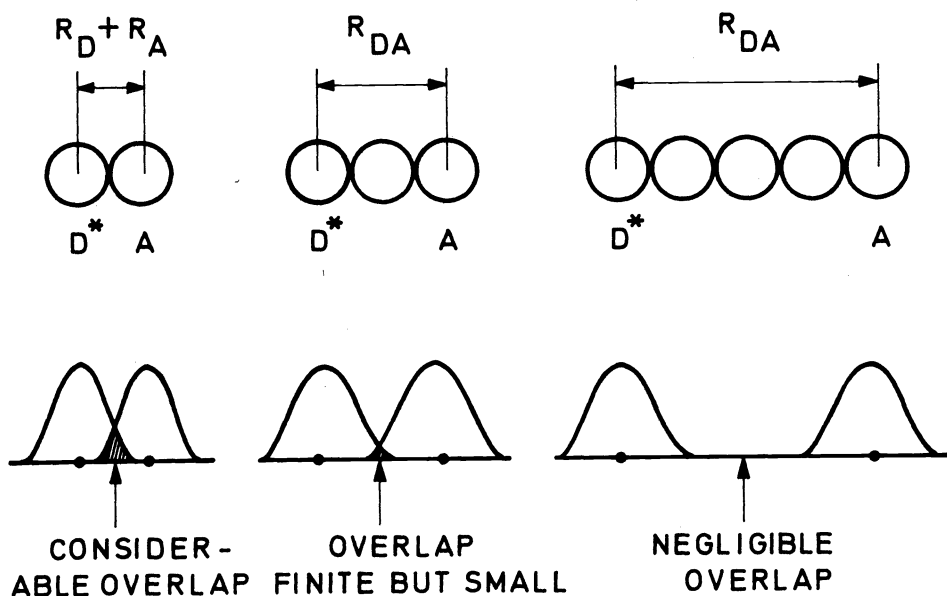


Fig. 3 Schematic of the overlap of electron clouds of molecules. The circles represent the van der Waals (or collisional) sizes of the molecules. These sizes underestimate the actual extension of the electron clouds in space. Below the van der Waals sizes a qualitative probability function for finding an electron is plotted as a function of nuclear electron distance. When D^* and A are in a state of "classical" collision ($R_{DA} = R_D + R_A$), the overlap of the electron clouds of D^* and A is considerable. When D^* and A are separated by a small solvent molecule (diameter $\sim 5 \text{ \AA}$) no "classical" collision between D^* and A is possible but the overlap of their electron clouds may still be finite; at separation distance of the order of 15 \AA ($R_{DA} \gg R_D + R_A$) or larger, the overlap of the electron clouds usually becomes completely negligible.

If we ignore the details of the orbitals overlap, then the rate constant for energy transfer by electron exchange is expected to fall off exponentially as the separation between D^* and A increases. Of course, the rate of energy transfer will also be directly related to J , the spectral overlap integral, so that

$$k_{ET} \text{ (electron-exchange)} \propto J \exp - R_{DA} \quad (14)$$

If we include the details of orbital interactions and overlap, we expect that k_{ET} will take on a form similar to that proposed for chemical reactions, i.e.,

$$k_{ET} \text{ (electron exchange)} \propto \frac{\langle \psi_{D^*A} | \psi_{DA^*} \rangle^2}{\Delta E} J \quad (15)$$

Notice that the key factors in an electron exchange interaction are quite different in several respects from those in a dipole-dipole interaction:

- (1) The rate of energy transfer by the exchange mechanism does not depend directly on k_D^0 nor ϵ_A .
- (2) The distance dependence of the rate of energy transfer by the exchange mechanism fall off exponentially with increasing separation of D^* and A
- (3) When D^* and A are close enough in space that they collide and their electron clouds overlap strongly, the rate of energy transfer will depend on the details of the orbital interactions that allow electron exchange.

EFFICIENCY OF ENERGY TRANSFER

Upon observation of electronic energy transfer one may follow a standard procedure in seeking to establish the mechanism of the process. The first classification should be whether the mechanism is short range (collisional or exchange in nature) or is long range (trivial emission-reabsorption or Coulombic in nature). We shall see that a number of experimental tests allow differentiation between short range or long range types, the most important of which is the distance dependence of the efficiency of energy transfer. The efficiency of energy transfer is given by:

$$\phi_{ET} = \frac{k_{ET}[A]}{k_{ET}[A] + k_D} \quad (16)$$

where k_{ET} is the rate constant for energy transfer and k_D is the rate constant for decay of the donor. If k_D is a constant and independent of the concentration of acceptor, we see that the efficiency of energy transfer depends on the relative magnitudes of $k_{ET}[A]$ and k_D . The predicted distance dependence of k_{ET} and hence ϕ_{ET} is quite different for the Coulombic and exchange mechanisms. For the former a relatively slow fall off into k_{ET} is predicted compared to exchange. If the energy transfer process can be qualitatively classified as dominantly Coulombic in nature, several quantitative tests of the Coulombic mechanism are possible from the Forster theory. If the energy transfer process can be qualitatively classified as dominantly exchange

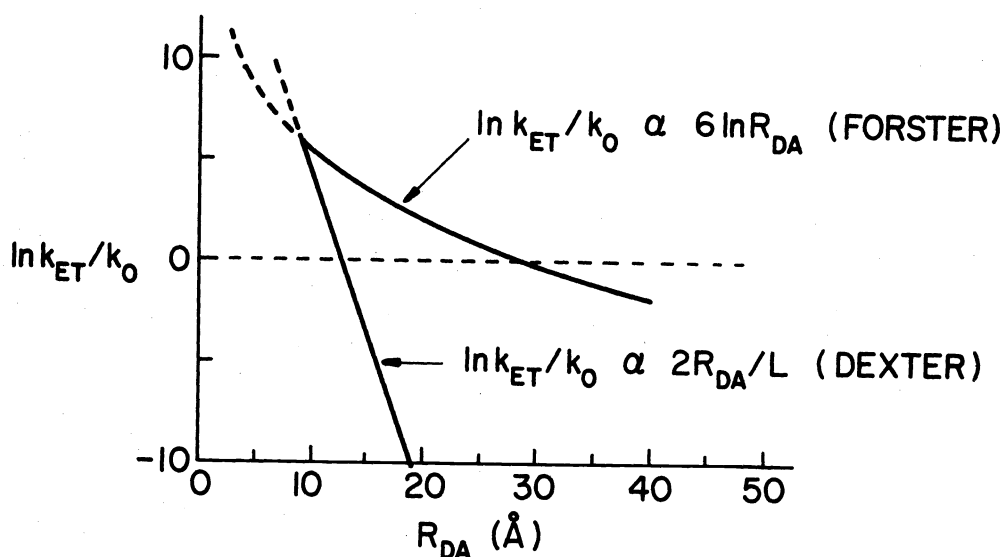


Fig. 4 Qualitative relationship between the ratio of the energy transfer rate constant to acceptor decay constant for Coulombic and electron exchange energy transfer to the separation between D^* and A.

in nature, the next chore is to decide whether a concerted mechanism, charge transfer mechanism or chemical bonding mechanism is involved. Finally, one should seek experimental evidence pertinent to the confirmation or exclusion of complexes in the energy transfer mechanism.

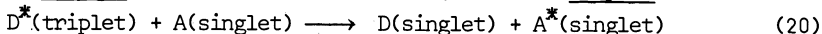
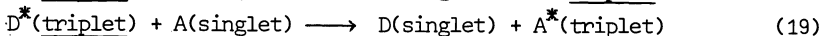
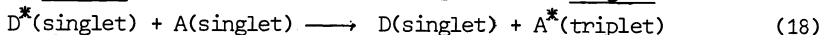
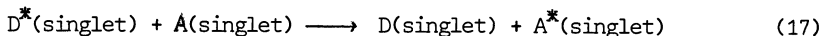
We have surveyed the two major mechanisms by which electronic energy is possible. From a practical standpoint, knowing the efficiencies of specific energy transfer is generally more important than knowing their inherent rates. The number of energy transfer events per donor lifetime, $k_{ET}\tau_D$, is the critical parameter for determining energy transfer efficiency. Thus, in order to anticipate the efficiency of energy transfer both k_{ET} and τ_D must be evaluable.

To appreciate the relationship of efficiency to rate and lifetime we should note that a slow rate of transfer may still be efficient if τ_D is long, i.e. although the probability of energy transfer per unit time is small, the period of time available to achieve energy transfer is large.

We shall now consider various parameters which influence the efficiency of energy transfer. We shall now consider how spin multiplicity, molecular diffusion and energy migration influence energy transfer efficiencies.

EFFECT OF SPIN MULTIPLICITY ON ENERGY TRANSFER PROCESSES

In general, chemical processes which proceed with a change in spin multiplicity ($\Delta S \neq 0$) are considerably slower than analogous processes which do not involve a change ($\Delta S = 0$) in spin multiplicity (Wigner Spin Rule). If we confine ourselves to energy transfer processes involving only singlet and/or triplet states, four general classifications according to spin types are possible.



Singlet-singlet (eq.17) and triplet-triplet (eq.19) energy transfers are spin-allowed but singlet-triplet (eq.18) and triplet-singlet (eq.20) energy transfers are spin-forbidden. Because of the Wigner Rule we might dismiss transfer types 18 and 20 as viable possibilities of general importance. However, since we are concerned with efficiency, we can imagine that energy transfers of type 20 may become significant if the donor triplet is very long lived. Energy transfer of type 18 is "forbidden" by the spin rule and does not enjoy the possibility of a long donor lifetime to compensate for the slow rate constant of energy transfer. In summary, spin selection rules automatically place prohibition factors on the rate constants of energy transfer processes. Of the four general types of energy transfers classified by spin types, we expect the following to be encountered in practice:

- (1) The spin is allowed singlet-singlet (Coulombic or exchange mechanism) and triplet-triplet (exchange mechanism only) energy transfers.
- (2) The spin forbidden triplet-singlet (Coulombic or exchange mechanisms) energy transfer.

ENERGY TRANSFER IN THE ABSENCE OF MOLECULAR DIFFUSION

We have discussed the electronic mechanisms which make electronic energy transfer viable. It was noted (eq. 13) that the rate of the dipole-dipole interaction falls off as R_{DA}^{-6} whereas the rate of the exchange interaction (eq. 14) falls off as $\exp-R_{DA}$. A qualitative comparison⁴ of how $k_{ET}\tau_D$ falls off for these two interactions is shown in Fig. 4. The efficiency of energy transfer by the exchange mechanism falls off much more sharply as a function of increasing separation of donor and acceptor than the efficiency of energy transfer by the dipole-dipole mechanism.

In order to appreciate the effect of molecular diffusion on the efficiency of energy transfer let us first consider several situations for donor-acceptor pairs which are held rigidly in space. We associate with D^* and A a rough "collisional radius" R_D and R_A which is related to the size of the molecule we commonly attribute to molecular structures. For example, the values of 2-5Å would be appropriate for common organic molecules whose molecular weights fall in the range of 100-200. This means that when D^* and A "collide", their separation is $\sim 4-10\text{Å}$.

Consider three situations with respect to a D^*A pair (Figure 3):

- (1) D^* and A are separated by distances comparable to the sum of $R_D + R_A$, i.e., the

molecules are undergoing collisions capable of inducing chemical interactions;

(2) D^* and A are separated by distances of the order of twice the sum of $R_D + R_A$, i.e., but molecules are incapable of undergoing strong chemical interactions, but the overlap of their electronic wavefunctions is still finite.

(3) D^* and A are separated by distances of the order of several times the sum of $R_D + R_A$, i.e., the overlap of electron clouds of the molecules is negligible.

For qualitative purposes, we may consider the rate constant of energy transfer may be written in the form $k_{ET}^* = k_0 \exp(-R)$ where k_0 is the maximum rate constant for energy transfer which occurs when D^* and A are in the state of a "classical" collision ($R_D + R_A + R_{DA}$) and R is the separation between the peripheries of D^* and A when they are further apart than the sum of their classical radii, i.e., $R = R_{DA} - (R_A + R_D)$. The maximum value of k_0 is expected of the order of 10^{13} sec^{-1} . Figure 5 shows a plot of $\log k$ versus R. The value of k_{ET} falls from 10^{13} sec^{-1} when D^* and A collide ($R = 0$) to $\sim 10^4 \text{ sec}^{-1}$ when R equals 10\AA . Although these calculations are not intended to be accurate, they indicate the sharp fall of k_{ET} by the exchange mechanisms as D^* and A are separated by more than one or two classical collisional diameters. Experimentally,⁶ a fall off of $k_{ET} \sim 10^8 \exp(-2R)$ was found for the carbazole (donor triplet) to naphthalene (acceptor triplet) system. When the acceptor is solvent,⁷ k_0 has been found to be of the order of 10^{12} sec^{-1} .

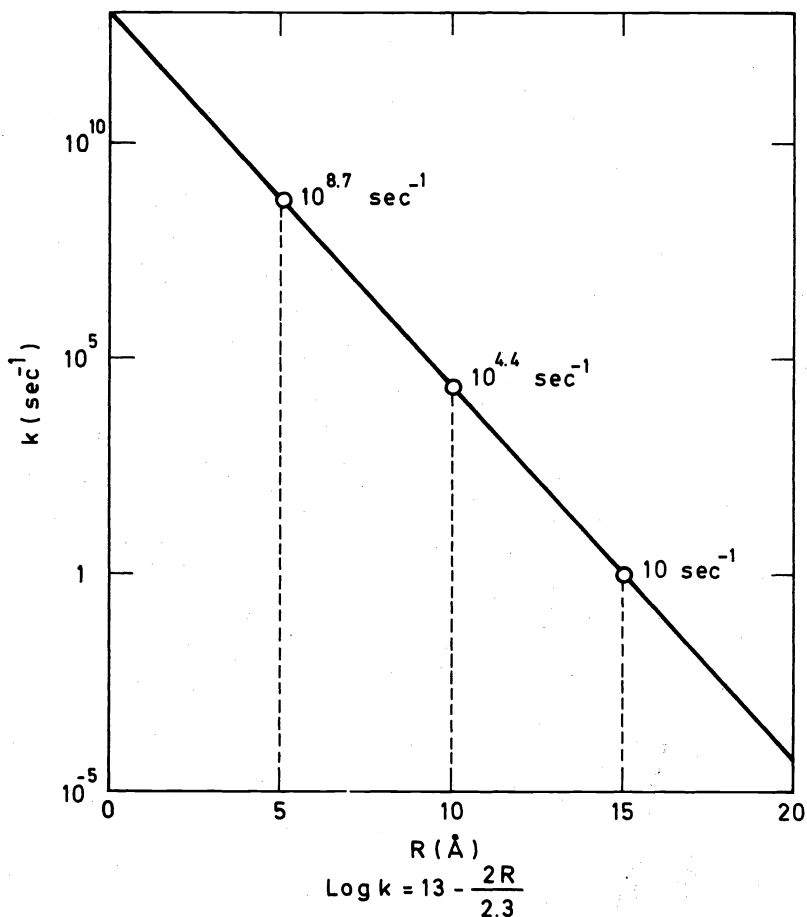


Fig. 5 Falloff of the rate constant for energy transfer by the electron exchange mechanism as a function of separation of donor and acceptor, for $k_{ET} = 10^{13} \exp(-2R)$

In figure 5 the rate constant for energy transfer by the exchange mechanism is plotted versus R , the distance of separation of D^* and A in excess of these collisional sizes. It is qualitatively clear that since the rate of energy transfer by electron exchange is a sensitive function of the extent of orbital overlap, that only when D^* and A are in a "state of chemical collision" will k_{ET} (exchange) be large. When D^* and A are separated by several times their collisional diameters ($\sim 20\text{\AA}$) the value of k_{ET} (exchange) has dropped by a factor of $\sim 10^{-13}$. Clearly, the exchange mechanism will be generally inoperative for this magnitude of separation. For the intermediate separations ($\sim 10\text{-}15\text{\AA}$), if τ_D is sufficiently long.

The dipole-dipole mechanism does not overlap of the electron clouds of D^* and A , so that we may ask what are the largest distances of separation for which this mechanism may be operative? A qualitative, approximate relationship between k_{ET} (dipole-dipole) and R_{DA} (in \AA) is given by:

$$k_{ET} \sim \frac{4 \times 10^4 \epsilon_{\max}^A k_D^0}{R_{DA}^6} \quad (21)$$

for a donor-acceptor pair possessing a typical value of J . If the donor possesses its maximal lifetime then $\tau_D = 1/k_D^0$ so that

$$k_{ET} \tau_D \sim \frac{4 \times 10^4 \epsilon_{\max}^A}{R_{DA}^6} \quad (22)$$

From eq. 14 it is expected that the efficiency of energy transfer by the dipole-dipole will be significant at values of $R_{DA} \sim 50\text{-}100\text{\AA}$ if ϵ_{\max}^A is of the order of 10^5 . It is also to be concluded from eq. 22 that if ϵ_{\max}^A is less than 1, the value of R_{DA} required for efficient energy transfer will be comparable to or smaller than that for energy transfer by electron exchange.

From this discussion several important conclusions concerning the efficiency of energy transfer arise:

- (1) When R_{DA} is of the order of $R_D + R_A$, both the dipole-dipole and electron exchange mechanisms may be effective.
- (2) When R_{DA} is much larger than $R_D + R_A$ only the dipole-dipole mechanism may be effective, but only when $\epsilon_{\max}^A \sim 10^5$.
- (3) When $\epsilon_{\max}^A < 1$, the dipole-dipole mechanism may be ineffective even at small separations of D^* and A .

Such is the situation when neither the molecules D^* and A nor the excitation energy are free to move in space from an initial location. We now consider the effect of molecular diffusion and energy migration on the mechanism of the energy transfer processes.

MOLECULAR DIFFUSION AND ENERGY MIGRATION

In general, we expect that D^* and A will be able to execute diffusional motions toward each other during the lifetime of D^* before energy transfer occurs.⁸ The rate constant for molecular diffusion in fluid media is given by:

$$k_{DIF} (\text{M}^{-1}\text{sec}^{-1}) = 2.2 \times 10^5 T/\eta \quad (23)$$

where T is temperature in $^\circ\text{K}$ and η is viscosity in Poise. In Figure 6 diffusion is depicted schematically as the relative motion of D^* and A through the empty space between solvent molecules. Since energy transfer by the exchange mechanism requires close approach of D^* and A we may assume that only if D^* and A are capable of becoming partners in a collision complex will energy transfer by the exchange mechanism be efficient. Does this mean that efficient energy transfer by an exchange mechanism is limited to fluid solutions and is generally not important in rigid or highly viscous solutions? There is an exception to this expectation and that occurs when energy migration can occur via a series of transfers initiated by energy transfer from D^* to a solvent molecule, mediated by hopping or migration of the excitation through the solvent and terminated by energy transfer from a solvent molecule to A . In this case the solvent serves as an electronic energy conductor. To gain an appreciation of distance time relations for molecular diffusion or energy migration

a plot of the distance r , a molecule will diffuse in a time period τ as shown in Figure 7.

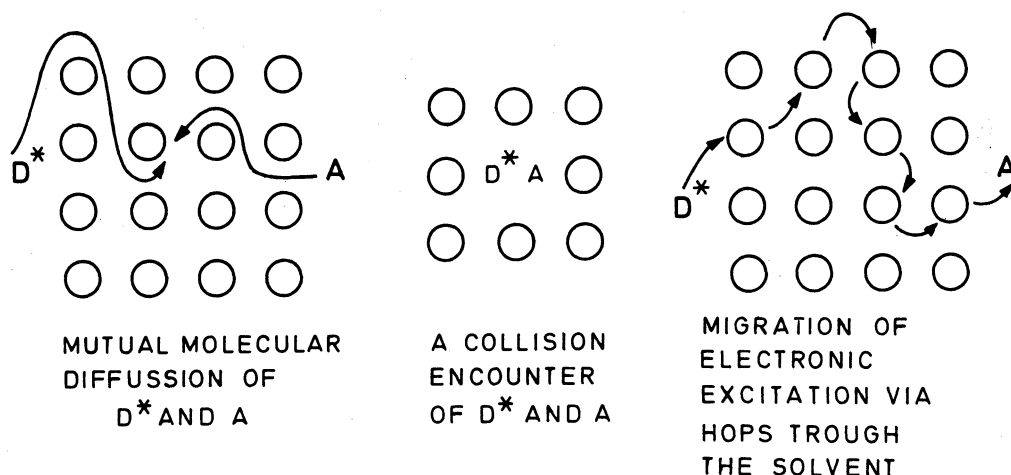


Fig. 6 Schematic of molecular diffusion, energy migration and collision encounters

The relationship between r and τ is given by the expression:

$$r = \sqrt{2D\tau} \quad (24)$$

where r is the average distance the molecule has diffused, τ is the time period and D is the diffusion coefficient. In figure 7, eq. 24 is plotted for $D = 10^{-5} \text{ cm}^2/\text{sec} = 10^{11} \text{ \AA}^2/\text{sec}$, a value typical for a molecule diffusing in a fluid organic solvent and for $D = 10^{-10} \text{ cm}^2/\text{sec} = 10^6 \text{ \AA}^2/\text{sec}$ a value typical of a very viscous, nearly rigid solvent. Suppose we take 1 ns as typical of the lifetime of a molecule in its singlet state. In the fluid solvent the molecule will diffuse roughly 15 \AA during its lifetime. In the more viscous environment, the same molecule will only diffuse about 10^{-1} \AA . In so far as the viscous environment is more typical of polymer systems, we conclude that only small displacements of molecules in space will occur during the lifetime of singlet states. On the other hand, a triplet molecule whose lifetime is 10^{-3} sec may, during its lifetime, diffuse up to $15,000 \text{ \AA}$ in the fluid solvent or up to 50 \AA in the viscous solvent.

Without specific reference to the mechanism of energy transfer, we can imagine that electronic excitation originally at a given point A in space and localized on a molecule M, will appear at some later time τ still on a molecule M at some different point B in space. If the system contains a number of identical molecules M, we cannot be certain whether the electronic excitation diffused through space was localized on a molecule M_0 through the journey from point A to point B or whether the excitation migrated from M molecule to M molecule n times and eventually was located on molecule M_n .

We call the movement of M through space molecular diffusion and associate with it a diffusion coefficient D . We call the movement or "hopping" of electronic excitation from M molecule to M molecule energy migration and associate with it a migration coefficient Λ . If both mechanisms for the displacement of excitation energy through space operate, a distance of net "molecular energy migration" r may be defined as:

$$r = \sqrt{2(D + \Lambda)\tau} \quad (25)$$

where τ is a time period of interest. In general, τ will be equal to the lifetime of an electronically excited molecule M^* .

If chromophores possessing low lying excited states are situated at more or less regular intervals along the backbone of a polymer molecule, such a situation may be crudely compared to that of a crystal. Energy migration, in pure crystals possessing a high degree of order among chromophores, is a very important process for the movement of excitation from an original excitation site. In organic crystals small quantities of guest molecules or defects act as energy traps. In most instances the guest molecules may be viewed as "point" or dimensionless energy traps embedded in a three-dimensional matrix of the host molecules. Qualitatively energy absorbed by the host is delocalized throughout the matrix and is ultimately observed as emis-

sion from the guest molecules. Analogously, a linear polymer chain through which similar delocalization of absorbed energy takes place might be likened to a one-dimensional crystal. The analogy is complete if some part of the polymer chain acts as a trap for the delocalized energy.

Thus, we may suppose that polymers, possessing ordered pendant chromophores which occur in regions of "one dimensional crystallinity" of the polymer, may undergo energy transfer processes involving energy migration.

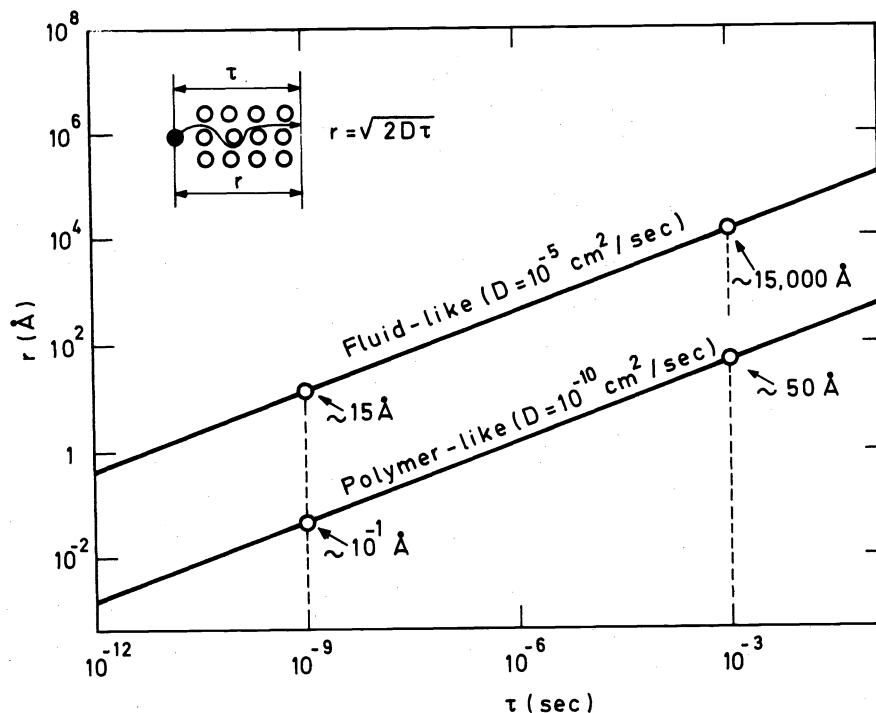


Fig. 7 Mean molecular displacement of a molecule in a non-viscous ($D = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) and a viscous ($D = 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$) solvent.

QUANTITATIVE STUDY OF ENERGY TRANSFER PROCESSES

Quantitative information concerning the rates and efficiencies of energy transfer processes may be obtained by the fitting of rate and efficiency equations (Rate Laws) to experimental data and then evaluating for the desired quantities. Usually (1) the quantum yield of quenched or sensitized emission is related to the concentrations of excited donor and ground state acceptor or (2) the decay of donor lifetime is related to the concentrations of excited donor and acceptor. In general, the concentration of D^* does not appear explicitly in the Rate Law. Each of the most commonly encountered formulations for handling experimental data makes certain assumptions concerning the basic electronic mechanism of energy transfer (dipole-dipole or electron exchange) and/or takes into account whether or not molecular diffusion or energy migration is possible.

From the standpoint of solutions of organic molecules there are two important general models for quantitative handling of experimental data:

(1) In the Stern-Volmer formulation, the rate constant for energy transfer is assumed to be independent of concentration of excited donor and acceptor, and that statistical mixing of donor and acceptor is completely achieved during the lifetime of D^* . If these conditions are met, then the decay of D^* may be viewed in terms of a simple kinetic competition between the normal decay rate of D^* in the absence of A and the decay rate of D^* in the presence of A, i. e.,

$$k_{D^*} = k_{D^*}^0 + k_{ET}[A] \quad (26)$$

where k_{D^*} is the rate constant for decay of D^* in the presence of A, $k_{D^*}^0$ is the rate constant for decay of D^* in the absence of A and k_{ET} is the rate constant for energy transfer. In terms of quantum yields of emission.

$$\phi_0/\phi = 1 + k_{ET}[A]/k_{D^*}^0 = 1 + k_{ET}\tau_{D^*}[A] \quad (27)$$

where ϕ_0 and ϕ are quantum yields for emission from D^* in the absence or presence of A, respectively, and τ_{D^*} is the lifetime of D^* in the absence of A ($k_{D^*}^0 = 1/\tau_{D^*}$).

If an experimental plot of ϕ_0/ϕ versus $[A]$ yield a straight line of intercept equal to 1.0, then the Stern-Volmer Rate Law is fit and the slope of the line is identified quantitatively as $k_{ET}\tau_{D^*}$. Since τ_{D^*} may be measured, in general, by an independent observation, the magnitude of k_{ET} may be evaluated explicitly.

(2) In the Perrin formulation, the notion of rate constant for energy transfer is replaced by an efficiency cross section or "active volume" about the excited donor molecule. It is assumed that a volume exists about each donor such that if a molecule of A is within the sphere, D^* is transfer energy to A with unit efficiency but if a molecule of A is outside of the sphere there is no energy transfer. If molecules of A are statistically distributed about D and if neither molecular diffusion nor energy migration is possible, then the Perrin model predicts the following efficiency relationship between the quantum yields of unquenched (ϕ_0) and quenched (ϕ) donor emission as a function of concentration of acceptor:

$$\phi_0/\phi = \exp NV[A] \quad (28)$$

$$\text{or } \ln \phi_0/\phi = NV[A] \quad (29)$$

where N is Avogadro's number and V is the volume of the "active sphere" of energy transfer about D^* . If a plot of $\ln \phi_0/\phi$ versus $[A]$ yields a straight line, the Perrin Rate Law is fit and the slope of the line is identified quantitatively with NV, and hence V may be evaluated. It is convenient to characterize systems that follow the Perrin Efficiency Law in terms of the radius (R) of V, since R is then directly comparable to familiar molecular dimensions. A useful relationship between R and the concentration of acceptor is:

$$R \text{ (in } \text{\AA}) \cong 7[A]^{-1/3} \quad (30)$$

where $[A]$ is in moles/l. A plot of R versus $[A]^{-1/3}$ is shown in Figure 8.

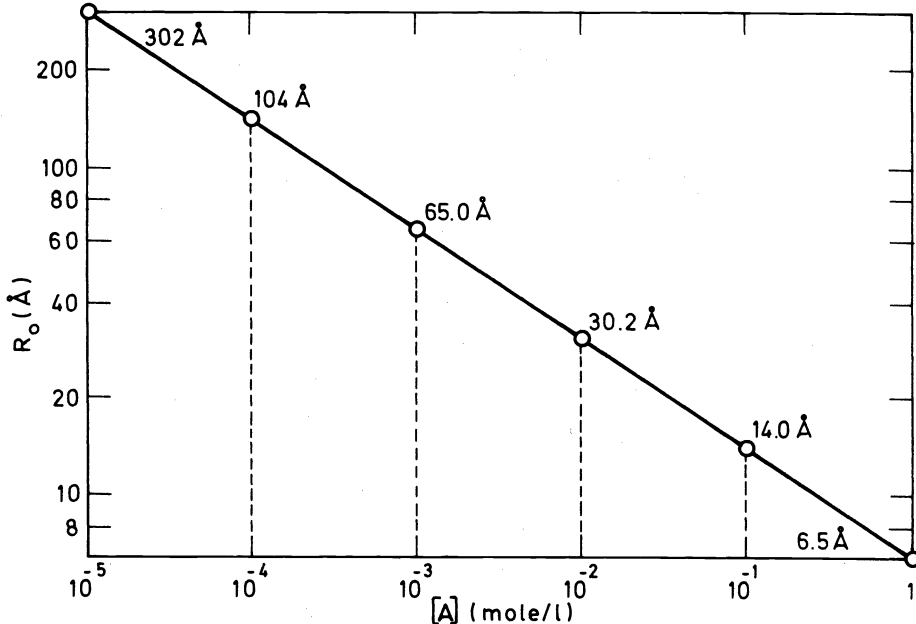


Fig. 8 The relationship of separation of D^* and A to the concentration of A.

The Stern-Volmer and Perrin equations allow quantitative characterization of the rate of efficiency of energy transfer independent of the mechanism of energy transfer. The basic ideas of the two models are the extreme situations of (1) statistical mixing of molecules or energy and a single rate constant for energy transfer (Stern-Volmer) or (2) no mixing of molecules or energy and a single volume of space about D^* in which energy transfer is totally effective (Perrin). Since the details of mechanisms do not enter into the fitting of the Kinetic Laws, the rate constants k_{ET} and radii R obtain from eqs. 27 and 30 are useful in comparing various

donor-acceptor systems. However, to determine whether energy transfer is occurring via a Coulombic or electron exchange interaction a more detailed theoretical formulation is required.

If the "critical" separation R_{DA}^0 determined for a solid polymer is larger than $\sim 15\text{\AA}$, it may be concluded that energy migration is operative. In such cases, the R_{DA}^0 values obtained are useful for qualitative comparisons although a quantitative evaluation of the energy transfer process is generally not possible.

When energy migration is sufficiently important that statistical mixing occurs, the Stern-Volmer formulation may be used to handle the experimental data. The Stern-Volmer parameter, $k_{ET}\tau_D$ is now interpreted in terms of "excitation hopping", and k_{ET} is viewed as the migration rate constant k_M for the process:



If migration does not result in reexcitation of a previously excited molecule then the number of hops per unit time is given by $k_M[D]$ and the number of hops per average donor lifetime is given by $k_M\tau[D]$. The mean displacement \bar{r} of excitation during the average lifetime, τ , of the excited state is then:

$$\bar{r} = R \sqrt{k_M\tau[D]} \quad (32)$$

where R is the distance the excitation travels per hop. For styrene vinylbenzophenone copolymer films up to 10^3 jumps of the triplet energy migration from benzophenone to benzophenone is indicated.

Let R_{DA}^0 be the critical transfer distance for which the probability of energy transfer equals the probability of deactivation of D^* by all other processes and let r be the distance of net molecular energy migration (eq. 31). Then two extreme situations may be envisioned:

(1) When $r \ll R_{DA}^0$, the D^* molecules are quenched at distances of separation much larger than the diffusional distances moved by the molecules or the excitation. In this case, the D^* and A molecules remain effectively stationary during the lifetime of D^* . These are conditions for which Forster², Perrin⁴ or Dexter-Inokuti-Hirayama^{3,10} Kinetic Laws apply.

(2) When $r \gg R_{DA}^0$, the excitation energy or D^* (or both) are effectively mobile and the energy transfer rate is not distance dependent in the sense of case 1. In this situation, the Stern-Volmer Kinetic Law may be applied. relative molecular diffusion coefficient
In polymer systems, we expect in general that D will be very small and incapable of allowing case 2 to apply if $R_{DA}^0 > 15\text{\AA}$. However, if the polymer structure allows, it may be possible that D will be large enough so that case 2 applies, i.e., only in the case of significant energy migration do we expect Stern-Volmer kinetics to apply to energy transfer in rigid polymers. Forster² demonstrated that for Coulombic interactions in the absence of molecular diffusion or energy migration, the rate constant for energy transfer is given by:

$$k_{ET} = \frac{ck_D^0}{R_{DA}^6} f_D \epsilon_A \nu \quad (33)$$

where c is an estimable constant for a given donor-acceptor pair, k_D^0 is the radiative rate constant for emission from D^* , R_{DA} is the distance separating the donor and acceptor, f_D is the spectral distribution of donor emission (normalized to unity), ϵ_A is the extinction coefficient of the acceptor at wavelength ν .

All of the quantities on the right hand side of eq. 33 are estimable from experimental data so that a quantitative measure of k_{ET} may be evaluated from experimental data. However, since k_{ET} depends on R_{DA}^6 , for each different separation of D^* and A, a different rate constant exists!

It is therefore not possible to discuss "the" rate constant for energy transfer if more than one donor-acceptor separation exists. It is convenient, therefore, to select an arbitrary separation which will be useful to make comparisons between different donor-acceptor systems.

For example, we may define a "critical" separation of R_{DA} such that the rate of energy transfer exactly equals the rate of decay of D^* in the absence of A. Let this distance be R_{DA}^0 . Eq. 33 may now be rewritten as

$$k_{ET}/k_D = \left(\frac{R_{DA}^0}{R_{DA}} \right)^6 \quad (34)$$

Recall from eq.29 that $R_{DA} \sim 7 \times [A]^{-1/3}$, so that if the concentration of [A] for which $k_{ET} = k_D$ is known, the value of $R = R_{DA}^0$ may be evaluated.

Based on the assumption of an electron exchange mechanism a general formula has been derived for the decay of donor phosphorescence when the donor and acceptor are fixed in space, randomly distributed and for which energy migration through the intervening medium is not possible. Thus, if the phosphorescence decay of a "donor triplet" is measured, the experimental result may be compared to theory.¹⁰ The resulting theoretical expression is a complicated expression whose detailed analytical form is not of interest to us except for its form:

$$\phi \text{ (Decay function)} = f(\tau_p, R_0/L, C_A/C_0, t) \quad (35)$$

We note that the decay function depends on τ_p the donor phosphorescence lifetime, R_0 , the effective interaction distance separating donor and acceptor, L is effective radius of the donor, C_A , the concentration of acceptor, C_0 the critical concentration corresponding to R_0 and t the time elapsed after excitation of the donor.

In the case of triplet-triplet energy transfer from benzophenone to naphthalene (rigid solution at 77°K)¹¹, agreement between the measured decay function and the theoretical expression is found. Because of the agreement a value $R_0 \approx 14\text{\AA}$ is found. This value is considerably greater than the molecular "radius" of the donor. Thus, an electron exchange mechanism which is effective over distances somewhat greater than molecule diameters.

The following important assumptions made in this theory are:

- (1) Brownian motion of all molecules is slow enough so that each individual energy-transfer process may be considered to occur at a definite donor-acceptor distance;
- (2) The rate constant for energy transfer is independent of molecular orientation.
- (3) Energy transfer occurs via a direct D^*A interaction, i.e., energy migration does not occur.

The decay function for D^* is not an exponential function because as the decay proceeds, excited donors having unexcited acceptors in their immediate neighborhood tend to become exhausted since the rate constant k_{ET} decreases with increasing distance of separation.

The distance dependence of triplet-triplet energy transfer between organic molecules has been established for a number of different donor-acceptor pairs. As predicted, the donor phosphorescence decay is non-exponential in the presence of acceptor, but can be fitted to an exponential variation of the triplet-triplet rate constant with intermolecular distance. The results, which show the possibility of slow, but efficient energy transfer over distances significantly greater than 10Å, emphasize the ability of molecular wavefunctions to extend from the nuclei and result in energy transfer over distances greater than the "collisional" radii of molecules. When the donor-acceptor pairs are rigidly fixed in space and energy transfer occurs by an electron exchange mechanism, the value of k_{ET} again depends on distance. A theoretical expression for this dependence was originally proposed by Dexter and is given by:

$$k_{ET} = [c/(R_{DA}^0)^2] (\exp-2R_{DA})J \quad (36)$$

where c is a constant of the system for a given donor-acceptor pair, R_{DA}^0 is the critical separation of D^* and A, and J is the spectral overlap integral. An explicit formula for the time dependence of the decay of D^* in the presence of A has been developed and is given by a complex expression which if obeyed experimentally, allows evaluation of R_{DA}^0 .

A number of formulations are available for quantitative evaluation of energy transfer parameters. When molecular diffusion or energy migration results allow the assumption of statistical mixing, the Stern-Volmer formulation may be employed to derive an average rate constant for the energy transfer process and this value of k_{ET} may be used to compare different donor-acceptor systems. When molecular diffusion and energy migration are not significant during the lifetime of D^* , the Perrin formulation, the Forster formulation or the Dexter formulation may be applied. In these cases instead of a rate constant, the pertinent parameter is the "critical" separation R_{DA}^0 which is used to compare different donor-acceptor systems. Before

dealing with actual examples of energy transfer processes in polymers we need some calibration points in order to appreciate how the values of k_{ET} and/or R_{DA}^0 may be used to form conclusions of energy transfer mechanisms.

Since electronic energy transfer is generally a function of the donor-acceptor separation, R_{DA} , determination of the distance dependence is important both for the determination and elucidation of the electronic and mechanical mechanisms and for the utilization of energy transfer in effecting or controlling photochemical reactions.

In conclusion we might emphasize that all of the quantitative formulations which use experimental data to evaluate k_{ET} and R_{DA}^0 make assumptions concerning the microscopic structure of the sample, in particular, the random or statistical distribution of D and A in space. Also, "trivial" donor emission acceptor reabsorption is assumed to be unimportant. If complexing of D and A results in a non-random distribution of D and A, the models no longer apply.

CALIBRATION POINTS FOR THE MAGNITUDE OF k_{ET} AND R_{DA}^0

Since values of k_{ET} and R_{DA}^0 may be extracted from energy transfer data, these quantities serve as useful guides to compare energy transfer processes in different donor-acceptor systems and as a means of elucidating mechanistic pathways. First let us consider energy transfer by the exchange mechanism. In fluid solution, we expect the maximum values of k_{ET} to be equal to the rate constant for diffusion of D^* and A into a collision encounter. Since the probability of electron exchange falls off rapidly as the separation of D^* and A increases (eq. 14) we expect that the maximum value of R_{DA}^0 will not be much larger than $R_D + R_A$, the sum of the "kinetic" collisional radii of D^* and A. The maximal value of k_{ET} (exchange) may be estimated from eq. 23. For non-viscous solvents (e.g., benzene, acetonitrile, methanol, etc.) near room temperature $\eta \sim 10^{-2}$ so that :

$$k_{ET}^{\max} \text{ (exchange)} \sim 10^{10} \text{ M}^{-1} \text{ sec}^{-1} \quad (37)$$

For small organic molecules, the pertinent chromophores possess R values of the order of $\sim 7\text{\AA}$ or smaller so that:

$$R_{DA}^0 \text{ (exchange)} \sim 15\text{\AA} \quad (38)$$

We now have two calibration points with which to consider experimental data: For energy transfer by the exchange mechanism k_{ET} can significantly exceed $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ and R_{DA}^0 cannot significantly exceed 15\AA . We should keep in mind the fact that k_{ET}^{\max} (exchange) is temperature dependent and should vary as T/η .

Consider now energy transfer by the dipole-dipole mechanism. From eq. 33, if the spectral distribution of emission, given by f_D and of absorption, given by ϵ_A are assumed to Gaussian and of half-width of $\sim 4000 \text{ cm}^{-1}$, then the rate constant for energy transfer is approximately given by:

$$k_{ET} \sim \frac{4 \times 10^4 \epsilon_A^{\max} k_D^0}{R_{DA}^6} \quad (39)$$

where ϵ_A^{\max} is the acceptor extinction coefficient, k_D^0 is the radiative lifetime of D^* and R_{DA} is the separation of D and A (in \AA).

The largest values of ϵ_A^{\max} encountered are of the order of $10^5 \text{ cm}^{-1} \text{ M}^{-1}$ and values of k_D^0 rarely exceed 10^9 sec^{-1} . Thus, if D^* and A are 10\AA apart

$$k_{ET}^{\max} \sim \frac{4 \times 10^4 \times 10^5 \times 10^9}{(10)^6} = \frac{4 \times 10^{18}}{10^6} = 4 \times 10^{12} \text{ sec}^{-1} \quad (40)$$

The value of k_{ET} is only qualitatively correct but it emphasizes that for separation of D^* and A as small as the order of molecular diameters, k_{ET} may reach a magnitude approaching vibrational rates! Suppose, $R_{DA} = 40\text{\AA}$ then, $k_{ET}^{\max} \sim 10^9 \text{ sec}^{-1}$.

We now see that both k_{ET}^{\max} and $(R_{DA}^0)^{\max}$ for dipole-dipole energy transfer may exceed the analogous maximal values for exchange energy transfer. Thus, experimentally derived values of k_{ET}

from experimental value data from eq. 34.

| <u>Singlet-Singlet Energy Transfer in Polymers</u> | | | | | |
|--|--------------------------|---------------------------|------------|-----------------|------|
| <u>Polymer</u> | <u>Donor</u> | <u>Acceptor</u> | R_{DA}^0 | k_{ET} | Ref. |
| Polyacrylonitrile | Pyrene | Sevron Yellow | 40 | 4×10^6 | 1 |
| Polystyrene | Polystyrene | Tetraphenyl- butadiene | 20 | 3×10^9 | 2 |
| Poly(vinylcarbazole) | Poly(vinyl- carbazole | Benzophenone | 26 | - | 3 |
| Poly(vinylnaphthalene)(PVN) | PVN | Benzophenone | 15 | 1×10^9 | 4 |
| Poly(vinylmethylketone)(PVM) | PVM | Benzophenone | 8 | $\sim 10^9$ | 5 |

(1) R.G. Bennett, R.P. Schwenker and R. Kellogg, *J.Chem.Phys.*, **41**, 3040 (1967)

(2) L.J. Basile, *Trans.Farad.Soc.*, **42**, 3163 (1965)

(3) G. Geuskens and C. David, IUPAC, special lectures, **8**, 19 (1971)

(4) C. David, W. Demarteau and G. Geuskens, *Europ.Polymer J.*, **6**, 1397 (1970)

(5) C. David, N. Putman and G. Geuskens, *ibid.*, **8**, 409 (1972)

Similarly, singlet-singlet energy transfer from photoexcited polystyrene to tetraphenylbutadiene exhibits a value of R_{DA}^0 equal to 21Å. The calculated value (eq. 33) is 20Å, so that a dipole-dipole interaction is indicated.¹³

In the case of singlet-singlet energy transfer from polyvinylcarbazole to benzophenone, the calculated value of R_{DA}^0 is considerably smaller (12Å) than the experimental value (26Å).

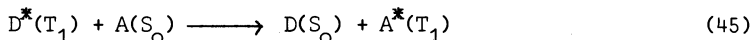
This discrepancy is consistent with singlet energy migration among the carbazole units.¹⁴

The small values of R_{DA}^0 for the donor-acceptor systems poly(vinylnaphthalene)-benzophenone¹⁵ and poly(vinylmethyl ketone)-benzophenone¹⁶ indicate a lack of both energy migration and of Coulombic interactions.

Quenching of the fluorescence of poly (methyl vinyl ketone) by biacetyl in ethyl acetate indicates that k_{ET} is about four time greater than that for quenching of the fluorescence of small ketones (e.g., 4-heptanone) by biacetyl.¹⁷ This result has been interpreted in terms of singlet-singlet energy migration along the polymer chain which results in a delocalization which somehow facilitates the transfer probability by effectively increasing the "cross section" for energy transfer.

TRIPLET-TRIPLET ENERGY TRANSFER

By triplet-triplet energy transfer in polymers we mean that an electronically excited donor in its triplet state produces an electronically excited acceptor in its triplet state (eq. 45).



Triplet-triplet energy transfer is "forbidden" by the dipole-dipole mechanism (exceedingly low ϵ_A , eq. 39) however, triplet-triplet energy transfer is "spin-allowed" by the exchange mechanism. We expect therefore that triplet-triplet transfer will generally occur via the exchange mechanism. Values of R_{DA}^0 of the order of 10-15Å are expected since close approach of donor and acceptor are required for effective exchange interaction.

Experimentally, triplet-triplet parameters are measured by quenching donor phosphorescence and/or sensitizing acceptor emission. Some examples of triplet-triplet energy transfer in polymers are given in Table 2.

From the R_{DA}^0 values given in table 2, it may be concluded that in the case of poly(vinylbenzophenone), poly(phenylvinylketone)¹⁸ and styrene-vinylbenzophenone⁹ copolymers substantial energy migration occurs via triplet-triplet energy transfer.

Notice that in solid solid (for which energy migration was unlikely) values of $R_{DA}^0 \sim 13-15\text{\AA}$ are found. Also note that "rate constant" for energy transfer at this separation is very small ($k_{ET} < 10^2 \text{ sec}^{-1}$)

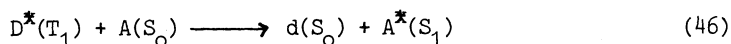
Triplet-Triplet Energy Transfer in Polymers

| Polymer | Donor | Acceptor | R_{DA}^0 | k_{ET}^{TT} | Ref. |
|---|--------------|----------------|------------|---------------|------|
| Poly(vinylbenzophenone)(PVB) | PVB | Naphthalene | 36 | 10^5 | 1 |
| Solid solution | Benzophenone | Naphthalene | 13 | 10^2 | 2a |
| Solid solution | Carbazole | Naphthalene | 15 | 10^{-1} | 2b |
| Poly(phenylvinylketone)(PPV) | PPV | Naphthalene | 26 | - | 3 |
| Poly(methylvinylketone)(PMV) | PMV | Naphthalene | 11 | - | 4 |
| Poly(vinylnaphthalene)(PVN) | PVN | 1,3-Pentadiene | ~ 15 | 10^2 | 5 |
| Styrene-Vinylbenzophenone Copolymer (SVB) | SVB | Naphthalene | 300 | - | 6 |

- (1) C. David, W. Demarteau and G. Geuskens, *Eur. Polymer J.*, **6**, 537 (1970)
 (2) (a) A.N. Terenin and V.L. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1956);
 M. Inokuti and F. Hirayama, *J. Chem. Phys.*, **43**, 1978 (1965);
 (b) G.B. Stambini and W.C. Galley, *ibid.*, **63**, 3467 (1975)
 (3) C. David, W. Demarteau and G. Geuskens, *Eur. Polymer J.*, **6**, 1405 (1970)
 (4) C. David, N. Putman, M. Lempereur and G. Geuskens, *ibid.*, **8**, 409 (1972)
 (5) C. David, M. Lempereur and G. Geuskens, *ibid.*, **8**, 417 (1972)
 (6) C. David, V. Naegelen, W. Piret and G. Geuskens, *ibid.*, **11**, 569 (1975)

TRIPLET-SINGLET ENERGY TRANSFER

By triplet-singlet energy transfer in polymers we mean that an electronically excited donor in its triplet state produces an electronically excited acceptors in its singlet state. (eq.46)



Triplet to singlet energy transfer may occur via the Coulombic mechanism if the donor triplet is very long-lived and if the acceptor possesses a large value of ϵ_A^{\max} . These conditions are somewhat antithetical to experimental study by photoexcitation techniques. Since the requirement of a large ϵ_A^{\max} and finite spectral overlap (J , eq.6), contribute to make direct excitation of the donor technically difficult. Chemiexcitation of an electronically excited donor allows this difficulty to be overcome, because the electronic excitation of the donor occurs selectively and the value of ϵ_A^{\max} is irrelevant to the chemiexcitation step. Chemiluminescence is chemiexcitation which is followed by luminescence. Chemiluminescence techniques have been employed to demonstrate the occurrence of energy transfer from triplet acetone to singlet dibromoanthracene in a polystyrene matrix. The process is long range in nature ($R_{DA}^0 \sim 25\text{\AA}$) and may involve a Coulombic mechanism and/or triplet energy migration through the polystyrene.¹⁹

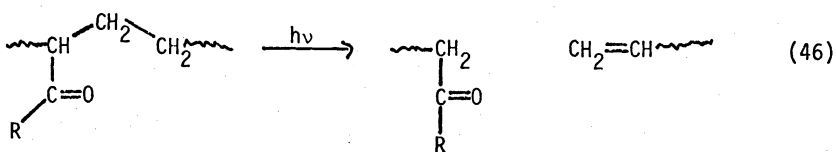
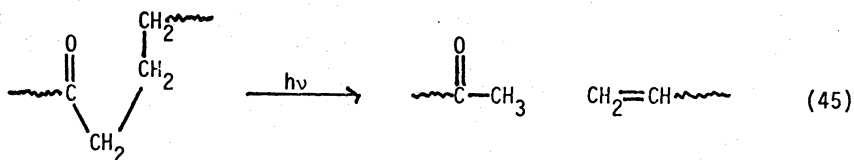
USES OF ENERGY TRANSFER PROCESSES FOR POLYMER STABILIZATION

The methods for stabilization of polymers against photodegradation may be classified in terms of:

- (1) Screening or coating of the polymer to prevent light from directly reacting the absorbing chromophores contained in the polymer;
 - (2) Addition of absorbers which preferentially absorb photoactive wavelengths and which are capable of degrading the absorbed energy without causing polymer degradation;
 - (3) Addition of scavengers which remove electronically excited states (or photochemically produced reactive intermediates) before the latter can cause polymer degradation.
- Let us consider stabilization method 3. Suppose a polymer absorbs a photon which excites one

of the chromophores on the main polymer backbone. Photoreactions of this excited unit may initiate degradation of the polymer via direct chain scission reactions, cross-linking reactions, chain alteration, etc. Alternatively, the excited unit may initiate degradation via formation of an intermediate which then proceeds to actually effect the deterioration of the polymer. If the excited chromophore is known, a rational selection of potential, effective energy transfer quenchers is possible.

As an illustration, irradiation of polymers containing ketone functions as part of the main chain or as pendant side chains results in chain scission via the well known "Type II" cleavage reaction.



For solutions of such polymers as well as in solid films, these reactions are strongly quenched by the well known acceptors of energy from ketone triplets, e.g., naphthalene and 1,3-dienes.²⁰ For illustration, the quantum yield for chain scission by the Type II process is 0.25 for poly(phenyl vinyl ketone) in benzene. Addition of triplet quenchers results in a substantial decrease in the scission efficiency.²¹

Interestingly, copolymers of vinyl phenyl ketone and 1-vinylnaphthalene are more stable to degradation than polymers of vinyl phenyl ketone containing free naphthalene units.²² The greater quenching efficiency of the bound naphthylene is probably due to energy migration followed by trapping. Since the R_{DA}^0 value of the poly(vinylphenyl ketone) - naphthylene system is $\sim 18\text{\AA}$, quenching in copolymers would be completely efficient if a naphthyl unit appeared regularly every 18\AA .

Experimentally, the photolysis efficiency of a copolymer containing 9% naphthyl units (ideal average random separation $\sim 15\text{\AA}$) is only 4% of the value of pure poly(vinylphenyl ketone). Poly(vinylbenzophenone) undergoes photochemical crosslinking as evidence by its insolubilization when a light of 365 nm is absorbed.²³ The reaction is probably the result of abstraction of a hydrogen atom by a triplet ketone unit followed by interchain radical couplings. This reaction is effectively prevented by the addition of naphthalene.

To the extent that a polymer undergoes photochemistry, it is possible that "impurities", either adventitiously present or as part of a few polymer chains (e.g., end groups), may have a dominant influence on the efficiency of reaction or of quenching of reaction. Energy migration or energy transfer along a polymer chain or between polymer chains may cause the electronic excitation to eventually become localized in a trap such that net photochemistry becomes controlled from the trap rather than by the polymer itself. The impurity traps may serve as stabilizers of the polymer by efficiently and harmlessly degrading the electronic excitation or may serve as a site for initiation of polymer degradation. Thus, the photochemistry of polymers may be partially dependent or completely controlled by energy transfer, energy migration and other photophysical events that occur after a photon is absorbed by a polymer but before the actual photochemical events that result in a net alteration of the polymer characteristics.

EXCIMER FORMATION

If an excited donor molecule D^* comes into the proximity of a ground state molecule D , the formation of an excimer is possible. An excimer is an electronically excited species of the type $D^* \cdots D$. Several important characteristics of excimers²⁴ are:

- (1) Excimer formation requires close approach of D^* and D and usually requires specific structural interactions;
- (2) Excimer formation is detectable by excimer emission, which is usually distinct from that of D^* ;

(3) Excimers are weakly bound species so that dissociation of the type $D^* \cdots D \longrightarrow D + D^*$ may occur readily as a mechanism for energy migration. The emission of films of poly (vinyl naphthylene) at 77°K or at room temperature consists exclusively of broad excimer emission. The near absence of "normal" naphthalene monomer fluorescence and phosphorescence at 77°K is noteworthy.²⁵ The lifetime of the excimer emission was found to be $\sim 10^{-3}$ sec, thereby indicating a rate limiting step involving triplets rather than singlets. Evidently, naphthalene singlet excitation, produced by triplet-triplet annihilation, migrates from naphthalene to naphthalene along the chain until the singlet excitation is trapped by a pair of chromophores that have the correct mutual spatial orientation for excimer formation. Thus, monomer fluorescence ($\tau_f \sim 100$ ns) cannot compete with excimer formation. It is extremely unlikely that excimer formation occurs significantly at the site of absorption by exciting photon, since this would require each naphthalene group to have at least one first neighbor satisfying the orientation requirements for excimer formation. The emission spectrum of solutions of polystyrene at room temperature indicates that singlet excimer formation is nearly 100 % efficient, i.e., only excimer fluorescence and no monomer fluorescence is observed.²⁶ This result indicates rapid intramolecular migration of singlet energy to sites favorable to excimer formation, and that these sites act as "traps" for singlet excitation. At the temperature of its glass formation (110°K) and below, excimer formation is not observed for dilute solutions of polystyrene. A neat film of polystyrene, however, displays excimer fluorescence at room temperature and at very low temperatures. The fraction monomer fluorescence increases and the temperature is lowered. Evidently, in the neat polymer film interchain singlet migration is possible. Phosphorescence from polystyrene is observed for dilute solutions at 77°K. However, at room temperature no phosphorescence is observed because of the very strong quenching by oxygen and other impurities that are capable of serving as diffusional quenchers of triplets in polystyrene at room temperature but not at 77°K. The occurrence of triplet energy migration in polystyrene is indicated, however, by the observation of delayed naphthalene fluorescence in polyvinyl naphthalene-polystyrene copolymers, even when the phenyl group absorbs most of the exciting radiation. The delayed nature of the fluorescence is thought to be the result of triplet-triplet annihilation processes. Since only the naphthyl groups emit, although the phenyl groups are excited, the observations may be interpreted as the result of triplet-triplet migration along the polystyrene chain followed by triplet transfer to a naphthyl unit. Further triplet migration along the naphthyl segment occurs until two triplets collide and generate a naphthalene singlet which then fluoresces. In summary, excimer formation has provided a means of identifying the occurrence of energy transfer along site chains (Figure 9) and across polymer chains. In addition, molecular motion and mobility in solid polymers may be investigated by studying the extent of excimer formation as a function of temperature.

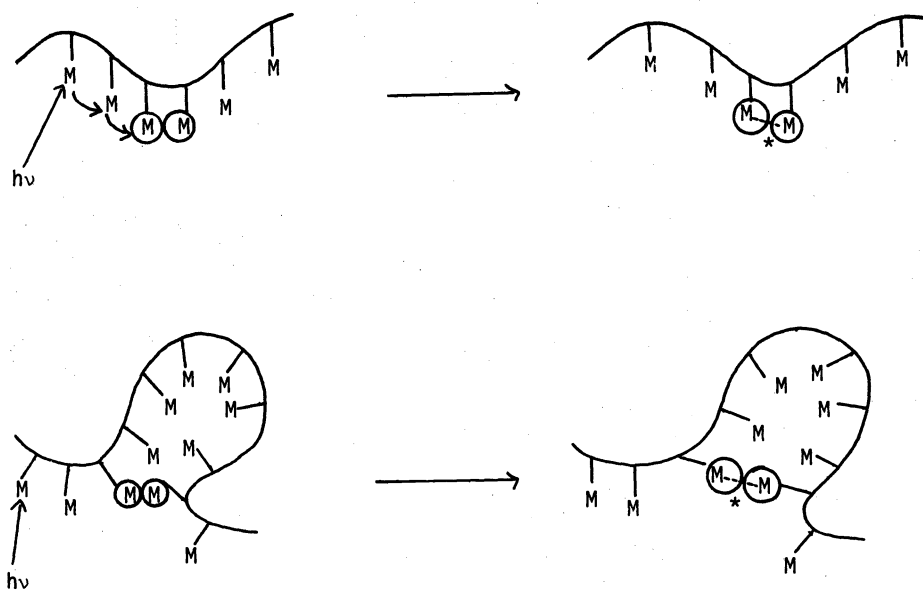
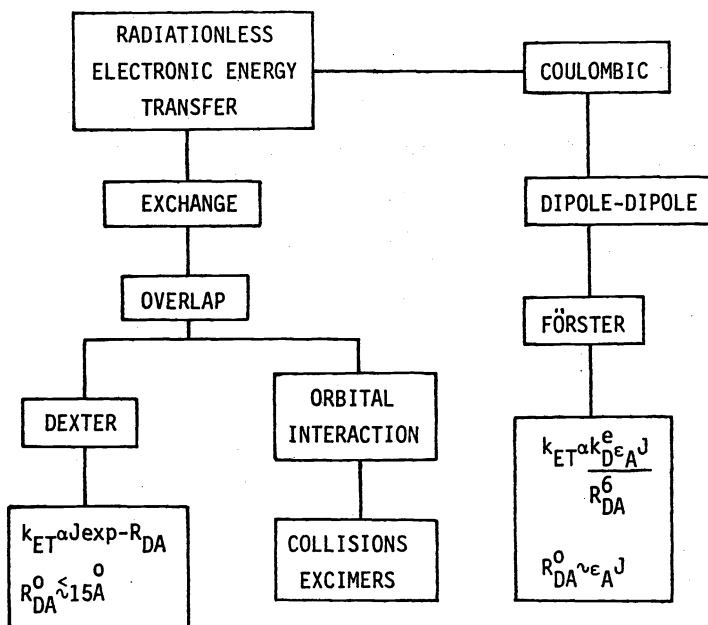
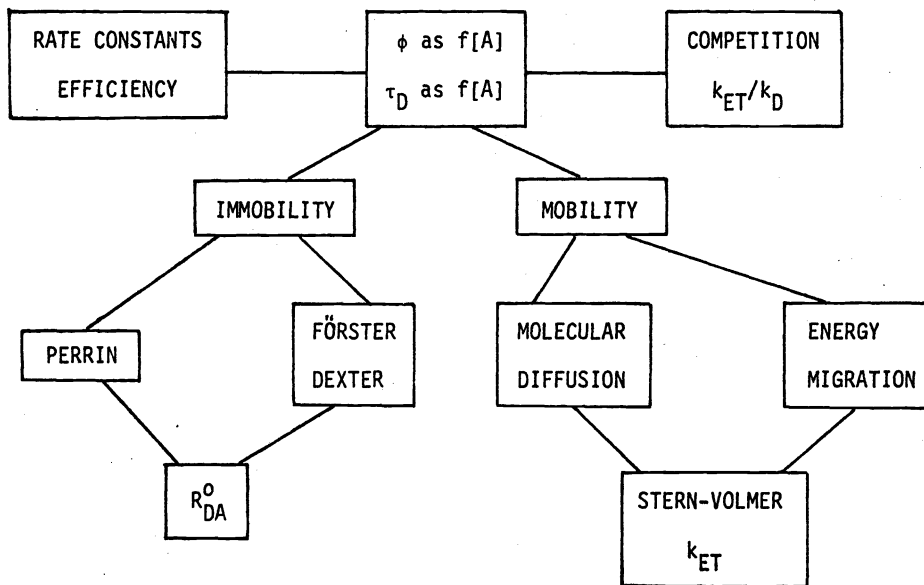


Fig. 9 Schematic description of excimer formation by energy migration between nearest neighbors along a polymer backbone and by intramolecular interactions between non-nearest neighbors.



Scheme 3 : Flow diagram of the major electronic mechanisms for electronic energy transfer and the relationship of energy transfer parameters to experimental and theoretical quantities.



Scheme 4 : Flow diagram of the procedure for determining energy transfer rate constants and critical separations.

CONCLUSION

In this review, we have attempted to provide an understanding of the nature of energy transfer processes and the relationship of rates and efficiencies to molecular structures and molecular mechanics. The broad general concepts which emerge are that two major types of electronic interactions provide the major mechanisms for electronic energy transfer (Schemes 3 and 4). The rate and efficiency of any actual system depends on the donor-acceptor pair with regard to the transfer energetics, the spin characteristics of the overall transfer, the distance of separation and the occurrence (or non-occurrence) of molecular diffusion and/or energy migration. Energy transfer processes can serve to protect polymers or to enhance their degradation. Systematic quantitative studies of energy transfer processes in polymer system have become more common in recent years. These investigations are providing a substantial basis for the rational selection of molecular structures to achieve control of electronic energy transfer processes in polymers.

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REFERENCES

1. Reviews of electronic energy transfer:
 - A. A.A. Lamola, "Energy Transfer and Organic Photochemistry", John Wiley, New York, (1969).
 - B. J.B. Birks, "Photophysics of Aromatic Molecules", John Wiley, New York, (1970) ch. 11
 - C. N.J. Turro, "Molecular Photochemistry", W.A. Benjamin, San Francisco, (1965) ch. 5
2. T. Forster, Disc. Faraday Soc., 27, 7 (1959).
3. D.L. Dexter, J. Chem. Phys., 21, 836 (1953).
4. V.L. Ermolaev, Bull. Natl. Acad. Sci., USSR, 32, 1193 (1968).
5. H.J. Heller and H.R. Blattmann, Pure Appl. Chem., 36, 141 (1973).
6. G. Stambini and W.C. Galley, J. Chem. Phys., 63, 3467 (1975).
7. R.W. Anderson, R.M. Hochstrasser, L. Lietz and G.W. Scott, J. Chem. Phys., 61, 2500 (1974).
8. For a general review of molecular diffusion and energy migration see J. Birks, "Photophysics of Organic Molecules", J. Wiley, 1970, p. 518 ff.
9. C. David, V. Naegelen, W. Pirit and G. Geuskens, Eur. Polymer J., 11, 569 (1975).
10. M. Inokuti and F. Hirayama, J. Chem. Phys., 43, 1978 (1965).
11. H. Kobashi, T. Morita and N. Mataga, Chem. Phys. Letters, 20, 376 (1973).
12. R. Bennett, R.P. Schwenker and R. Kellogg, J. Chem. Phys., 41, 3040 (1967).
13. L.J. Basile, Trans. Farad. Soc., 42, 3163 (1965).
14. G. Geuskens and C. David, IUPAC, special lectures, 8, 19 (1971).
15. C. David, W. Demarteau and G. Geuskens, Eur. Polymer J., 6, 1397 (1970).
16. C. David, N. Putnam and G. Geuskens, ibid., 8, 409 (1972).
17. A. Somersall and J.E. Guillet, Macromol., 5, 410 (1972).
18. C. David, W. Demarteau and G. Geuskens, Eur. Polymer J., 6, 537 (1970).
19. H.C. Steinmetzer and N.J. Turro, J. Am. Chem. Soc., 96, 4677, 4679 (1974).
20. M. Heskins and J.E. Guillet, Macromol., 3, 224 (1970).
C. David, W. Demarteau and G. Geuskens, Eur. Polymer J., 6, 1405 (1970).
21. F.J. Golemba and J.E. Guillet, Macromol., 5, 212 (1972).
22. I. Lukac, P. Hrdlovic, Z. Manosck and D. Bellus, J. Polymer Sci., Part A-1, 9, 69 (1971).
23. C. David, W. Demarteau and G. Geuskens, Polymer, 10, 21 (1969).
24. For a review of excimers see ref. 8, p. 403.
25. C. David, W. Demarteau and G. Geuskens, Eur. Polymer J., 6, 1397 (1970).
26. Review: R.B. Fox, Pure Appl. Chem., 34, 235 (1973).