

ENERGY TRANSFER PROCESSES

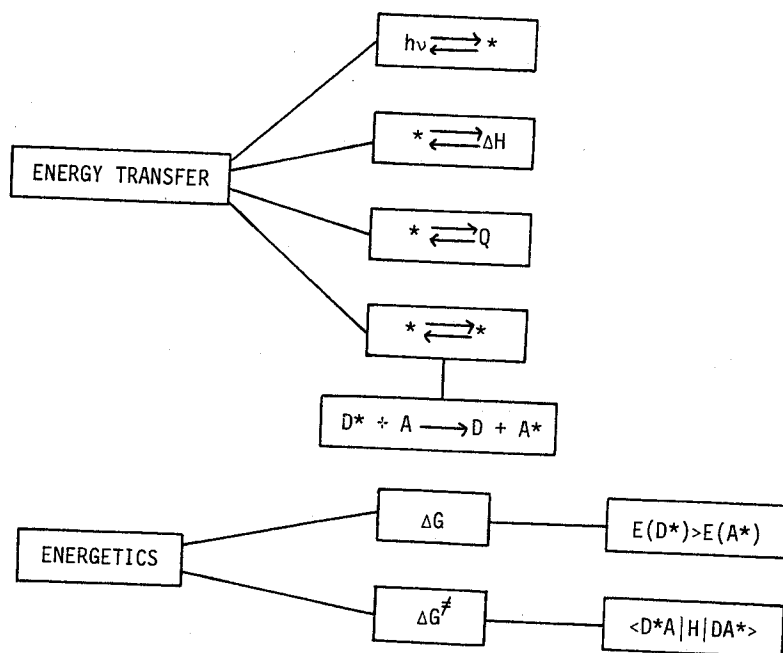
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Abstract: A discussion of the major mechanisms for electronic energy transfer for organic molecules is presented. Application of the techniques and ideas of electronic energy transfer to study the properties of polymers is given.

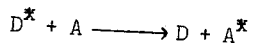
INTRODUCTION

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



(1)

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

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 influence 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,

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 $\phi_D^* \rightarrow \phi_D$ and $\phi_A \rightarrow \phi_A^*$. 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).

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

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

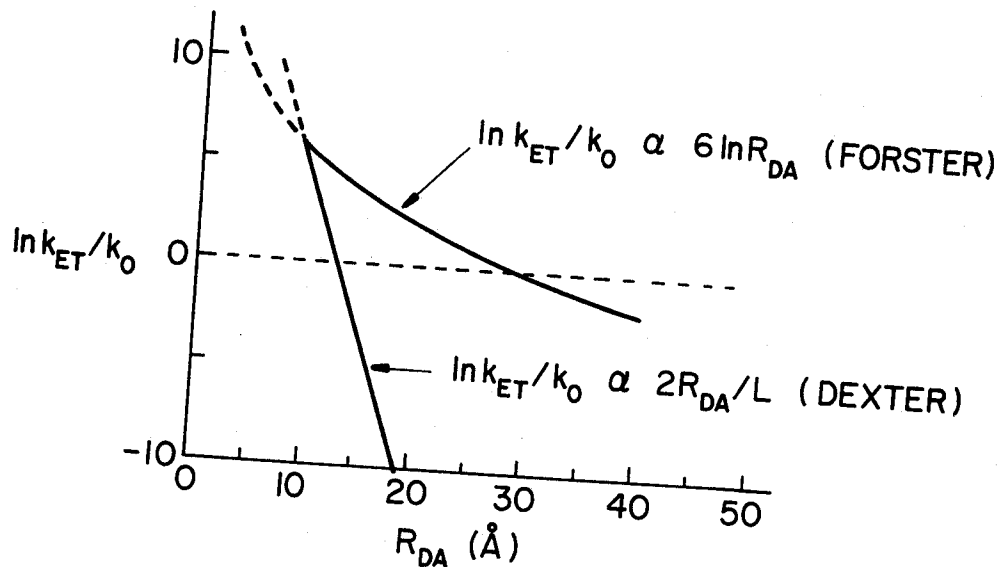


Fig. 4 Qualitative relationship between the ratio of the energy transfer rate constant to acceptor decay constant for Coulombic and electron exchange energy transfer to the separation between D^* and A.

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} .

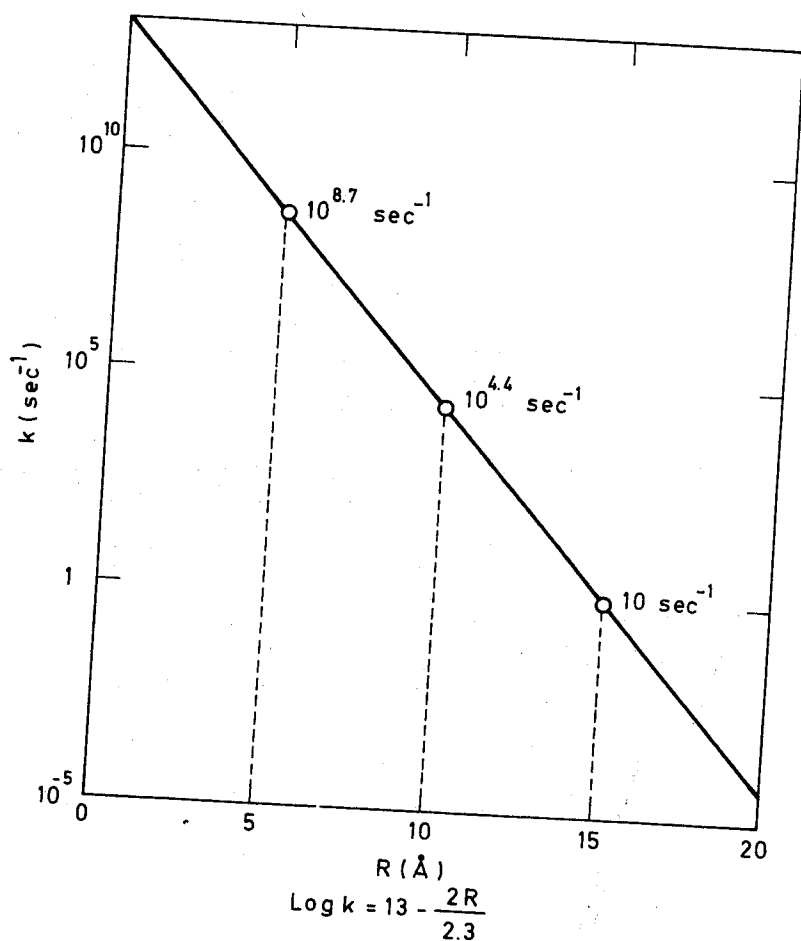


Fig. 5 Falloff of the rate constant for energy transfer by the electron exchange mechanism as a function of separation of donor and acceptor, for $k_{ET} = 10^{13} \exp(-2R)$

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

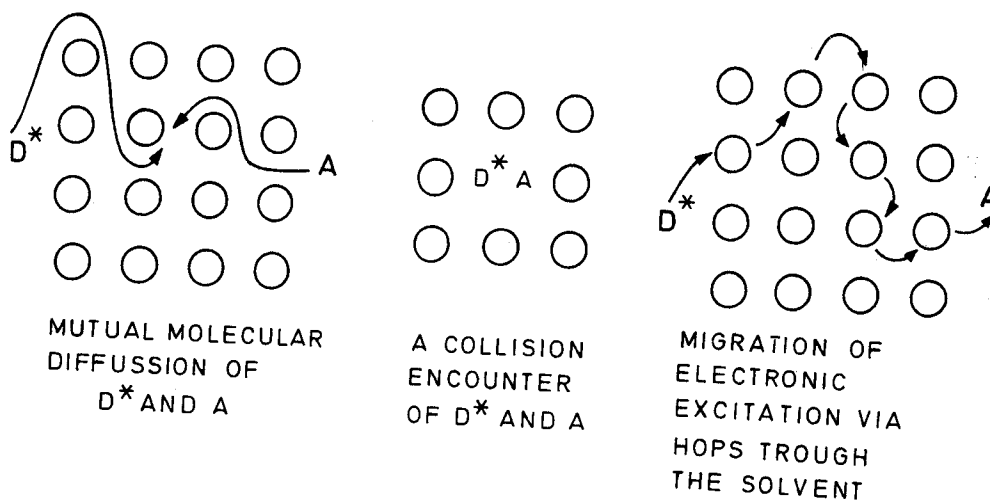


Fig. 6 Schematic of molecular diffusion, energy migration and collision encounters

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

$$r = \sqrt{2Dt}$$

(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 150 \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 \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:

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

(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-

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

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.

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

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

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

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

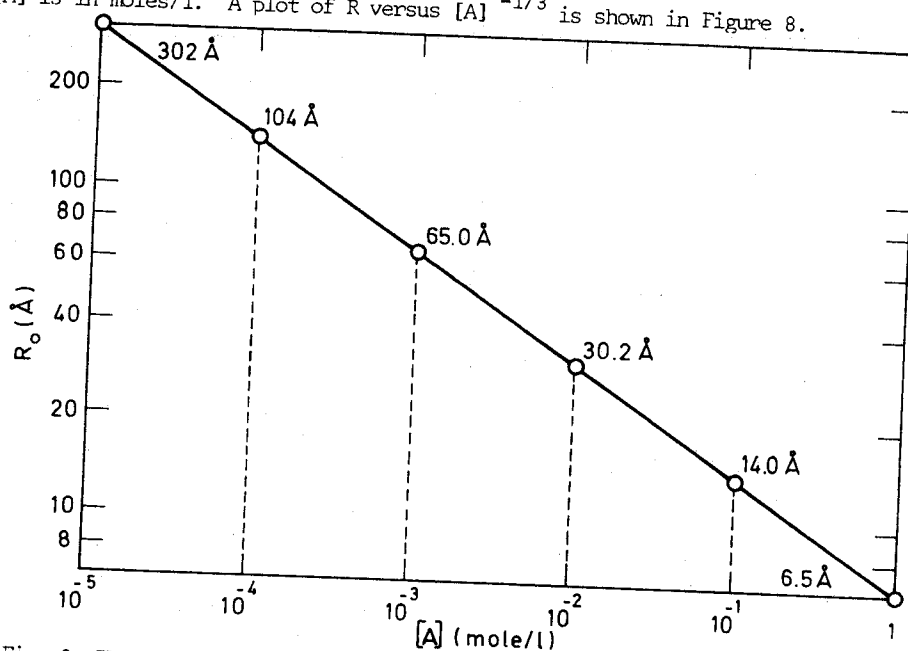


Fig. 8 The relationship of separation of D^* and A to the concentration of A.

For example, we may define a "critical" separation of R_{DA}^0 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 $R_{DA}^0 \sim 7 \times [A]^{-1/3}$, 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 functions 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 10\AA , 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

which are significantly in excess of $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ are inconsistent with a single step exchange mechanism as are R_{DA}^0 values in excess of 15\AA .

ENERGY TRANSFER PROCESSES IN POLYMERS

We shall consider briefly some examples of energy transfer processes in polymers. A basic assumption made in the interpretation of energy transfer processes in polymers is that concepts developed for energy transfer between low molecular weight chromophores in solution are valid for chromophores inbedded in polymer systems. A major new feature is the inhibition of molecular diffusion and molecular conformational motions imposed upon the polymer backbone and pendant groups by the polymer structure. The inhibition of molecular motions restricts the possibilities of molecular mechanics which may be involved in energy transfer processes. A second distinctive feature of macromolecules such as polymers is the occurrence of sequential structural units containing chromophores which are attached to the backbone or main chain of a polymer. This permanent spatial relationship between neighboring and well separated chromophores contrasts with the dynamic relationship between a small solute molecule and its solvent neighbors. If the pattern of sequential bonding is repetitive and orderly, domains of the polymer may exist which are crystalline in nature. This situation may be favorable to certain types of energy transfer processes. If we assume that molecular diffusion is not significant during the excited state lifetime, and ignore intermolecular energy transfer, we are concerned with the following situations:

(1) Energy transfer from D^* to A occurs via direct interactions during which the polymer serves as an inert matrix which prevents molecular diffusion of D^* and A during the lifetime of D^* , i.e.,



(2) Energy transfer from D^* to A occurs via initial transfer to a chromophore, M, of the polymer, followed by energy transfer along the polymer chain until an M^* interacts with and transfers energy to an acceptor, i.e.,



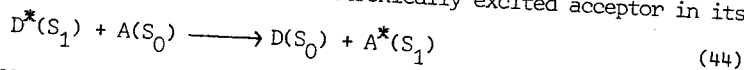
(3) Energy transfer occurs from D^* to M as in eq. 32, but A is now part of the polymer chain (end group or copolymerized group), i.e.,



We may also image situations in which M^* is produced by direct light absorption and then processes analogous to eqs. 41, 42 and 43 ensue. With the above classifications in mind let us now consider some experimental examples of energy transfer processes in polymers.

SINGLET-SINGLET ENERGY TRANSFER IN POLYMERS

By singlet-singlet energy transfer in polymers we mean that an electronically excited donor in its singlet state produces an electronically excited acceptor in its singlet state (eq. 44).



This process may occur in one step via a dipole-dipole interaction (favored by a large value for k_D^F and ϵ_A^{max}) or via an exchange interaction (favored by a small value of k_D^F and ϵ_A^{max}). In addition, an indirect mechanism involving energy migration through polymer segments may operate. The energy migration may occur via dipole-dipole or exchange interactions. Some examples of singlet-singlet energy transfer in which the polymer serves as an inert matrix are given in Table 1.

The large value of R_{DA}^0 for the singlet-singlet energy transfer in the pyrene-Sevron Yellow system in polyacrylonitrile indicates that transfer is occurring via a dipole-dipole mechanism. Energy migration via the solvent is unimportant because polyacrylonitrile does not possess low energy singlet excited states. Furthermore, the value of R_{DA}^0 calculated from eq. 33 (an assumption of a dipole-dipole interaction) is in excellent agreement with the value calculated

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

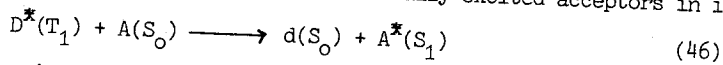
Triplet-Triplet Energy Transfer in Polymers

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);
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- (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

(3) Excimers are weakly bound species so that dissociation of the type $D \text{---}^* \text{---} D \longrightarrow D + D^*$ 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 polystyrene copolymers, even when the phenyl group absorb 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.

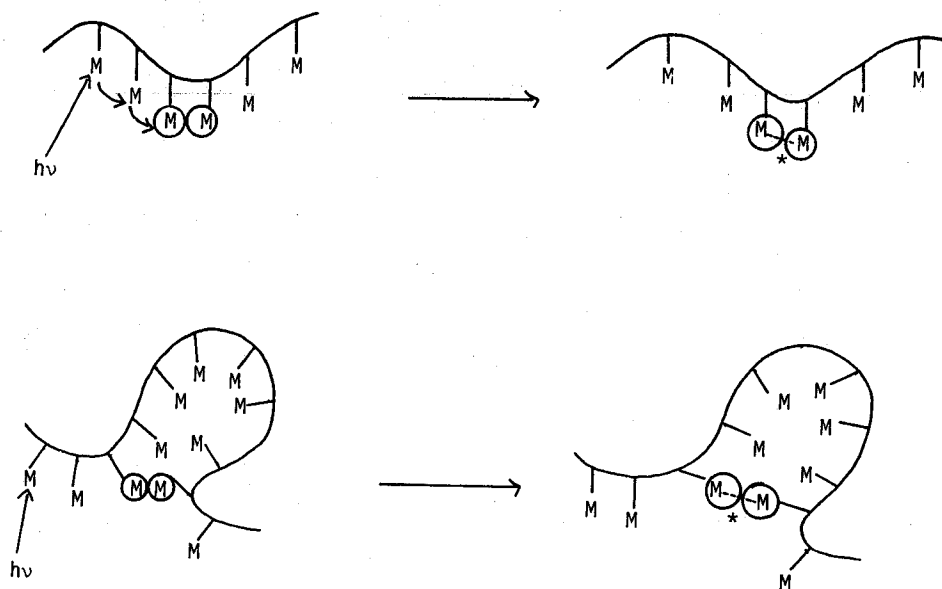


Fig. 9 Schematic description of excimer formation by energy migration between nearest neighbors along a polymer backbone and by intramolecular interactions between non-nearest neighbors.

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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