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Intramolecular Long-Distance Electron Transfer in Organic Molecules

GERHARD L. CLOSS AND JOHN R. MILLER

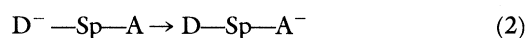
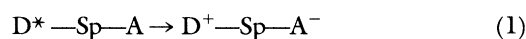
Intramolecular long-distance electron transfer (ET) has been actively studied in recent years in order to test existing theories in a quantitative way and to provide the necessary constants for predicting ET rates from simple structural parameters. Theoretical predictions of an "inverted region," where increasing the driving force of the reaction will decrease its rate, have begun to be experimentally confirmed. A predicted nonlinear dependence of ET rates on the polarity of the solvent has also been confirmed. This work has implications for the design of efficient photochemical charge-separation devices. Other studies have been directed toward determining the distance dependence of ET reactions. Model studies on different series of compounds give similar distance dependences. When different stereochemical structures are compared, it becomes apparent that geometrical factors must be taken into account. Finally, the mechanism of coupling between donor and acceptor in weakly interacting systems has become of major importance. The theoretical and experimental evidence favors a model in which coupling is provided by the interaction with the orbitals of the intervening molecular fragments, although more experimental evidence is needed.

ELECTRON TRANSFER (ET) REACTIONS HAVE A CENTRAL position in chemistry and biochemistry. The key steps in photosynthesis and metabolism, as well as many simple chemical reactions, involve ET reactions. Thus experimental and theoretical research on the subject has been actively pursued for many decades (1-3). However, there has been an unprecedented flurry of activity in the field in recent years, partially stimulated by the exciting developments in photosynthesis research, (4) where x-ray structure analyses (5) of reaction center proteins have focused attention on the mechanism of the primary steps of photoinduced charge separation. Physical organic and inorganic chemists have also been attracted to the problem and made valuable contributions. Their skills in synthesizing specific molecules for the solution of particular problems have had an enormous impact on the field. In this article we emphasize intramolecular ET in organic model systems. Space restrictions do not allow us to include protein-based model systems in spite of their fundamental importance (6, 7).

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The Basic Models and the Foundation of Their Theoretical Description

In recent years several research groups have recognized that intramolecular ET in molecules, in which donor (D) and acceptor (A) are separated by inert rigid spacers (Sp), have definite advantages over freely diffusing systems because the distance of the electron "jump" is well defined (8-15). They are also better models for many biological systems, because frequently D and A are bound to proteins that maintain a well-defined separation distance. Thus the chemical systems and reactions we are concerned with here are given by Eqs. 1 and 2. The first corresponds to charge separation from an excited donor (or acceptor) state



and the second is a simple charge-shift reaction, and both have analogs in important biochemical reactions (16). Since many recent experiments have been designed to test theories, we present at this point a brief outline of the basics upon which quantitative theories are built.

The rates of most ET reactions, like any other chemical reactions, can be expressed in terms of an Arrhenius expression (Eq. 3) with a preexponential factor A and an exponential temperature (T) dependence (17), the magnitude of which depends on an activation energy, E_a .

$$k = A \exp[-E_a/k_B T] \quad (3)$$

In Eyring's transition state theory (TST), the preexponential term is replaced by $\kappa k_B T/h$, where κ is the transmission coefficient, h ($=2\pi\hbar$) is Planck's constant, and k_B is Boltzmann's constant. The activation energy is replaced by the free energy of activation ΔG^\ddagger . In ET, where usually no bonds are broken or made, both terms differ from those associated with conventional TST. The next few paragraphs will outline those differences.

The electronic interactions between D and A in molecules presented by Eqs. 1 and 2, as well as in many natural systems, are extremely weak (much less than one kilocalorie) compared with the energies of bonds broken or made in most chemical reactions. Thus one must ask whether the reaction is adiabatic, nonadiabatic, or perhaps on the borderline, because the theory is different for each of those limits (18, 19). A definition of the extreme cases is given with the help of Fig. 1. The left and right sides of Eqs. 1 and 2 represent in zero order two different electronic states. An as yet undefined reaction coordinate takes the system from one state to the other. Somewhere along this coordinate the curves for the zero-order states cross (Fig. 1A), but in higher order this crossing is avoided by mixing between the states (Fig. 1B). According to the time-

Fig. 1. Schematic representations of free energy crosssections of two electronic states: (A) zero-order presentation without mixing, followed in nonadiabatic reactions; and (B) presentation of eigenstates after mixing, followed in adiabatic reactions.

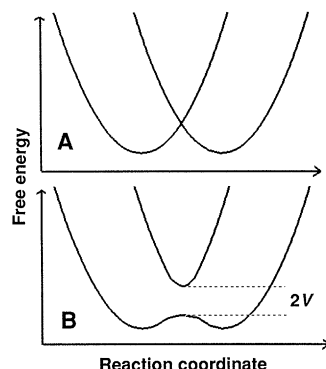
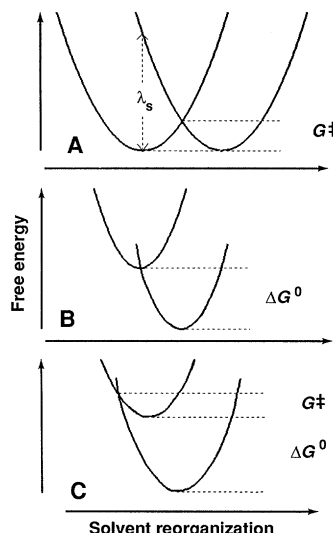


Fig. 2. Schematic, one-dimensional representation of free energy surfaces relevant in nonadiabatic electron transfer reactions for (A) thermally neutral reactions; (B) the special case where $-\Delta G^0 = \lambda_S$; and (C) highly exoergic reactions with $|\Delta G^0| \gg \lambda_S$.



dependent Schrödinger equation, it takes time for the wave function to evolve from one zero-order state to another and that time becomes longer as the mixing between the states becomes weaker. In adiabatic reactions the mixing is strong enough to ensure that the system remains an eigenfunction of the true Hamiltonian at all times and follows the pathway of Fig. 1B. In nonadiabatic cases the mixing can be so weak that there is not enough time spent in the curve-crossing region for the wave function to evolve, and the system continues on the zero-order reactant surface and gets reflected back many times before it finally jumps to the other surface. In that case, the curve crossing might become rate determining. The dividing line for ET reactions can be roughly estimated by the inequalities 4 that compare the matrix element V , which mixes the two states, with the thermal energy $k_B T$.

$$\text{adiabatic: } V \gg k_B T; \text{ nonadiabatic: } V \ll k_B T \quad (4)$$

For the systems to be discussed here, it is usually assumed that they are nonadiabatic. In that case another possible starting point for a rate expression is the so-called golden rule (Eq. 5), which treats ET as radiationless transitions. In this expression, derived from time-dependent quantum mechanical perturbation theory, the rate is given as the product of an electronic term, $|V|^2$, and the nuclear coordinates as the Franck-Condon-weighted density of states (FCWD).

$$k = 2\pi\hbar^{-1}|V|^2 \text{FCWD} \quad (5)$$

As such, Eq. 5 is not very descriptive and a more physical model and comparison with TST (Eq. 3) would be helpful. What is the meaning of V ? In terms of our model, it is approximately equal to

the resonance energy associated with the structures of reactant and product zero-order wave functions at the curve-crossing point if the motions of all the nuclei were frozen (20). To make a connection with Eq. 3, V is contained in the preexponential factor A . The second term in Eq. 5 is not as straightforward. By necessity, however, it must account for the exponential dependence associated with the activation energy and temperature of Eq. 3. The theory we use here is based on Marcus' classical papers (21, 22) and was further developed in the 1970s by several authors (19–25). Although the model outlined here is not the most sophisticated, it does yield a physically understandable picture.

Some of the key parameters are introduced in Fig. 2. Figure 2A represents a schematic, one-dimensional picture of an ET reaction, say of type (2). The potential curves represent the equilibrium free energies of the reactant and product states for a thermally neutral reaction as function of solvent coordinates. In this representation the reaction coordinate is the reorganization of the solvent, which is assumed to change its coordinates in a continuous fashion along the coordinate. If the electron moved from donor to acceptor without rearranging the solvation shell, an energy λ_S , the solvent reorganization energy, would be necessary to move the system from curve 1 to curve 2. However, there is an energetically less expensive pathway to get from curve 1 to curve 2 involving thermal activation of the solvent molecules to a configuration where the free energy of the ion is unchanged regardless of whether the electron is on the donor or the acceptor. As Marcus recognized 30 years ago, that is the pathway the system will take. For isoenergetic parabolic potential curves, the energy of this point is $\lambda_S/4$. In terms of the Arrhenius equation or TST, this is the activated state or transition state. In Fig. 2B we have singled out a reaction in which the free energy change equals λ_S . In this case the activation energy vanishes altogether. Finally, Fig. 2C shows the case in which the free energy change is even greater than the solvent reorganization energy, causing the activation energy to reappear. Within the approximation of parabolic potential curves, the free energy of activation is easily calculated by analytical geometry and shows a quadratic dependence on ΔG^0 and λ_S , given by Eq. 6. The associated rate constant is shown in Eq. 7.

$$G^\ddagger = (\Delta G^0 + \lambda_S)^2/4\lambda_S \quad (6)$$

$$k_{ET} = A' \exp[-(\Delta G^0 + \lambda_S)^2/4\lambda_S k_B T] \quad (7)$$

This classic result (26), obtained by Marcus (21), contains a most interesting prediction: as the driving force of the reaction increases and the free energy becomes more negative, the reaction rate rises to a maximum when $\lambda_S = -\Delta G$, but then unexpectedly falls off again. The prediction of this so called “inverted region” was one of the more startling and controversial results of Marcus' theory. This result is independent of whether the reactions are adiabatic or not (27). Experimental tests will be discussed below.

As outlined above, for reactions in the nonadiabatic regime, the probability of crossing from reactant to the product surface at the activated state is much less than unity and becomes rate limiting. In the framework of TST, this corresponds to κ being much smaller than 1. Using the golden rule (5), Levich (19) obtained Eq. 8 for nonadiabatic ET rates, giving the explicit dependence of the prefactor on V , λ_S , and T . Once again, this has the general form of an Arrhenius equation and connects with Marcus theory by substituting G^\ddagger with Eq. 6.

$$k_{ET} = (\pi/\hbar^2 \lambda_S k_B T)^{1/2} |V|^2 \exp(-G^\ddagger/k_B T) \quad (8)$$

The model discussed so far includes only the reorganization of the solvent molecules. It can be improved by taking into account bond length and angle changes accompanying the addition or removal of an electron. One of the simpler models, and the one adopted here,

(24) assumes that the reactant donor molecule is in its vibrational ground state, but that the acceptor may be produced in higher vibrational states as well. For a single vibrational mode of energy $h\nu$, where ν is the frequency, the schematic picture of Fig. 3 results, where the donor surface intersects the ground and higher vibrational surfaces of the acceptor. This is especially important for highly exothermic reactions and makes the inverted region less pronounced. Incorporating this vibrational reorganization energy, λ_ν , into Eq. 8 yields Eq. 9. In it we recognize the electronic coupling term of the golden rule and

$$k = (\pi/\hbar^2 \lambda_S k_B T)^{1/2} |V|^2 \sum_{w=0}^{\infty} (e^{-S} S^w / w!) \times \exp \{ -[(\lambda_S + \Delta G^0 + w h\nu)^2 / 4 \lambda_S k_B T] \} \quad (9)$$

$$S = \lambda_\nu / h\nu$$

the properly weighted summation over the activation free energies leading into all the product vibrational levels. This weighted sum may be called the effective Franck-Condon factor. If this theory is adequate, we should be able to predict ET rates for any system as function of four parameters, ΔG^0 , λ_S , λ_ν , and V . The free energy change of the reaction can usually be estimated with the desired accuracy from electrochemical redox potentials of the donor and acceptor. If photochemical ET is involved, excitation energies will also be required. Marcus (22) derived an expression for the solvent reorganization energy and related to it the high frequency (ϵ_{op}) and static (ϵ_S) dielectric constant of the solvent and donor and acceptor radii (r_D and r_A) and separation (R_{DA}). In its simplest form λ_S is given by Eq. 10

$$\lambda_S = e^2 [(2r_D)^{-1} + (2r_A)^{-1} - (R_{DA})^{-1}] (\epsilon_S^{-1} + \epsilon_{op}^{-1}) \quad (10)$$

where e is the charge of an electron. The vibrational reorganization energy is more difficult to estimate and requires the knowledge of the most important vibrational modes coupled to ET. Finally, the coupling matrix element V is in principle obtainable from molecular orbital (MO) theory and calculations for simple systems have proved quite acceptable (28, 29); rapid progress in this area can be expected in the near future.

Equation 9 constitutes essentially the outcome of theoretical efforts up to the end of the 1970s. More recently, there have been substantial theoretical developments (30) particularly concerned with the effects of solvent dynamics (31). Although these are at the frontier of ET research, we will not cover them in this article, because they are of minor importance to the understanding of the experiments to be discussed below.

From this discussion it should be clear that two types of experiments are needed to test the theory. The first should address the problem of the effective Franck-Condon factors and the second the electronic coupling.

Experiments on ET Rates as Function of Free Energy and Reorganization Energy

Perhaps the most dramatic prediction of Marcus theory is the existence of an inverted region. Experiments on intermolecular systems seemed to be at variance with Marcus' prediction (32). As expected, the rate would rise with increasing driving force, but then would level off and fail to show a clear inverted region. There were a few isolated examples that seemed to show a fall off at high exoergicity (33), but the cases were few. The first real evidence for an inverted region came from the work of Miller and co-workers (34) on intermolecular ET in rigid glasses. But since the analysis of

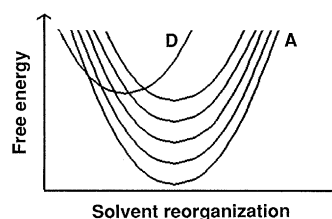
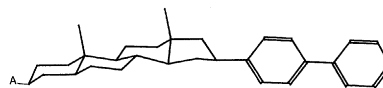


Fig. 3. Schematic, one-dimensional representation of the intersection between the zero point energy surface of the donor with the acceptor surface with its fundamental and overtones of a single vibration.

the data is based on random distance distributions between donor and acceptors, it was desirable to have a series of experiments that were easier to interpret. Those were provided in our laboratories by intramolecular ET processes in a series that was designed to test the dependence of the rate on free energy changes (8, 9).

The experiment involved the synthesis of a series of compounds with the general structure **1** in which a steroid spacer (androstane) carries a 4-biphenyl group at position 16 and different electron acceptors at position 3. These compounds were then subjected in liquid solution to a pulsed electron beam from a linear accelerator producing a pulse of solvated electrons, which are captured by the substrate.



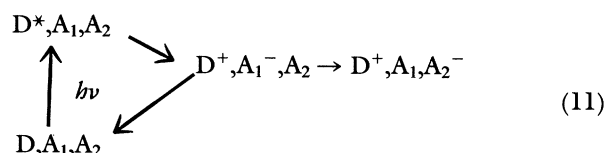
Electron capture is not very selective and the initial ion distribution is almost statistical, far away from the equilibrium. The rate of attaining equilibrium was then monitored by absorption spectroscopy. Variation of the substrate concentration allowed the separation of intermolecular from intramolecular reaction rates. The experiment has the advantage that the ions are free ions and that reactions can be run in several solvents, including hydrocarbons.

Figure 4A shows the structures and the intramolecular rates obtained for a series of eight compounds as measured in methyltetrahydrofuran (MTHF) and plotted versus the free energy of the ET reaction. As indicated, all of the reactions involve ET from the biphenyl group to the acceptor at position 3. As is evident from the plot, the rates go through a maximum and show a pronounced inverted region. The solid line is a best fit through the data with Eq. 9 with its adjustable parameters shown in Fig. 4A, and by assuming a single vibrational mode close to the aromatic skeleton vibrational frequencies. This result was the first relatively unambiguous confirmation of the Marcus inverted region for a simple reaction in liquid solution.

An equally striking confirmation of Marcus theory comes from the solvent dependence of the rates in the same series. A close examination of Eq. 9 shows that the maximum rate occurs when the free energy change of the reaction equals the sum of the solvent and vibrational reorganization energies. In MTHF for the series under discussion this value is 1.2 eV, with the major part due to the solvent reorganization energy λ_S . If a less polar solvent than MTHF is used, the maximum rate should occur at a less negative free energy of the reaction. This prediction is born out strikingly by the results obtained for dibutyl ether and isooctane solvents (Fig. 4, B and C). Inspection shows that switching to less polar solvents causes the rates of the less exoergic reactions to increase drastically, while at the same time retarding the rates of the reactions with large driving forces. Figure 4C also shows two points that are much faster than predicted. This deviation can be explained by invoking the formation of product in an electronic excited state, which reduces the free energy of the actual ET step by the excitation energy.

This highly nonlinear solvent effect has some practical implica-

tions for cases where competing pathways with different driving forces exist in ET reactions. For example, in photoinduced charge separation (Eq. 11) in photosynthesis, it is often necessary to shift the electron quickly to a second acceptor to prevent the undesirable back reaction with the donor. If the back reaction is more exoergic than the charge shift, a nonpolar solvent is the medium of choice because it will partition the reaction in the desired direction.



Although these experiments gave the first strong evidence for an inverted region, there are now additional reports of similar behavior (14, 35). A series of charge-separation and charge-recombination reactions involving rigidly attached porphyrin donors and quinone type acceptors were reported by Wasielewski *et al.*

Earlier attempts to verify Marcus' prediction of an inverted region were unsuccessful mainly for two reasons. First, the tests were performed on intermolecular ET reactions, which, in comparison with intramolecular processes, include the additional step of bringing the reactants together by diffusion. In the fast reactions this step becomes rate limiting, and thus produces a flat region on the rate versus free energy curve. Also, compounds were chosen for the very exoergic region, which allowed product formation in the excited states to give artificially high rates, as do the two points in Fig. 4C. Most recent studies (36), have overcome these problems and show an inverted region in intermolecular reactions as well.

Distance and Stereochemical Dependence of Intramolecular ET Rates

Any discussion on long-distance ET must address the problem of how the rates respond to distance between donor and acceptor. In terms of the simple theory outlined above, the distance dependence will be reflected mostly in the coupling matrix element V , although the reorganization energy also shows a distance dependence. Before discussing experimental results, it may be useful to discuss theoretical models.

The most common expression for the distance dependence of ET rates can be derived from Eq. 12, which assumes an exponential decay of the wave function and the coupling matrix element.

$$V = V_0 \exp[-\beta(R - R_0)/2] \quad (12)$$

Here V_0 is the coupling matrix element for a donor-acceptor pair at van der Waals separation R_0 , and β is a constant scaling the distance dependence. If the reorganization energy were distance independent, an equivalent expression could be written for the ET rate

$$k = k_0 \exp[-\beta(R - R_0)] \quad (13)$$

Equations 12 and 13 have the correct form for a through-space coupling mechanism. However, it is in principle possible, and as will be shown below, very likely, that the coupling will be provided by a pathway involving intervening bonds of the spacer. In linear molecules (2), the distance is approximately proportional to the number of bonds, and the different mechanisms will give similar results. But in highly nonlinear geometries, as shown schematically by 3, some differences may become apparent. In that case a better expression may be given by Eq. 14, in which the distance dependence is normalized to a one-bond connection between donor and acceptor.

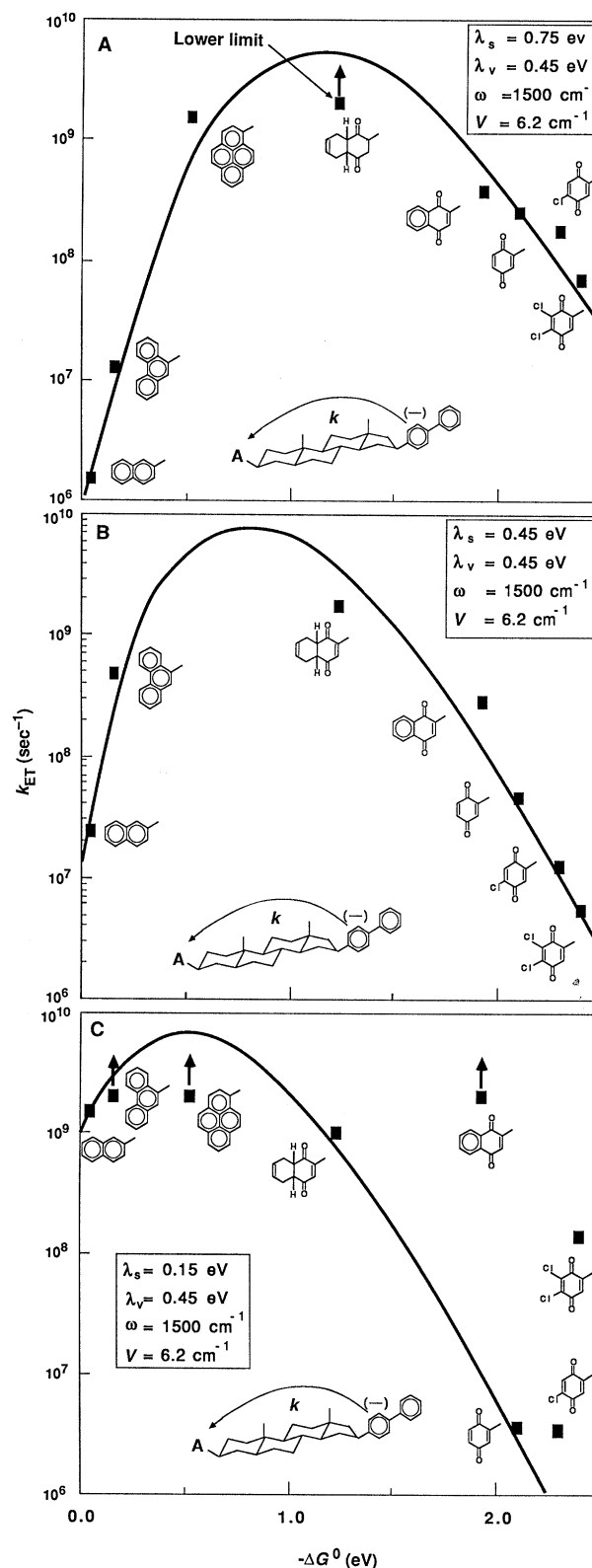


Fig. 4. Logarithmic plots of experimental rate constants obtained at room temperature in the solvents listed versus free energy changes of the ET reactions indicated in the figure (structures are the various acceptors). Solid lines are computed from Eq. 9 with the parameters listed in the figures. Solvents are: (A) methyltetrahydrofuran (MTHF); (B) di-*n*-butylether (47); and (C) isooctane.

$$\begin{array}{ccc}
 \text{D} \text{---} \text{A} & \text{D} \text{---} \text{A} \\
 2 & 3
 \end{array}$$

$$V = V_0 \exp[-\beta'(N-1)/2] \quad (14)$$

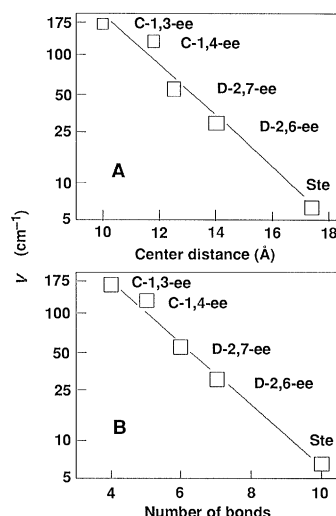
where N is the number of bonds.

Many experiments have been designed to probe the distance dependence in ET in a quantitative manner. Table 1 lists the compounds synthesized in our laboratory and their ET rates mea-

Table 1. Distances, ET rates, and electronic interaction matrix elements in model compounds. Abbreviations: Naph, naphthalene; Biph, biphenyl; D, decalin; C, cyclohexane; e, equatorial; and a, axial.

Symbol	Compound	$R_{DA}(\text{\AA})$	$k(\text{sec}^{-1})$	$V(\text{cm}^{-1})$
Ste	Naph-Steroid-Biph	17.4	1.5×10^6	6.2
D-2,6-ee	Naph-Biph	14.0	5.0×10^7	30
D-2,6-ea	Naph-Biph	11.4	5.9×10^7	23
D-2,6-ae	Naph-Biph	11.0	2.3×10^7	13
D-2,6-aa	Naph-Biph	11.9	5.8×10^7	24
D-2,7-ee	Naph-Biph	12.5	2.9×10^8	54
D-2,7-ea	Naph-Biph	11.4	3.0×10^8	53
D-2,7-ae	Naph-Biph	10.9	1.75×10^8	38
D-2,7-aa	Naph-Biph	6.2	25×10^8	52
C-1,4-ee	Naph-Biph	11.8	1.6×10^9	128
C-1,4-ea	Naph-Biph	9.5	2.5×10^9	120
C-1,4-ae	Naph-Biph	9.3	0.45×10^9	50
C-1,3-ee	Naph-Biph	10.0	4.2×10^9	168

Fig. 5. Logarithmic plots of the coupling matrix elements of ET in the equatorial-equatorial isomers of the compounds listed in Table 1 versus (A) center-to-center distance and (B) the minimum number of bonds separating donor from acceptor.

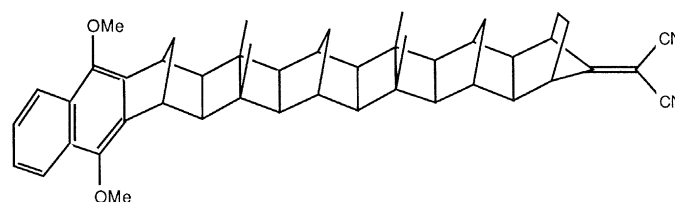


sured in pulse radiolysis experiments of the same kind as described above for the steroid series (8). To keep the Franck-Condon factors as constant as possible, ET was designed to occur in all of the compounds from the negative ion of the 4-biphenyl group to the 2-naphthyl substituent with a driving force of approximate 50 mV. If Eq. 13 were a valid description of the distance dependence, a plot of the rates on a logarithmic scale versus distance should give a line with slope $-\beta$. An attempt to obtain such a correlation gave poor results. A plot against the number of intervening bonds improved the correlation somewhat but was still unsatisfactory.

There are two obvious reasons for the failure. The reorganization energy depends on the separation between donor and acceptor and therefore is not constant throughout the series (22). The use of Eq. 10 can remedy this situation. With data obtained from the steroid series, a solvent reorganization energy can be computed for any distance, and from the measured rate constant and Eq. 9, a coupling matrix element can be computed for each of the compounds listed in Table 1. Also, a more serious problem arises from the fact that stereochemistry and its consequences are not specifically included in Eq. 12, 13, or 14 (37).

To demonstrate the effect of stereochemistry, we make use of Eq. 13 and examine what to expect for the different stereoisomers in the decalin series. The preexponential factor k_0 is the rate constant expected for a donor-acceptor pair in van der Waals contact. If the spacer is removed and the donor acceptor are moved together by translation, the resulting van der Waals complex will have different geometries depending on whether donor acceptor attachments to the spacer were equatorial or axial. Thus the data listed in Table 1, with four different attachment patterns, should be plotted in four separate correlations, each with a different k_0 . The largest number of experimental points exist for the series with both substituents attached equatorially. The coupling matrix elements as function of distance and number of bonds are plotted in Fig. 5, A and B, respectively. In this case either Eq. 12 or 14 gives a satisfactory fit, because with an all-equatorial geometry, distance is roughly proportional to the number of intervening bonds. The values of β and β' are $0.95 \pm 0.05 \text{ \AA}^{-1}$ and 1.12 ± 0.05 per bond, respectively (38). In line with ab initio MO calculations (29), any isomer with axial substituents has ET rates slower than the all equatorial isomers because of a smaller k_0 . There are not enough points for the other isomers for meaningful correlations, but it appears that β' in a number-of-bond plot is similar to the one obtained for the equatorial series.

There are several other studies that have aimed at obtaining a distance dependence for intramolecular ET rates (10, 12). One contribution is based on the synthesis of a remarkable series of polycyclic compounds with its largest member having structure 4.



The ET studied in this series is the charge separation occurring on photoexcitation of the dimethoxynaphthalene fragment that causes ET to the dicyanoethylene end of the molecule. By using fluorescence quenching to measure the transfer rates, a three-point correlation with distance was obtained that followed Eq. 13 with a β of 0.85 \AA^{-1} ($\beta' = 1.15$ per bond) that was similar to results obtained in our series. Pulse radiolysis experiments on the same series of compounds in an attempt to measure charge transfer in the negative

ions yielded only lower limits for the rate constants even for the longest molecule (39). From these results it was suggested that the donor-acceptor coupling in these cases might be strong enough to make the transfer adiabatic.

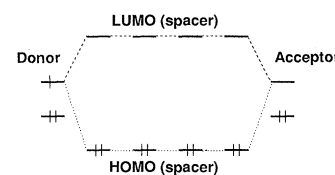
Other work has yielded distance dependencies not very different from the ones discussed here (40). Among those, results obtained for proteins (6) and for random distributions in glasses (34) are particularly relevant. In general, the value of β in Eq. 13 does vary within the small range from 0.85 to 1.2 Å⁻¹. However, β occurs in the exponent of Eq. 13 and seemingly small variations in this constant have a large effect on the spread of rates over large distances.

The Mechanism of Long-Distance ET

An important question arising from the results mentioned above is how the electron gets from donor to acceptor when the intervening medium essentially has no electron affinity by itself. The golden rule (Eq. 5) requires electronic coupling between the donor and acceptor and there are two different ways of providing it. One is by simple overlap of their wave functions through space, which is generally referred to as the through-space mechanism. In contrast, the so-called through-bond mechanism makes use of the wave function of the spacer itself to propagate the interaction. Some of the results reported above show that edge-to-edge distances between donor and acceptor of as much as 15 Å will still give rates in the nanosecond regime if the Franck-Condon factors are maximized. Although the tail ends of wave functions are very hard to estimate, it is difficult to imagine a direct overlap of the required magnitude. The possibility of through-bond coupling has been recognized as long as 28 years ago by McConnell (41) and by Halpern and Orgel (42). An even earlier suggestion was made by Anderson (43) who introduced the concept of superexchange, a different name for the same phenomenon, to explain long-range antiferromagnetic coupling. Over the years, the through-bond mechanism has won acceptance by most investigators.

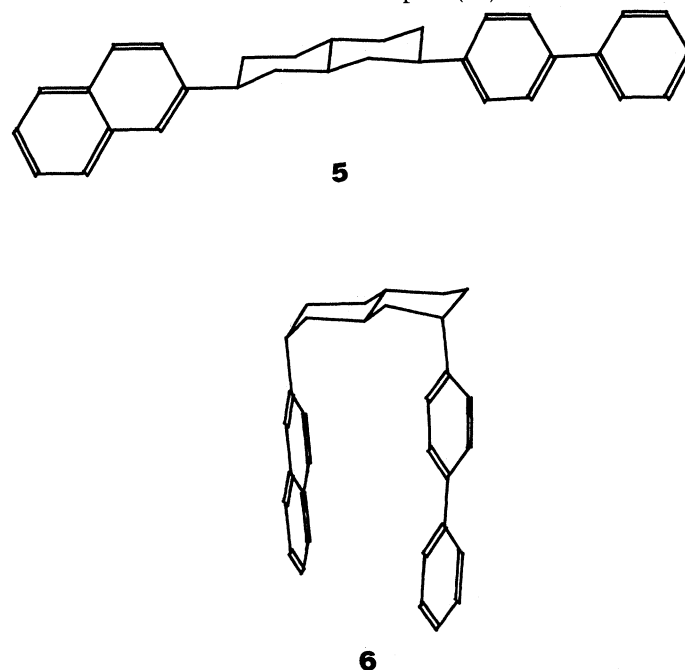
A qualitative description of the through-bond mechanism within the frontier MO framework is schematically depicted in Fig. 6. In a typical charge shift reaction of the kind described above, the transferring electron is initially in the lowest unoccupied molecular orbital (LUMO) of the neutral donor and is transferred to the LUMO of the acceptor. Donor and acceptor are bound to the σ -bond framework of the spacer made up of a string of saturated carbon atoms to be viewed as a chain of beads. To each bead we can assign a HOMO (highest occupied molecular orbital) and LUMO as shown in Fig. 6. The energies of the spacer LUMOs are above the donor and acceptor LUMOs, which in turn are above the spacer HOMOs. There are now two possible pathways to couple the donor LUMO with that of the acceptor. One involves mixing of the donor LUMO with the nearest spacer LUMO and the mixing from one spacer LUMO to the next and finally mixing of the last spacer LUMO with the acceptor LUMO. This pathway leads to electron transfer. Another way is to couple the acceptor LUMO with the nearest HOMO of the spacer, followed by coupling within the HOMO chain of the spacer and then with the donor LUMO. This process is sometimes referred to as hole transfer. Which pathway predominates depends on the relative energy gaps, because effective mixing is inversely proportional to the energy spacings between orbitals. This picture yields an exponential decay of the coupling with the number of spacer carbon atoms and is the basis of Eq. 14. An intuitive objection is that this mechanism requires mixing across the large energy gap separating the donor LUMO and the nearest spacer LUMO (or HOMO) and the similarly large gap at the

Fig. 6. Schematic representation of the coupling between donor and acceptor LUMOs through spacer orbitals. The dashed pathway, involving LUMOs of the spacer, may be called electron transfer, and the dotted pathway, involving the HOMOs of the spacer, may be called hole transfer.



acceptor end. However, this objection becomes less convincing when it is realized that with maximum Franck-Condon factors a coupling matrix element of less than 10 cm⁻¹ (0.028 kcal/mol) is sufficient to let an electron cross from one end of a steroid to the other on the picosecond time scale.

The through-bond mechanism probably dominates intramolecular long-distance electron and hole transfer. MO calculations from simple extended Hückel through sophisticated ab initio levels (29, 44) show that without the intervening spacer molecules, ET rates would be many orders of magnitude slower. However, direct experimental evidence is not abundant. A kinetic approach would be to compare rates in stereoisomeric molecules with the same number of bonds between donor and acceptor but at different distances. One such example is the coupling in the two decalin isomers (5 and 6) taken from the series discussed above (8). The center-to-center distance of donor and acceptor differs by a factor of 2 (12.5 versus 6.2 Å) in the two isomers, yet the coupling matrix element as deduced from the ET rates are almost the same (63 versus 58 cm⁻¹, with the larger one being associated with the longer distance). Of course, it is not unreasonable to assume that direct through-space coupling will contribute, or even predominate, in cases with direct face-to-face contact of donor and acceptor (35).



Other evidence is based on photoelectron and electron transmission spectroscopy (45) results that show a shift in the HOMO and LUMO levels of the spacers when they are attached to donors and acceptors. Nevertheless, more evidence for the through-bond mechanism is desirable.

Finally, some mention should be made of intermolecular ET where donor and acceptor are separated, either by solvent molecules in rigid glasses (34), or by parts of a protein (6, 7), that are not bonded directly to a donor or an acceptor. Although the experimental evidence is still missing, the coupling in those cases is probably

provided again by the intervening medium. Since the direct pathway involves bridging intermolecular van der Waals gaps, it will be interesting to find out how much each of the discontinuities contributes to the attenuation of the total coupling. The available data [β_{intra} (8) versus β_{inter} (34)] make it appear that this attenuation is not too large.

Summary

Studies on intramolecular ET in organic model compounds have established that current theories give an adequate description of the process. The separation of electronic from nuclear coordinates is only a convenient approximation applied to many models, but in long-distance ET it works remarkably well. It is particularly gratifying to see Marcus' ideas finally confirmed after three decades of skepticism. By obtaining the numbers for quantitative correlations between rates and distances, these experiments have shown that saturated hydrocarbon fragments can "conduct" electrons over tens of angstroms. A dramatic demonstration of this fact has recently been obtained by tunneling electron microscopy on Langmuir-Blodgett films, showing in a pictorial fashion that electrons prefer to travel from cathode to anode through the fatty-acid chains (46).

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The Vibrational Spectroscopy and Dynamics of Weakly Bound Neutral Complexes

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A growing number of binary and tertiary van der Waals and hydrogen-bonded complexes are being studied by means of near-infrared laser spectroscopy. Studies of this type have generated a wealth of detailed structural and dynamical information that provides exacting tests of the corresponding theoretical methods. An additional incentive for the investigation of such clusters arises from the fact that they may be considered as intermediates between the gas and condensed phases of matter. As a result, these systems represent a fertile meeting ground for researchers from both fields and can often be studied with a variety of methods.

THE FIELD OF GAS-PHASE CLUSTER RESEARCH HAS GROWN tremendously over the past decade, to the point where a wide array of experimental (1-6) and theoretical (7-10) methods has been developed for the study of clusters. For the purposes of the present discussion, these clusters may be defined as a collection of two or more chemically bound molecules or atoms (or both) held together by weak van der Waals, hydrogen, or metallic type bonds. Much of the interest in these systems is therefore related to the fact that they represent intermediates between the gas and condensed phases (6, 11). Indeed, clusters of argon consisting of as few as three atoms have been shown to undergo modifications that are entirely analogous to the phase transition from liquid to solid (7, 12). For small molecular systems of this type, the "liquid" phase is more traditionally thought of as simply a "floppy" molecule that undergoes wide-amplitude vibrational motion, whereas the "solid" phase can be correlated with the rigid-molecule limit. In view of these associations, the study of clusters of this type provides a fruitful meeting ground for scientists from a wide range of fields, and these clusters are often amenable to study with techniques from both the gas and condensed phases.

From the computational standpoint, the advantages of studying clusters of finite size are obvious. Not only do these systems allow for the systematic inclusion of a larger number of intermolecular interactions, but the reduced computational effort, in comparison to

the effort required for the bulk phases, makes more realistic calculations feasible. For example, the problems associated with the inclusion of periodic boundary conditions are eliminated. Through the systematic study of clusters, varying in size from two or three to perhaps several hundred molecules, detailed information can be obtained on the intermolecular interactions responsible for their existence. For example, although the structure of a binary complex depends on only a single pair interaction, the structure of a tertiary complex (13) may depend on not only the sum of the corresponding pair interactions but also the effects of three-body forces.

Binary and tertiary complexes also may be thought of as prototype systems in the study of photochemical processes. The interest here stems from the fact that the intermolecular bond is much weaker than all of the chemical bonds of the constituent molecules so that dissociation can occur at very low energies of excitation. For example, vibrational excitation of one of the constituent molecules in the complex is often sufficient to vibrationally predissociate the complex by breaking the intermolecular bond (3). This process occurs on a single electronic potential surface (9), at energies sufficiently low to enable essentially exact closed coupled calculations to be carried out in favorable cases (14, 15). As a result, it is possible to make quantitative comparisons between experiment and theory.

The intense activity in the field of gas-phase cluster research has given rise to a body of literature far too extensive and diverse to be discussed in a single article. In fact, even within the field of gas-phase infrared spectroscopy of clusters, the literature is quite extensive. As a result, what follows is not meant to be a critical review of the literature but rather a way of highlighting some of the more important aspects of these studies, with work from my laboratory used as illustrations. These results include the observation of rotational fine structure, which gives detailed structural information (16, 17), as well as of line broadening (18, 19) and photofragment distributions (20, 21), which give important new clues on the nature of the vibrational predissociation dynamics.

Experimental Methods

Despite its early application to the study of van der Waals molecules (22), gas-phase infrared spectroscopy has only recently become a method that is generally applicable to their study. These recent advances are mainly a result of the blending of tunable

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