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Free Energy and Structure Dependence of Intramolecular Triplet Energy Transfer in Organic Model Compounds

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A series of compounds, each containing a triplet energy donor and an acceptor separated by a rigid spacer, has been designed and synthesized. The 1,4-cyclohexanediyl moiety is employed as the spacer for the series. The rates of intramolecular triplet energy transfer (TT) have been measured for the series. The rate of TT shows an inverted parabolic, i.e., Marcus, dependence on the thermodynamic driving force for a selected subset of the compounds wherein the donor is maintained constant throughout and the acceptors are "rigid", having no low-frequency internal degrees of freedom. The internal low-frequency torsional mode of a biphenylyl acceptor can be accounted for quite satisfactorily as an additional contribution to the solvent reorganization energy, λ_s. The driving force dependence of the rate of TT is not modeled well by the conventional Marcus-Jortner equation for weakly coupled nonadiabatic electron transfer. Generalization of the Marcus-Jortner equation to include coupling to a high-frequency harmonic mode which is both displaced and distorted along the reaction coordinate provides a somewhat better fit to the experimental data with fewer adjustable parameters.

Introduction

It has been recognized for some time that electron transfer (ET) and energy transfer, particularly triplet energy transfer (TT), have certain features in common.[1] This similarity becomes apparent when it is realized that, at least in the cases of nonadiabatic transfers, both processes may be viewed as radiationless transitions between two electronic states. Experimental work, mostly on transition-metal complexes, has given qualitative support to this hypothesis.[2]

Recent work in these laboratories has developed this concept further, leading to a quantitative relationship between intramolecular ET, hole transfer (HT), and TT rates.[3] The experimental basis for the relationship was obtained by comparing the rate constants measured in three reaction series as summarized by eq 1. In all series, ET, HT, and TT, the acceptor group (A) was

$$\text{(ET)}\ D^- \text{–Sp–A} \rightarrow \text{D–Sp–}A^- \quad (1a)$$

$$\text{(HT)}\ D^+ \text{–Sp–A} \rightarrow \text{D–Sp–}A^+ \quad (1b)$$

$$\text{(TT)}\ {}^3D'\text{–Sp–A} \rightarrow D'\text{–Sp–}{}^3A \quad (1c)$$

a 2-naphthyl group. The donor (D) in the ET and HT series was 4-biphenylyl, while in the TT series it was 4-benzophenonyl. The spacers (Sp) were *trans*-2,6- and 2,7-decalindiyls and 1,4-cyclohexanediyl. The attachment of the D and A groups were either equatorial (e) or axial (a). Each series contained 10 compounds with the same spacers and stereochemistry.

The triplet energy transfer rate constant was found to be proportional to the product of the rate constants obtained for ET and HT with the same proportionality constant throughout the series. This finding is consistent with an exchange mechanism, referred to as the Dexter mechanism,[4] which views TT as a simultaneous ET and HT and therefore might be expected to depend on a similar way on the spacer size and stereochemistry.

This successful correlation raises the question: Do other features of ET and HT have a counterpart in TT? It is known that this is definitely not the case for the solvent dependence which plays a major role in ET and HT but not in TT.[3d] This is as expected because there is little charge migration in TT and therefore the solvent reorganization energy is expected to be much smaller. Instead of the several orders of magnitude changes in rate constants observed when the polarity of the solvent is changed, as is typical for ET reactions, the TT rate constants change very little.

A more difficult question to answer from first principles has to do with the free energy dependence of the TT rates. In ET there has been a flurry of activity in recent years resulting in a qualitative confirmation of Marcus theory, although a more quantitative description of ET rates requires a quantum mechanical extension of that theory to include high-frequency vibrational modes of the donor and acceptor.[5] To put the general question of similarity between ET, HT, and TT processes into perspective, it helps to remember that all three reactions of eq 1 can be classified as occurring in weakly coupled systems in which the transfer step is nonadiabatic and therefore should obey the Golden Rule, eq 2.

$$k = (2\pi/\hbar)|V|^2\text{FCWDS} \quad (2)$$

The above-mentioned excellent correlation between the three series is due to the fact that it has its origin in the electronic coupling matrix element, V, and that the Franck-Condon weighted density of states (FCWDS) was held relatively constant throughout each series. Solvent and free energy dependencies are contained in the nuclear term (FCWDS) and there is no a priori reason for them to correlate among the three series. It was the purpose of the work described in this paper to investigate the free energy dependence of the rate constants in a series of model compounds with the general structure as shown in eq 1c.

Results

To uncover a possible relationship between free energy and TT rate, a series of compounds had to be designed and synthesized

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TABLE I: Experimental Intramolecular Triplet Energy Transfer Rates[a]

donor	acceptor	$-\Delta G$, eV	$-\Delta G$, kcal/mol	$k_{e,a}$, s^{-1}	$k_{e,e}$, s^{-1}
4-benzophenonyl	9,9-dimethylfluorenyl	0.026	0.6	1.82E+06[b] ± 4.9E+05	
4-benzophenonyl	9-spirofluorenyl	0.026	0.6	2.26E+07 ± 2.3E+06	
4-benzophenonyl	4-biphenylyl	0.07	1.6	1.83E+05 ± 1.17E+05	4.0E+07 ± 4.0E+06
4-benzophenonyl	2-naphthyl	0.33	7.7	4.00E+07 ± 4.0E+06	1.3E+09 ± 2.6E+08
4-acetophenonyl	4-biphenylyl	0.347	8.0	6.30E+07 ± 6.3E+06	
4-acetophenonyl	2-naphthyl	0.556	12.8	1.48E+08 ± 1.5E+07	
4-benzophenonyl	2-benzoquinonyl	0.808	18.6	2.20E+06 ± 4.3E+05	

[a] All rates measured at 25 °C in benzene. [b] 1.82E + 06 ≡ 1.82 × 10^6.

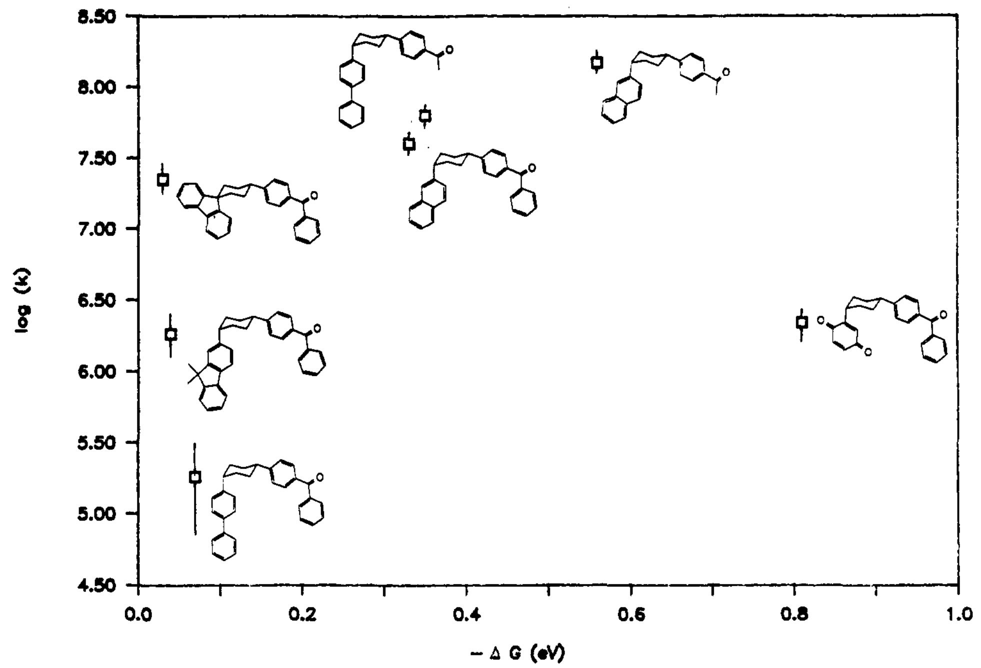

Figure 1. All 1,4-e,a-cyclohexanediyl TT rates (uncorrected).

following a set of requirements. These are (i) a large variation in the free energy of TT; (ii) comparable HOMO and LUMO coefficients of the donor and acceptors at the atom of attachment to the spacer to assure little variation of the electronic coupling; (iii) rapid population of the donor triplet state; (iv) the appropriate energetics of the excited states to allow triplet energy transfer but not singlet energy transfer; (v) $T_1 \rightarrow T_n$ absorption characteristics allowing monitoring of the TT process; (vi) the rates of the TT processes falling into a time scale readily accessible by the available nanosecond flash photolysis apparatus; (vii) the compounds not too difficult to synthesize.

Because of requirement (vii) we chose the 1,4-cyclohexanediyl spacer. From previous work it was known that the trans compounds with the predominant e,e conformations would be on the borderline for measurements on our spectrometer.[3d] We therefore chose the slower *cis*-1,4-cyclohexanediyl compounds as the main series. The *cis*-1,4-cyclohexanediyl compounds are an equilibrium mixture of two conformers, one with the donor axial and the acceptor equatorial, and the other with the donor equatorial and the acceptor axial. This conformational equilibration can theoretically result in the observation of different rates of TT for each conformer. However, we were only able to discern a single exponential decay of the ^3D in our data. Since the synthesis of the materials used in this study (vide infra) always produces a separable mixture of cis and trans isomers, some of the measurements were also made on the trans series.

Because of requirement (iii) the donor fragments of the molecule are restricted to aromatic ketones 4-benzophenonyl and 4-acetophenonyl known to produce the triplet states from the photoaccessible singlet states on the picosecond time scale.[6] As acceptors we chose the hydrocarbon fragments 2-naphthyl, 4-biphenylyl, 9,9-dimethyl-3-fluorenyl, spiro-9-fluorenyl, and 2-benzoquinonyl. The triplet energies of the fragments were equated with the literature values listed for the triplet energies[7] of the corresponding molecules or were determined from equilibrium measurements carried out in our and other laboratories.[8] The rates of energy transfer were measured by conventional nanosecond laser flash photolysis in benzene as a solvent. The rate constants and the structures of the compounds measured are listed in Table I.

Discussion

The rate constants for the *cis*-1,4-cyclohexanediyl isomers are plotted on a logarithmic scale versus the free energy change in the transfer reactions in Figure 1. It is apparent that, in contrast to similar plots obtained for electron-transfer reactions, no clear and simple correlation between the rates and the free energy changes exists for the complete data set. This is perhaps not too surprising if the diversity of the structural variations of the compounds is taken into account. This variation is a necessity for obtaining a large enough range in free energy change. However, it is possible to assess some of the consequences of structural changes in a semiquantitative way in order to identify a subset of the data meeting the criteria previously outlined for an ideal series.

As has been well established in ET, the coupling matrix element, V, is strongly determined by the through bond component which is dictated by the nature of the spacer and the stereochemistry of attachment of D and A.[3] The spacer and the stereochemical attachments are held constant throughout the series listed in Table

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I with one notable exception, the spiro-9-fluorenyl acceptor. Examining the data in Table I reveals a significant difference in the rate of TT for the spiro-9-fluorenyl and the 9,9-dimethyl-3-fluorenyl acceptors. The free energy change for TT from benzophenoyl triplet to both of these acceptors is the same to a first approximation. The difference in the TT rate for these compounds, approximately 1 order of magnitude, is the direct result of two factors. First, the acceptor is attached to the spacer via two bonds, one equatorial and one axial. These two pathways will increase the through-bond coupling compared to the remaining compounds. Second, the spiral linkage at the point of attachment of the acceptor to the spacer also removes rotational degrees of freedom which are available to other compounds in the series and fixes the acceptor orientation relative to the spacer in such a way as to maximize the electronic coupling matrix element, V.[9] This substantially increases the rate of TT making the spiro-9-fluorenyl containing compound significantly different from the others listed in Table I. While the increased rate constant is an interesting observation by itself, it makes it impossible to compare this compound with the others listed in Table I.

While the stereochemistry of attachment of the donor and acceptor have been shown to be important in controlling the rate of TT,[3d] the electronic character of the triplet state of the donor is also important. In the series of compounds listed in Table I, two different donors have been used, 4-benzophenonyl and 4-acetophenonyl. The T_1 state of benzophenone and 4-substituted benzophenones is primarily n,π^* while the T_1 state of acetophenone and 4-substituted acetophenones contains considerably more π,π^* character.[10] The electronic structure of both the HOMO and the LUMO are important in TT since V is determined, in first approximation, by a two-center two-electron integral as opposed to ET or HT where V is a two-center one-electron integral.[3] The compounds in Table I which contain 4-benzophenonyl donors must therefore be considered separately from those containing 4-acetophenonyl donors.

The data for the biphenylyl-containing compounds in Table I also require some consideration. It is known that the lowest energy conformation of the S_0 state of biphenyl in solution corresponds to an approximately 15–30° angle between the planes of the two phenyl rings.[11] In the T_1 state of biphenyl the two rings are coplanar.[12] The torsion about the single bond between the two phenyl rings in the S_0 state of biphenyl is predicted by ab initio calculations to have an approximately 2.4 kcal/mol energy barrier[13] and the frequency of the torsional mode has been measured at 60–63 cm^{-1} in a supersonic jet.[13,14] The effect of this low-frequency conformational change would be to slow TT because of unfavorable Franck–Condon factors. Since the torsional motion corresponds to a very low frequency mode, it can be treated classically, as is the solvent low-frequency mode in Marcus theory. With a small driving force, this leads to an additional activation energy. Computationally, this low-frequency mode can be lumped together with the solvent reorganization energy, λ_s, which is used to compute the Franck–Condon factors in ET and HT.

The same conformational change is known to result in bimolecular quenching of triplet benzophenone by biphenyl at less than the diffusion-controlled rate.[15] The magnitude of the contribution by this torsional motion to λ_s can be approximated computationally.[16] The geometry and heat of formation of the singlet state of biphenyl were determined by a semiempirical SCF calculation with full geometry optimization employing the AM1 Hamiltonian. This geometry was then used to calculate the heat of formation of the geometrically unrelaxed triplet state. The difference between the energy of the unrelaxed triplet state and the energy found for the geometrically optimized triplet state is the total internal reorganization energy. To obtain the fraction of this energy due to the torsional mode, the same calculations were carried out for fluorene in which the two benzene rings are held coplanar by a methylene bridge thus eliminating any torsional degree of freedom. The difference of the computed total reorganization energies between biphenyl and fluorene, 5.6 kcal/mol (0.24 eV), is then considered to be due to the torsional mode in biphenyl. As shown below, this will make it possible to compare the biphenyl-containing compounds directly with those with rigid acceptors.

Given these considerations, the largest subset of data from Table I which is consistent with the requirement of maintaining a constant V and eliminating undesired contributions to λ_s contains only three compounds. The set consists of the compounds with the 4-benzophenonyl donor and the 9,9-dimethyl-2-fluorenyl, 2-naphthyl, and 2-benzoquinonyl acceptors. We shall subsequently refer to this subset of data as set $\{S\}$. Although the number of compounds in this subset of the data is quite small, theoretical assessment of the data is still possible.

The driving force dependence of the rate of ET in weakly coupled nonadiabatic systems can be expressed mathematically as in eq 3[3] which contains an explicit expression for the FCWD of eq 2. This equation has been quite successful in modeling a

$$k = \left(\frac{\pi}{\hbar^2\lambda_s k_B T}\right)^{1/2} |V|^2 \sum_{w=0}^{\infty}\left[\exp(-S)\frac{S^w}{w!}\right] \times \exp\left\{-\left[\frac{(\lambda_s + \Delta G + wh\nu)^2}{4\lambda_s k_B T}\right]\right\} \tag{3}$$

$$S = \lambda_v/h\nu \tag{4}$$

large set of experimental data on ET obtained in these laboratories. Inherent in eq 3 is the quantum mechanical treatment of high-frequency vibrational modes, averaged to a single mode, $h\nu$, and the classical treatment of all low-frequency modes, contributing to ν_s. The quantum mechanical treatment of the high-frequency mode in eq 3 involves the calculation of the Franck–Condon factors for the vibration coupled to the reaction. The term in the summation in eq 3 which premultiplies the exponential term explicitly calculates the Franck–Condon factors for two harmonic oscillators which are displaced at their origin and have the same force constant or curvature. In eq 3 the summation is over the quantum levels, w, in the final state and ν is the frequency of the oscillator. An approximate fit of eq 3 to the data set $\{S\}$ using an average vibrational frequency of 1500 cm^{-3}, an electronic coupling matrix element, V, of 0.3 cm^{-1}, a solvent reorganization energy, λ_s, 0.2 eV, and a vibrational reorganization energy, λ_v, of 0.15 eV is shown in Figure 2. Also shown in Figure 2 is the calculated rate for the benzophenonyl donor and biphenylyl acceptor containing compound after correcting λ_s by 0.24 eV for the torsional mode. This correction places the rate of the biphenyl-substituted compound within experimental error of the compound with the fluorenyl group, a quite satisfying result. It should be noted that different values for the parameters did not give a more satisfactory fit to the data.

The part of eqs 3 and 4 which calculates the Franck–Condon factors is the same as that previously given by Siebrand, $F(E)$, using different symbols as shown in eq 5.[17] Equation 5 is spe-

$$F(E) = \exp(-\gamma)\gamma^w/w! \tag{5}$$

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[16] These types of calculations have been done previously by: Nelsen, S. F.; Blackstock, S. C.; Kim, Y. *J. Am. Chem. Soc.* **1987**, *109*, 677. Nong Liang has used the same method to calculate internal reorganization energies on radical anions used in ET reactions. The values obtained compare well with experimental results (private communication).

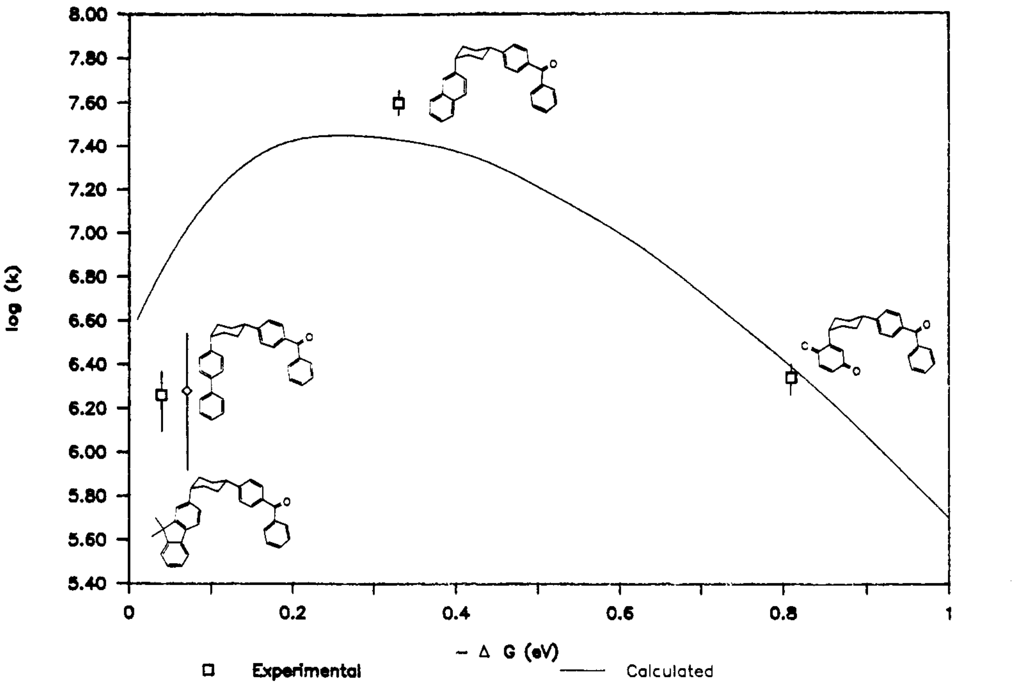

Figure 2. Rates of TT for data set {S} and the theoretical curve for eq 3 with $V = 0.3$ cm^{-1}, $\lambda_s = 0.2$ eV, and $\lambda_v = 0.15$ eV. The corrected TT rate of the benzophenonyl donor and biphenylyl acceptor containing compound is also shown.

cifically for calculating the overlap between the lowest vibrational level in the initial state and the vibrational level w in the final state. The term γ given by eq 6 is equivalent to S in eq 4 and is referred

$$\gamma = \tfrac{1}{2}k(q_F - q_I)^2/h\nu \qquad (6)$$

to as the displacement parameter by Siebrand. In eq 6, q_F and q_I are the equilibrium minima for the final and initial states, and k is the force constant for the vibration.

The poor fit of the model to the data points may be in part due to a major contribution of the carbonyl stretching mode in the benzophenonyl group. It is known that the bond length, and therefore the force constant, changes considerably when going from the triplet state to the singlet state of the ketone. In the triplet state the CO bond has much less double bond character than the ground state. If the CO bond frequency makes a major contribution to the TT process, one has to calculate the Franck–Condon factors for a model with displaced and distorted oscillators in which the force constants are different in the initial and final state.

Siebrand has given the expression for calculating the Franck–Condon factors between the zeroth vibrational level of an initial state and the wth vibrational level of a final state where the oscillators are both displaced and distorted, eqs 7–11.[17] In eq

$$F(E) = \frac{F(0)(\tfrac{1}{2}\xi)^w|H_w(ix)|^2}{w!} \qquad (7)$$

$$F(0) = (1 - \xi^2)^{1/2}\exp(-\gamma) \qquad (8)$$

$$\gamma = (k_I k_F)^{1/2}(q_I - q_F)^2/h(\nu_I + \nu_F) \qquad (9)$$

$$\xi = (\nu_I - \nu_F)/(\nu_I + \nu_F) \qquad (10)$$

$$x = \left[\frac{\gamma(1 - \xi)}{2\xi}\right]^{1/2} \qquad (11)$$

7, $F(0)$ is the Franck–Condon factor for the overlap of the zeroth quantum level in the initial state with the zeroth level in the final state and is calculated with eq 8, γ is the displacement parameter, now calculated by eq 9, and ξ is the distortion parameter, calculated by eq 10. The term $|H_v(ix)|$ in eq 7 is the Hermite polynomial with an imaginary argument where x is calculated by eq 11. Substituting into eq 3 we obtain a more general expression for the rate constant of a weakly coupled nonadiabatic system where the reaction is coupled to a single high-frequency vibration demonstrating both displacement of the equilibrium position and distortion of the frequency along the reaction coordinate, eq 12.

$$k = \left(\frac{\pi}{\hbar^2\lambda_s k_B T}\right)^{1/2}|V|^2\sum_{w=0}^{\infty}\left[\frac{(1 - \xi)^{1/2}\exp(-\gamma)(\tfrac{1}{2}\xi)^w|H_w(ix)|^2}{w!}\right]\times \exp\left\{-\left[\frac{(\lambda_s + \Delta G + wh\nu_F)^2}{4\lambda_s k_B T}\right]\right\} \qquad (12)$$

In the numerator of the exponential term which weights the Franck–Condon factor in eq 12, the energy gap is now corrected by $wh\nu_F$, the energy spacing of the vibrational levels in the final state.

To fit eq 12 to the rates for the subset of data, {S}, chosen from Table I, a few additional pieces of information will be needed. Equation 12 no longer formally contains a collective vibrational reorganization parameter, λ_v. Instead, it is necessary to provide information about the vibration which is coupled to the energy transfer. For TT in the selected compounds from Table I, the change in both frequency and bond length for the benzophenone carbonyl carbon to oxygen bond is considerable. The benzophenone carbonyl stretching frequency is 1665 cm^{-1} in the ground state (S_0) and 1222 cm^{-1} in the triplet state (T_1).[18] The equilibrium bond length for the singlet state has been calculated to be 1.208 Å and the bond length in the triplet state has been calculated to be 1.246 Å.[19] Given these values, there are only two parameters in eq 12 which can be adjusted to fit the data, V and λ_s, leaving one statistical degree of freedom for fitting of eq 12 to the selected data. The electronic coupling matrix element, V, simply scales the rates and moves the curve up or down. Figure 3 shows a plot of the subset of data from Table I and the calculated curve for V equal to 0.3 cm^{-1} and λ_s equal to 0.3 eV. Also shown in Figure 3 is the rate of TT for the benzophenonyl donor and

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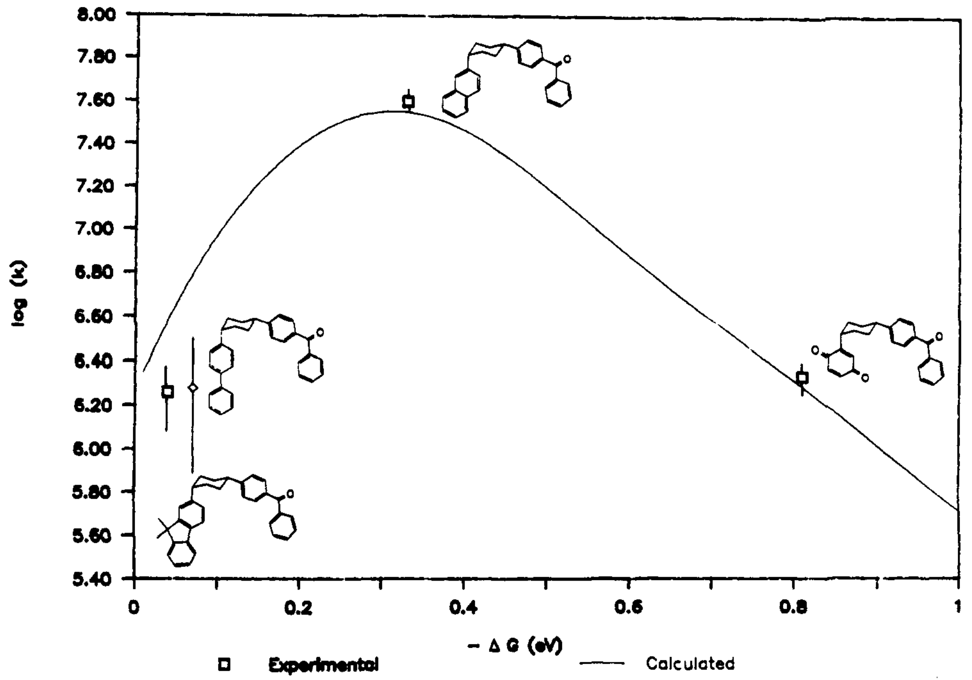

Figure 3. Rates of TT for data set {S} and the theoretical curve for eq 12 with $V = 0.3\ \mathrm{cm}^{-1}$, $\lambda_s = 0.3$ eV. The corrected TT rate of the benzophenonyl donor and biphenylyl acceptor containing compound is also shown.

biphenylyl acceptor containing compound calculated from eq 12 after λ_s is corrected by 0.217 eV. Equation 12 is seen to provide a better model for the data with fewer adjustable parameters.

The value of λ_s required to fit the data, 0.3 eV, is larger than expected for triplet energy transfer in benzene. Previous work in intramolecular electron transfer has indicated solvent reorganization energies of 0.75 eV for methyltetrahydrofuran, 0.45 eV for di-*n*-butyl ether, and 0.15 eV for isooctane.[3] Although it is known that a 0.88 D change in dipole moment accompanies the transition from T_1 to S_0 in benzophenone,[20] the actual solvent reorganization energy in TT is certainly very small. A possible explanation for the large value of λ_s used to fit the data may be related to the additional contribution to λ_s by the low-frequency torsional motion of the biphenyl substituent.

The torsional angles in benzophenone are almost certainly different in the ground and triplet states.[19] The torsional motions are must be of low frequency and can contribute to the classical reorganization energy λ_s. At present there do not exist calculations reliable enough to estimate those contributions. But if they are of comparable magnitude as in biphenyl, most of the magnitude of λ_s can be attributed to that effect. Studies of the temperature dependence of the TT rates in these model compounds are planned for the future and should shed some light on these problems.

Conclusion

Among the seven bifunctional compounds synthesized only three proved to be sufficiently similar to allow a direct comparison. This subset was expanded to four by making allowance for the low-frequency modes in the biphenyl substituent. The attempted fit to a theoretical model based on classically treated low-frequency modes and an average high-frequency mode with displaced but undistorted oscillator gave a poor fit to the data. A more extensive model in which the high-frequency mode is treated as displaced and distorted oscillators gave a better, but still not very good, fit. This is almost certainly due to the unrealistic simplification of including only one high-frequency mode in the model. A better model could probably be obtained by including both undistorted and distorted oscillators, the former for changes in the carbon skeleton and the latter for changes in the bond length of the carbonyl group of the donor. Such a mixed model, however, will be of considerable mathematical complexity and no attempts have been made to develop it. Also, the number of parameters will increase to the point where a fit to the data will involve several unsupported guesses.

Even from the limited number of experimental points presented in this study, it appears that TT is similar to ET in its dependence on the energy gap of the reaction. Because the TT reaction rates depend to a higher power on factors influencing the electronic coupling than ET reactions, it should be much easier to obtain information on the electronic coupling from TT rates. This, together with the previously demonstrated close relationship between TT and ET rates,[3c] makes the study of TT a valuable tool for the understanding of processes governed by weak electronic coupling.

Experimental Section

The general synthetic scheme used to obtain the compounds listed in Table I is the following. Approximately 10 g of the appropriately brominated acceptor was dissolved in 150 mL of dry THF and cooled to −78 °C in a dry ice/acetone bath. One equivalent of butyllithium was added as a solution in hexane (Aldrich) and the resulting solution was allowed to stir for 1 h. A solution of 0.8 equiv of 1,4-cyclohexanedione–monoethylene ketal in dry THF was slowly added and the solution was allowed to stir for an additional 30 min at −78 °C. The solution was then warmed to room temperature and the lithium salt was converted to the alcohol by pouring the reaction mixture into water. The alcohol was isolated by extraction into ether.

The alcohol was dehydrated by refluxing in a minimal amount of acetic anhydride required to give a homogeneous solution upon heating. The dehydration was followed by TLC and was usually complete in 30 min. The olefin was isolated by crystallization from the acetic anhydride on cooling and subsequently hydrogenated over a 10% Pd/C catalyst in THF under 1 atm of H_2. The resulting 4-substituted cyclohexanone–ethylene ketal was converted to the ketone by transketalization in acetone with a catalytic amount of aqueous HCl under refluxing conditions. The resulting ketone (I) was later attached to the donor (vide infra).

The appropriate 4-bromo donor (acetophenone or benzophenone) was ketalized by refluxing in benzene with an excess of ethylene glycol and a catalytic amount of pTSA. The equilibrium reaction was driven to completion by removal of water in a Dean–Stark trap as it was generated. An amount of the bromo ketal, 20% in excess of the amount of ketone (I) produced earlier, was dissolved in dry THF and cooled to −78 °C. One

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equivalent of butyllithium in hexane was added to the bromo ketal. After stirring for 1 h, I was slowly added as a solution in THF. The reaction mixture was allowed to stir for an additional hour at −78 °C and then warmed to room temperature. The resulting alcohol was isolated and subsequently dehydrated and hydrogenated by using the procedures previously outlined.

The ketal was removed from the donor by reflux in acetone with aqueous HCl giving a mixture of the e,e- and e,a-1,4-cyclohexanediyl compounds. The isomers were separated by selectively crystallizing the trans (e,e) compound out of the mixture in an ethanol/benzene solvent system.

Kinetic measurements were made on a nanosecond flash photolysis apparatus consisting of a Lambda Physic Excimer pumped dye laser. The output of the terphenyl containing dye laser (360 nm) was attenuated as necessary and focused into a 1 cm path cell perpendicular to the probe direction of a flashed broad-band white light source. The wavelength to be monitored was extracted from the continuum by a monochromator with a 5-nm band-pass. The laser and probe timing and data collection were controlled by a LeCroy transient digitizer which was connected to an IBM-PC/AT through a GPIB interface. Identical results were obtained on the nanosecond flash photolysis system when the sample was excited with the third harmonic (355 nm) from a Quantel NdYAG laser.

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Picosecond Time Resolution of Barrier Crossing in Isolated Perylene/Alkyl Halide Complexes

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van der Waals complexes of perylene with 1-chlorobutane and 1-chloropentane, when prepared in the zero-point state in S_1 by a supersonic expansion, each exist at the 1:1 aggregation level in three principal isomeric forms. All three forms of each complex exhibit the same fluorescence decay time (10.4 ± 0.1 and 10.8 ± 0.1 ns, respectively) when excited into the zero–point level. When excitation is into the 355-cm^{-1} level of S_1, the fluorescence decay time is shortened to a different degree for the different isomeric forms of each complex (4.9–6.3 ns for 1-chlorobutane; 6.9–9.2 ns for 1-chloropentane). This indicates a different degree of singlet–triplet coupling for the different geometrical structures represented. Also at this energy, vibrational relaxation, indicated by time evolution of the spectral bandwidth and Franck–Condon profile, and isomer exchange, causing a shift in the emission spectra, are observed. For the most part, isomer exchange occurs on the same time scale as vibrational relaxation (i.e., 100–300 ps), indicating that the isomerization process is limited by coupling of the optical promoting mode. One case, the A isomer of the chlorobutane complex, indicates the presence of a bottleneck in the conformational relaxation process.

1. Introduction

There is currently much interest in the structural and dynamical properties of molecular clusters doped with aromatic chromophores. Such systems offer a variety of opportunities to study molecular aspects of condensed-phase interactions and to explore new dimensions in microscopic photochemistry. Levels of aggregation can be determined by mass-resolved two-photon ionization techniques, and electronic spectral shift data permit some assignments of structural types. For example, the sign of the shift or the amount of Franck–Condon activity in "van der Waals" modes may be used to distinguish between different attachment sites of small molecules onto larger aromatic substrates,[1] although few actual structures have been determined.[2,3] For some aggregates possessing a low degree of rotational asymmetry, structural information has been obtained through the application of polarization anisotropy techniques.[4–6]

Numerous instances have been reported where van der Waals complexes are present in more than one ground-state conformation or exhibit barriers to the interchange of indistinguishable conformers.[7–9] Yet, there is little information available on the overall binding energies of molecular aggregates, the relative energies of different isomers, and, most importantly, the energy barriers separating different isomers. Another factor difficult to predict is the distribution of vibrational isomers likely to occur in a given experiment. Such considerations involve detailed comparison of the dynamics of expansion cooling and conformational interchange.

Potential energy calculations of medium and larger clusters rely heavily on semiempirical techniques. These commonly involve Lennard-Jones (e.g., 6–12) or Buckingham type (6-exp) formulas, augmented by terms to accommodate electrostatic interactions.[10] Although such approaches are widely used, such as in applications of molecular dynamics calculations,[11] their applicability to cluster

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