Supplementary Material Available: The low-temperature ^{13}C NMR spectra and data for acetophenone, pivalophenone, and a mixture of these ketones with MAD added in different molar ratios (8 pages). Ordering information is given on any current masthead page.

Determination of Long Distance Intramolecular Triplet Energy Transfer Rates. A Quantitative Comparison with Electron Transfer[1]

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Recent efforts in these laboratories have been directed toward understanding the factors governing long distance intramolecular electron transfer (ET).[2] In the models chosen for study the electronic coupling between donor and acceptor is sufficiently weak to assure nonadiabatic reactions. It occurred to us that long distance triplet energy transfer by the Dexter mechanism[3] (TT) of which there are several examples in the literature[4] should exhibit features similar to nonadiabatic electron transfer because both reactions are governed by the same theory of radiationless transitions. We therefore have started a program aimed at finding quantitative similarities and differences in these two processes when studied on directly comparable systems. Also, with one exception,[5] the absolute rates of intramolecular triplet energy transfer have never been measured directly in liquid solution. In this communication we report our first results and conclusions.

One of the series studied in ET, **1**, involves compounds in which a 4-biphenylyl group (D) is connected via a rigid spacer (Sp) with a 2-naphthyl group (A).[2a] The spacers used were cyclohexane
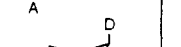
1: A = 2-naphthyl; D = 4-biphenylyl

2: A = 2-naphthyl; D = 4-benzophenoneyl

A-Sp-D

and decalin ring systems. Simply by replacing the 4-biphenylyl group with 4-benzophenonyl, the series can by converted to an almost ideal series **2** for triplet energy transfer. The spacers are

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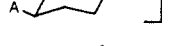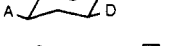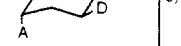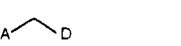(2) (a) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986,** *90,* 3673. (b) Ohta, K.; Closs, G. L.; Morokuma, K.; Green. N. J. *J. Am. Chem. Soc.* **1986,** *108,* 1319. (c) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984,** *106,* 3047. (d) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983,** *105,* 670.

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Table I.

compound		$k_{r}{}^{a}$ (s^{-1})	$k_{ET}^{COR b}$ (s^{-1})
D-2,6ee		3.1×10^{6}	5.0×10^{7}
D-2,7ee		9.1×10^{7}	1.7×10^{8}
D-2,7ae		1.1×10^{7}	7.6×10^{7}
C-1,4ee		1.3×10^{9}	8.6×10^{8}
C-1,4ea	[c]		7.2×10^{8}
C-1,4ae		4.0×10^{7}	1.3×10^{8}
C-1,3ee		7.7×10^{9}	1.5×10^{9}
C-1,3ea	[c]		
C-1,3ae		3.3×10^{9}	
M			5.0×10^{10}

^{a} Measurement at room temperature, in benzene. The estimated errors are ±20%, with the exception of D-2,7ee, where the error is ±10%, and M, for which it is ±30%. ^{b} Rates from ref 2, but corrected for changes in solvent reorganization, normalized to D-2,6ee. ^{c} Assignment to either conformer is open at this time.
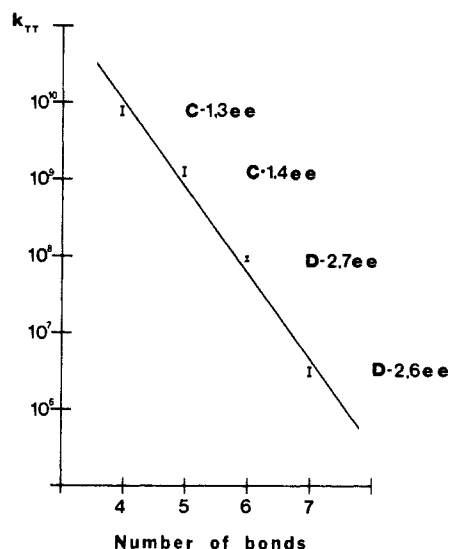

Figure 1. Logarithmic plot of the rate constants of the all-equatorial compounds against the minimum number of σ-bonds separating donor and acceptor. See Table I for key of compounds.

listed in Table I. The triplet transfer rates were measured in benzene at room temperature by flash photolysis exciting the benzophenone chromophore and monitoring the decay of the T_1 − T_n absorption of the benzophenone or the buildup of the naphthalene T_1 − T_n absorption. The slower compounds were excited with a nitrogen laser, while the faster ones were measured on a picosecond spectrometer previously described.[6] Measurements at different concentrations allowed the separation of intermolecular from intramolecular processes.[7] The rate constants are listed in Table I. As expected the rate falls off with increasing number of bonds separating triplet donor and acceptor. In analogy to the findings of electron transfer in the equivalent systems, the

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(7) The intermolecular rates are approximately 5×10^{9} M^{-1} s^{-1}.
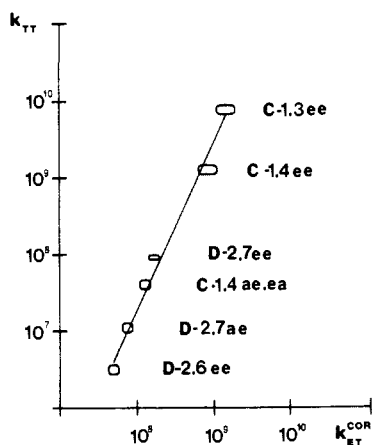
Figure 2. Logarithmic plot of the TT rate constants versus ET rate constants for the compounds indicated. Compound key in Table I.

maximum rates among stereoisomers are found for the equatorial–equatorial substituent patterns.

Both long distance ET and TT are nonadiabatic processes and therefore should be describable by the Golden Rule (eq 1), expressing the rate as a product of an electronic coupling term, V,

$$k = 2\pi\hbar^{-1} |V|^2 \text{ FCWDS} \qquad (1)$$

and the Franck–Condon weighted density of states. Assuming through-bond coupling with an exponential decay of V with the number of intervening σ-bonds as in

$$V = V_0 \exp - [\alpha(\text{no. of bonds} - 1)/2] \qquad (2)$$

we can write

$$k = 2\pi\hbar^{-1} \text{ FCWDS } |V|^2 \exp - [\alpha(\text{no. of bonds} - 1)] \qquad (3)$$

$$k = k_0 \exp - [\alpha(\text{no. of bonds} - 1)] \qquad (4)$$

where k_0 contains the Franck–Condon factors and the coupling matrix element when donor and acceptor are separated by one σ-bond. A correlation of a series of compounds with different spacers by eq 4 will only be successful if k_0 is kept constant throughout the series. Using identical donors and acceptors will assure a reasonable invariance of the Franck–Condon factors. However, as has been shown in the electron-transfer work, a constant V_0 can only be expected for a series of compounds with identical stereochemical attachment to the spacer.

Figure 1 shows a logarithmic plot of the rate constants versus numbers of bonds separating donor and acceptor of the cyclic compounds with both donor and acceptor being attached equatorially. The least-squares line has a slope $\alpha = 2.6/\text{bond}$ and an intercept $k_{0TT} \simeq 3 \times 10^{13} \text{ s}^{-1}$. A corresponding correlation for electron transfer on the same spacer series gave an exponent of $\beta = 1.15/\text{bond}$ and $k_{0ET} \simeq 10^{11} \text{ s}^{-1}$.[2a] With the aid of eq 4, we can derive the relationship between TT and ET rate constants for any spacer as

$$k_{ET}{}^{\alpha/\beta}/k_{TT} = k_{0ET}{}^{\alpha/\beta}/k_{0TT} \qquad (5)$$

Figure 2 shows a logarithmic plot of the rates for TT versus ET for all the compounds where both rates are available.[8] The fact that (5) correlates compounds of different stereochemical attachment with a single line shows that the k_0's obey the same power dependence as the other points. The least-squares line has a slope of $\alpha/\beta = 2.2 \pm 0.2$.

This slope is close to the slope of 2 predicted from a rather simple model, viewing triplet transfer as simultaneous two-electron transfer. The matrix element determining the rate in electron transfer can be written as a two-center, one-electron resonance integral (6).

$$\langle \psi^D{}_{LUMO}(1)|H_{ion}|\psi^A{}_{LUMO}(1)\rangle = H_{DA} = V_{ET} \qquad (6)$$

The appropriate integral in triplet transfer is a two-center (four orbital) two-electron exchange integral (7).[9]

$$\langle \psi^D{}_{LUMO}(1)\psi^A{}_{HOMO}(2)|e^2/r_{1,2}|\psi^A{}_{LUMO}(1)\psi^D{}_{HOMO}(2)\rangle =$$
$$K_{DA} = V_{TT} \qquad (7)$$

The distance dependence of both integrals will parallel the distance dependence of the corresponding overlap integrals. Inspection shows that elimination of the operator converts (6) to a simple two orbital overlap integral, while (7) will become a product of two such integrals. If the overlap for all orbitals falls off with the same exponent $-\gamma R$, the product of two integrals will give an exponent of $-2\gamma R$, remarkably close to the α/β ratio found experimentally.

Besides these similarities between TT and ET, there are important differences. ET rates, involving charged particles, show strong solvent dependencies caused by large changes in the Franck–Condon factors. Triplet transfer occurs in neutral molecules with little solvent reorganization. Preliminary results show rate changes in some of the compounds studied here to be less than a factor of three upon switching from hexane to acetonitrile. In ET the corresponding changes would amount to many orders of magnitude.[2a] It is therefore much easier to separate electronic coupling from Franck–Condon factors in TT than in ET, and the study of TT may sometimes be a preferred way to learn about electronic coupling in ET.

(9) This expression is strictly correct only for a direct exchange mechanism. For through bond coupling, it must be replaced by the appropriate superexchange Hamiltonian.

[2 + 1] versus [4 + 2] Cycloadditions of Fischer Carbene Complexes with 1,3-Dienes. Evidence for a Zwitterionic Intermediate in a Cyclopropanation Reaction[†]

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The reactions of transition-metal carbene complexes with alkenes are known to occur under the proper conditions to give cyclopropane products in a formal [2 + 1] cycloaddition.[2] We report herein the first examples of the cyclopropanations of 1,3-dienes with isolable transition-metal carbene complexes,[3,4] the first nonstereochemical evidence for the intermediacy of a zwitterion in a reaction in which a cyclopropane is formed from a carbene complex in a stoichiometric reaction,[2a,5,6] and a dramatic example

†Dedicated to Professor Gerhard L. Closs on the occasion of his 60th birthday.
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