

Triplet Energy Transfer through the Walls of Hemicarcerands: Temperature Dependence and the Role of Internal Reorganization Energy

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Abstract: The dependence of the rate of electronic excitation transfer from a triplet donor (biacetyl) trapped inside a hemicarcerand cage to a range of triplet quenchers in free solution was studied as a function of the driving force and the internal reorganization energy of the acceptor, $\lambda_{\text{acceptor}}$. Acceptors with internal reorganization energies ranging from ~ 0 to more than 1.1 eV were investigated. It was found that quenchers with nearly identical triplet energies can lead to transfer rates differing by almost 3 orders of magnitude as a result of large differences in their internal reorganization energies. The data were analyzed in terms of the semiclassical Marcus–Jortner theory. Variable-temperature measurements were performed in order to independently evaluate the activation energies and thus to unequivocally determine which acceptors belong to the “normal” and which to the “inverted” Marcus region. Four distinct groups of triplet acceptors emerged from the analysis: (a) rigid aromatics with small geometry changes and modest internal reorganization energies; (b) acyclic olefins exhibiting a large-amplitude internal relaxation and correspondingly large reorganization energies; (c) cyclic olefins with exceptionally large λ_v values; and (d) molecular oxygen, O₂, with negligibly small internal reorganization energy.

Introduction

One of the remaining fundamental issues in the field of intermolecular charge and electronic excitation transfer studies is the role of a disorganized medium separating the donor and the acceptor sites in providing the electronic coupling necessary for the transfer process to occur.¹ While the medium contribution to the coupling has been unequivocally demonstrated in the case of glasses (e.g., the very first triplet energy-transfer measurements of Terenin and Ermolaev,² or the seminal work of Miller et al.³ on the driving force dependence of electron transfer), the similar role of isotropic solvent is much less understood and agreed upon. The investigations are complicated by the free diffusion of the donor and acceptor and the resulting free distribution of distances and rates. It is generally agreed that, because of the short-range nature of the electronic interaction, the transfer process is overwhelmingly dominated by the donor–acceptor encounter complexes. However, some notable exceptions, where because of energetic reasons the transfer between more distant sites can be faster than that between nearest neighbors, have been reported in the case of electron transfer.^{4,5} The possible role of solvent molecules in mediating electron

transfer in linked donor–acceptor systems has been investigated in detail by Zimmt and collaborators.⁶

In this contribution we address yet another case of an intervening material which is not bound to either to the donor or the acceptor, but where a fixed barrier is placed between the reactants. This intervening barrier is imposed by the encapsulation of the donor, i.e., the 2,3-butanedione (biacetyl), within one of Cram’s closed surface hemicarcerand hosts.⁷ The donor is free to rotate inside its cage; however, as shown in the space-filling representation (Figure 1b), it is not possible for molecular oxygen to enter freely into the interior of **1**, and the larger organic triplet energy acceptors cannot come in direct van der Waals contact with the encapsulated biacetyl donor.⁸ As a result, the energy transfer must occur through the walls of the hemicarcerand, with an intervening center-to-center distance between the donor and the acceptor of approximately 7 Å. Triplet excitation transfer is mediated by a two-electron exchange interaction between the localized orbitals of the donor and the acceptor, which falls off steeply with increasing distance (approximately twice as rapidly as the analogous single-electron exchange interaction, which is responsible for electron-transfer

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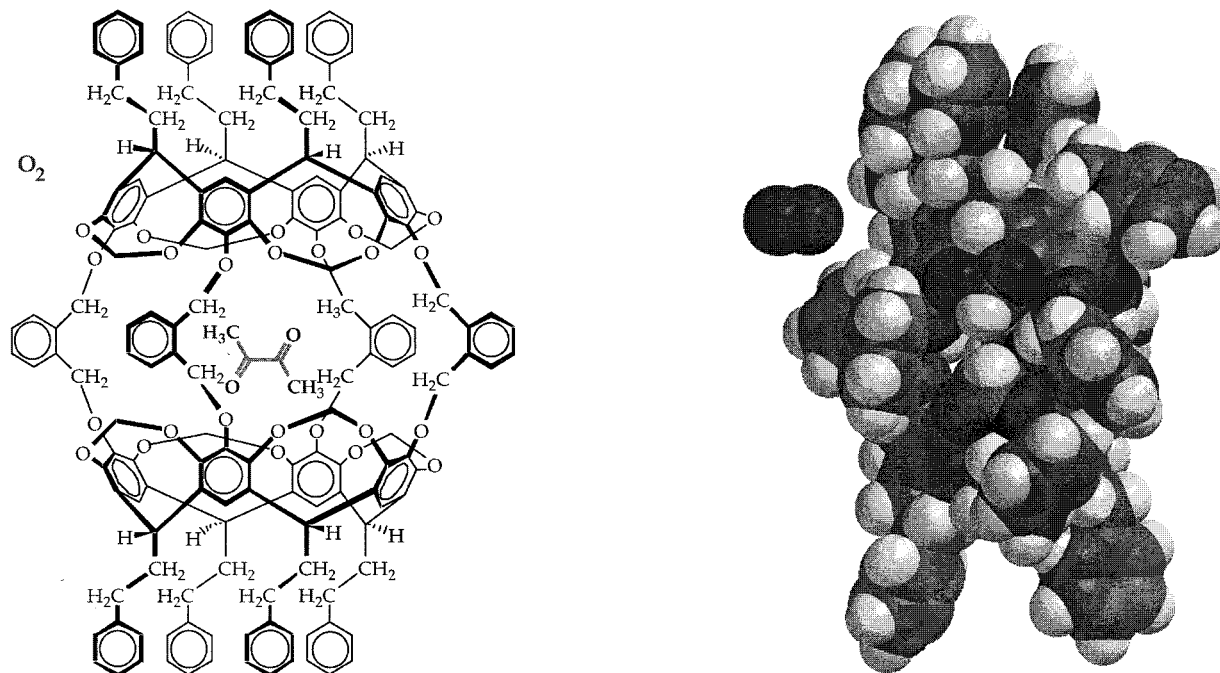


Figure 1. Structure of the 1-biacetyl hemicarciplex (a, left) and a space-filling representation (b, right) with molecular oxygen shown for size comparison.

reactions).⁹ We have previously communicated that, thanks to the greatly reduced electronic coupling in the encounter complex, the rate constants for triplet energy transfer between the incarcerated biacetyl and a variety of acceptors fall well below the diffusion-controlled limit.¹⁰ As a result, the characteristic Marcus relationship between rate constant and driving force is obtained, instead of the Sandros¹¹ or Weller¹² type behavior typical of a diffusion-controlled process. These findings have been largely verified by the independent and nearly contemporaneous work of Balzani and collaborators.¹³

Since the donor/acceptor electronic coupling in the encounter complex is small, the rate of the process can be treated using the standard nonadiabatic theory of nonradiative transitions,

$$k = \frac{2\pi}{\hbar} |V|^2 \rho \quad (1)$$

where V is the electronic coupling, which in the case of triplet transfer is given by the aforementioned two-electron exchange integral, and ρ is the Franck–Condon weighted density of states. The density of states is most frequently expressed classically, or semiclassically, in terms of the driving force $-\Delta G^\circ$ and the nuclear reorganization of both the reactants and the solvent (Marcus theory). In the present paper we demonstrate that the widely accepted semiclassical Marcus–Jortner formalism (eq 2) can be applied to explain the observations of both Deshayes et al.⁸ and Balzani et al.¹³ in a quantitative manner, provided that the wide distribution of the internal reorganization energies of the various triplet acceptors is properly accounted for.

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

Inherent in eq 2 is the dependence of the transfer rate constant, k , on the reorganization energy of the medium, λ_s , and the internal reorganization energy of the reactants, $\lambda_v = \lambda_{\text{donor}} + \lambda_{\text{acceptor}}$. The solvent term is treated classically, while the internal component is approximated by one average quantized vibrational mode with a frequency ν ; however, if warranted, the extension to include multiple internal modes is straightforward. As it has been shown in the case of intramolecular electron transfer, it is meaningful to plot and analyze the transfer rate vs the driving force dependence, $k = f(\Delta G^\circ)$, only if the total reorganization energy of the studied systems is reasonably constant.¹⁴ Figure 2 illustrates how any change in the overall reorganization energy is reflected in the shift of the position of the optimum rate, and in an altered shape of the ΔG° dependence. Similarly, a different partitioning between the λ_s and λ_v , or a major change of the average frequency of the quantized modes, ν , will have an influence on the appearance of $k = f(\Delta G^\circ)$.

In the case of electron transfer, the overall reorganization energy is dominated by the contribution of the solvent, λ_s , which depends on the radii of the donor and the acceptor, the separation between them, and the polarity of the medium. The magnitude of the solvent reorganization energy can be in excess of 1 eV (~ 23 kcal/mol). Consequently, a correction for the large variation in λ_s , usually based on the Born expression for solvation of ions, has been included in the analysis of virtually all reported electron-transfer data. The magnitude of λ_v is much smaller (typically ~ 0.1 – 0.2 eV, 2.3–4.6 kcal/mol), and the variations between different electron donors and acceptors are

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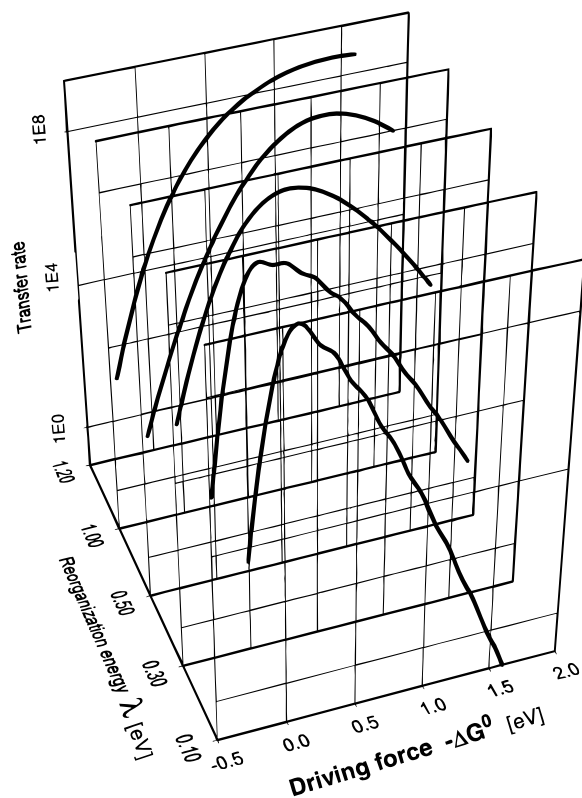


Figure 2. Relationship between driving force, $-\Delta G$, total reorganization energy, λ , and transfer rate for nonadiabatic energy transfer. The electronic coupling term is held constant for all values of λ . Different ratios of λ_s and λ_v were used for different curves.

usually ignored without much detriment to the agreement with the experimental results.¹⁶

The partitioning between the internal and external components of the reorganization energy in triplet transfer is the opposite of that found for electron transfer.¹⁵ Triplet energy transfer does not involve a major redistribution of charges between the donor and the acceptor. Indeed, often even the dipole moments of the individual moieties, and of the entire assembly, remain unchanged, e.g., in biacetyl, naphthalene, anthracene, pyrene, etc. Therefore, the corresponding solvent reorganization energy is very small, 0.1 eV or less. On the other hand, the magnitude of λ_v associated with the $S_0 \leftrightarrow T_1$ and $S_0 \leftrightarrow S_1$ transitions is usually considerably larger than that in the case of the formation of the corresponding radical anions or cations.¹⁷ As a result, λ_v is the

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(16) The internal reorganization energy is nearly constant in all studies of the distance dependence of electron and energy transfer because the donor and acceptor are kept the same throughout a given family of model compounds. However, any ΔG° dependence study necessitates an introduction of a wide range of donor and/or acceptor moieties, with the corresponding variation in values of $\lambda_{\text{internal}}$. Nevertheless, to our knowledge, all reported studies used a single average value of the internal reorganization energy for the entire set of donors and acceptors.

(17) In the zero-order picture, triplet energy transfer to and from a typical closed-shell organic molecule involves the change in occupancy of both the HOMO and the LUMO orbitals of the donor and the acceptor. For a conjugated or aromatic triplet acceptor, it can be represented as $\pi^2\pi^{*0} \rightarrow p^1\pi^{*1}$. This results in lowering of the overall bond order by 1. The analogous reduction and oxidation processes involve only one occupancy change, $\pi^2\pi^{*0} \rightarrow p^2\pi^{*1}$ or $\pi^2\pi^{*0} \rightarrow p^1\pi^{*0}$, with the corresponding bond order decrease of $1/2$. The magnitude of the nuclear reorganization is appropriately lower. Indeed, for symmetric aromatics, MO calculations return triplet reorganization energies which are approximately twice as high as those associated with the formation of the corresponding radical anions or cations.

dominant component of the overall reorganization energy in triplet transfer, and the rates become extremely sensitive to this parameter. Furthermore, a very wide distribution of magnitudes of the internal reorganization energy, covering the range from nearly zero to more than 1 eV, is found for different families of organic triplet energy donors and acceptors.

In accordance with the above considerations, the triplet energy acceptors used in the present work were divided into four distinct classes and analyzed separately, depending on the average magnitude of the internal reorganization energy. The respective groups are the following: (a) rigid aromatics, which undergo very minor geometric changes upon formation of the triplet state and have correspondingly modest reorganization energies; (b) acyclic olefins with large, primarily low frequency, internal reorganization energies originating from the 90° twist of one of the double bonds upon formation of the T_1 state; (c) cyclic olefins, which have similarly large, but primarily high frequency, reorganization energies stemming from the planarization of the ring in the lowest triplet state; and (d) oxygen, a diatomic molecule with one vibrational mode and a negligibly small reorganization energy.

The initial division into separate classes of acceptors was performed primarily on the basis of computational results, and, when available, the literature values of the Franck–Condon and fully relaxed energies of the relevant T_1 states.^{18,19} These predictions were then verified by direct variable-temperature measurements of activation free energies for triplet energy transfer in all investigated donor/acceptor pairs. This approach has been used successfully in the past in electron-transfer studies, which confirmed that, in the vicinity of the maximum of the $k = f(\Delta G^\circ)$ curve, i.e., for optimum Franck–Condon factors, the rates are virtually independent of temperature. As the “inverted region” is entered, the transfer rates begin to decelerate with increasing temperature, and negative values of activation energy are obtained.^{14b,20} In this work, the dependence of the rate constants on temperature served as the crucial diagnostic in determining whether a reaction is in the “normal” or “inverted” region, and as an aid in partitioning the reorganization energy between the high- and low-energy modes. While the importance of the structural relaxation in triplet energy transfer was recognized in the past,²¹ we believe that this is the first systematic investigation of how the internal reorganization

(18) Because of the lack of comprehensive experimental data on both the Franck–Condon and the fully relaxed triplet energies of the commonly used acceptors, particularly the olefins, we relied primarily on computational results. The $S_0 \rightarrow T_1$ reorganization energies of over 40 common organic triplet acceptors were calculated at the AM1 level. There was a clear pattern of the average values of λ_v obtained for chemically distinct groups of acceptors: 9.8 kcal/mol for the rigid aromatics, 20.5 kcal/mol for the olefins, 8.1 kcal/mol for aryl ketones, and 3.2 kcal/mol for aryl thioketones (this class was not used in the experiments). The computed value obtained for the biradicaloid triplets of olefins is very close to the one which emerged from the analysis of our experimental data. The calculated λ_v for rigid aromatics is much higher than the one used in the plot in Figure 4. The complete set of the calculated reorganization energies can be found in the Supporting Information.

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energy of different classes of acceptors affects the effective Franck–Condon factors and the dependence of the rate of electronic energy transfer on the driving force.

Experimental Section

Materials and Methods. All chemicals were reagent grade, and all solvents were spectroscopic grade, purchased from Aldrich, and used without further purification. **1**·DMA was prepared by methods described elsewhere.²² The synthesis of **1**·biacetyl is given in the Supporting Information, along with the NMR and FAB-MS data.

Emission Measurements. Emission spectra were recorded on a SPEX Fluorolog phosphorimeter. Samples were kept in a jacketed cell holder attached to a circulator bath, which kept temperature constant to ± 0.1 °C. The excitation wavelength was 430 nm. All spectra were corrected for detector sensitivity and background signals.

Determination of Bimolecular Rate Constants with Organic Acceptors. All organic quenchers were purchased from Aldrich and used without further purification. The lifetime of the **1**·biacetyl triplet for each quencher concentration was determined by exciting **1**·biacetyl at 430 nm and fitting the decay of emission at 534 nm with a single exponential. The lifetime was determined for each acceptor concentration at 15, 25, 35, 45, and 55 °C. The equation $1/\tau = 1/\tau_0 + k_q[Q]$ was used to calculate the rate constants, where τ is the observed lifetime, τ_0 is the lifetime in the absence of quencher, k is the bimolecular rate constant, and $[Q]$ is the concentration of quencher. The rate of decay was plotted against acceptor concentration at each temperature. The energy-transfer rate constant was obtained from the slope of the resulting line. Correlation coefficients better than 0.99 were obtained in all cases.

Determination of Bimolecular Rate Constants with Molecular Oxygen. A 0.7 mM solution of **1**·biacetyl was placed in a jacketed cell equipped with a pressure gauge and attached to a circulator bath that kept temperature constant to ± 0.1 °C. The **1**·biacetyl was excited at 430 nm, and the emission decay was monitored at 534 nm. The triplet lifetimes were determined at O₂ concentrations that ranged from 0.38 to 7.2 mM. Oxygen concentrations were calculated using the measured pressure while correcting for the temperature dependence of O₂ solubility.²³ The rate constants were calculated in the same manner as described above.

Reversible Energy Transfer. Reversible triplet energy transfer occurs for endothermic and weakly exothermic reactions when the acceptor T₁ state is sufficiently long-lived.¹¹ This situation was addressed by quenching the external triplet with O₂. Fortuitously, the **1**·biacetyl triplet is extremely long-lived, even in oxygen-saturated benzene, while external triplets are quenched by O₂ with rate constants greater than 10^9 M⁻¹ s⁻¹. The naphthalene triplet has lifetimes of approximately 1.0 and 0.1 μ s in aerated and O₂-saturated benzene, respectively, compared to 175 μ s in degassed solution. Thorough degassing yielded a rate constant of approximately 10^4 M⁻¹ s⁻¹ for 1 mM solutions of **1**·biacetyl, with the observed rate constant inversely proportional to the **1**·biacetyl concentration. The same series of experiments carried out in either aerated or O₂-saturated benzene gave a single rate constant of 1.1×10^6 M⁻¹ s⁻¹, which is independent of the **1**·biacetyl concentration. This shows that triplet transfer from biacetyl to naphthalene is reversible in the absence of O₂ and irreversible in an aerated solution. Oxygen quenching of the external acceptor was used when reverse energy transfer was likely, and the transfer rate constant was sufficiently high that the direct O₂ quenching of **1**·biacetyl was not competitive. This method was not applicable to some of the alkene acceptors, for which rate constants as low as 10^4 M⁻¹ s⁻¹ were observed. However, since these triplets are short-lived, back transfer cannot occur.²⁴

MO Calculations. The nuclear reorganization energies associated with the S₀↔T₁ transitions in the various acceptors were calculated at the AM1 level. In the case of cycloheptatriene, cyclohexadiene, O₂, and biacetyl, ab initio calculations were performed using the 6-31G** basis set. It should be noted that the reorganization energies following

an “up” or “down” electronic transition are generally not identical. To obtain the reorganization energy of a triplet energy acceptor, its T₁ energy was first calculated in the frozen geometry of the S₀ state, which subsequently was allowed to relax to the optimum triplet geometry. The reorganization energy of the donor was obtained by first calculating the S₀ energy in the frozen optimized geometry of the T₁ state and then allowing it to relax to the S₀ optimum. All calculations employed either the Spartan 4.0 or Gaussian 94 software packages running on an IBM 43P computer.

Results and Discussion

The pseudo-unimolecular triplet energy-transfer rates from the incarcerated biacetyl to the various acceptors in free solution, and the experimentally determined activation energies, are gathered in Table 1. The appropriate thermodynamic parameters (energies of the relaxed triplet states and the driving force) are also included. The results are presented graphically in Figures 4 and 5. Thanks to the presence of the hemarcerand wall, the electronic interaction between the colliding donor and acceptor moieties is greatly diminished. As a result, all measured rates fall well below the diffusion-controlled limit and exhibit a strong dependence on the ΔG° .

As it was outlined in the Introduction, a quantitative description of the ΔG° dependence of the structurally different classes of acceptors requires different sets of parameters. Therefore, each class will be discussed separately. Common to the analysis of all acceptors are the internal reorganization energy of the incarcerated biacetyl, λ_{donor} , and the solvent reorganization energy, λ_s . It is important to note that the equilibrium structures of the singlet ground state and the lowest triplet state of biacetyl are very similar, and that the reorganization energy associated with the T₁→S₀ transition is correspondingly small. Only minor bond length and bond angle adjustments take place, and the molecule remains planar, with the oxygen atoms in a trans arrangement (Figure 3). Indeed, the strong room-temperature phosphorescence and the extremely long triplet lifetime of biacetyl are clear manifestations of such structural similarity. In accordance with the results of our semiempirical and ab initio calculations, we assign 0.02 eV (~0.5 kcal/mol) as the internal reorganization energy of biacetyl and treat it as a high-frequency quantized mode, $\nu = 1500$ cm⁻¹. Vibrational states from $w = 0$ to $w = 10$ were included in the summation, and the electron–phonon coupling, for both the donor and the acceptor, was expressed as $S = \lambda_\nu/h\nu$ (eq 2).

As was mentioned earlier, the solvent reorganization energy accompanying electronic energy transfer is very small. In the case of our system, the magnitude of the classical λ_s is reduced even further. Since the triplet donor is insulated from the surrounding medium by the cage, it is reasonable to assume that essentially only the resolution of the acceptor will contribute to the solvent reorganization. The value of 0.1 eV (2.3 kcal/mol) was found to give a satisfactory agreement with experimental results. The detailed discussion of the behavior of the specific families of triplet energy acceptors is presented below.

(24) When the rate constant of triplet transfer is low, $k \leq 10^4$ M⁻¹ s⁻¹, even small amounts of impurities that are efficient quenchers can cause difficulties, and obtaining accurate rate constants becomes challenging. For example, 0.1% of an impurity that quenches with a rate constant of 10^7 M⁻¹ s⁻¹ would account for a significant portion of the observed decay of the **1**·biacetyl triplet. A rate of 9.2×10^6 M⁻¹ s⁻¹ was reported for *cis*-piperylene in ref 8. However, this value could not be reproduced with any other sample, and therefore we have attributed the original value to the presence of an impurity. Repeated measurements on purified *cis*-piperylene yielded a reproducible value of 1.0×10^4 M⁻¹ s⁻¹. In the case of cyclohexadiene and cycloheptatriene, consistent results were obtained in several trials, with the cycloheptatriene value in good agreement with the rate constant reported by Balzani et al. in ref 13.

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Table 1.

acceptor	triplet energy, ^a kcal/mol	−ΔG ^o , ^b kcal/mol	E _{a,corrected} , ^c kcal/mol	k _{ET} , M ^{−1} s ^{−1}	
				1•biacetyl	[biacetyl]
Aryl Acceptors					
naphthalene* ^h (NAP)	61.0	−3.1	4.6	1.1 × 10 ⁶	[2.0 × 10 ⁶] ^d
2-phenylnaphthalene* (PNAP)	58.6	−0.7	3.0	2.4 × 10 ⁶	[6.5 × 10 ⁸] ^e
fluoranthene* (FLA)	52.8	5.1	−0.2	1.0 × 10 ⁷	[5.2 × 10 ⁹] ^e
pyrene* (PYR)	48.6	9.3	−0.9	2.2 × 10 ⁷	[6.0 × 10 ⁹] ^d
acridine* (ACR)	45.4	12.5	−1.4	8.6 × 10 ⁶	[9.0 × 10 ⁹] ^d
anthracene (ANT)	42.5	15.4	−2.0	4.0 × 10 ⁶	[8.0 × 10 ⁹] ^d
9-bromoanthracene (BANT)	41.4	16.5	−4.9	1.8 × 10 ⁶	[6.6 × 10 ⁹] ^e
9,10-dibromoanthracene (DBA)	40.2	17.7	−4.4	4.2 × 10 ⁵	[1.2 × 10 ⁹] ^e
Alkene Acceptors					
<i>cis</i> -piperylene ^f (PIP)	59.0	−1.1	5.2	1.0 × 10 ⁴	[1.6 × 10 ⁷] ^e
1,3-cyclohexadiene (CHD))	52.4	5.5	4.2	2.0 × 10 ⁴	[2.9 × 10 ⁸] ^e
triphenylethylene (TPP)	50.0	7.9	2.9	1.1 × 10 ⁵	[1.6 × 10 ⁸] ^e
1,4-diphenyl-1,3-butadiene (DPB)	42.5	15.4	0.9	5.3 × 10 ⁵	[9.0 × 10 ⁸] ^e
cycloheptatriene (CHP)	38.0	19.9	5.0	3.4 × 10 ⁴	[3.0 × 10 ⁹] ^e
1,6-diphenyl-1,3,5-hexatriene* (DPH)	35.6	22.3	1.7	8.2 × 10 ⁵	[9.0 × 10 ⁸] ^e
<i>all-E</i> -retinol* (RET)	33.5	24.4	1.1	1.0 × 10 ⁶	[4.8 × 10 ⁷] ^e
1,8-diphenyl-1,3,5,7-octatetraene* (DPO)	31.6	26.3	1.7	2.2 × 10 ⁶	[4.3 × 10 ⁸] ^e
oxygen ¹ Σ	37.5	20.4	−1.9	1.7 × 10 ⁴	[4.3 × 10 ⁸] ^g

^a From ref 19a, 1993. ^b −ΔG, the driving force, is calculated as the difference in triplet energy between 1•biacetyl (57.9 kcal/mol) and the organic acceptor. In the case of oxygen, the driving force is the difference in energy between 1•biacetyl triplet and the ¹Σ state of oxygen. ^c All the measured activation energies were corrected for the barrier to diffusion. An activation energy of 2.1 kcal/mol was obtained from the diffusion-controlled benzophenone triplet energy quenching by naphthalene, in benzene solvent, and subtracted from the activation energy obtained with each quencher. ^d From ref 11. ^e Determined experimentally. ^f *cis*-Piperylene experiment performed in He freeze-pump-thaw degassed solutions. ^g From Darmanyan, A. P.; Foote, C. S. *J. Phys. Chem.* **1995**, *99*, 11854. ^h An asterisk indicates that experiments were performed in aerated solutions.

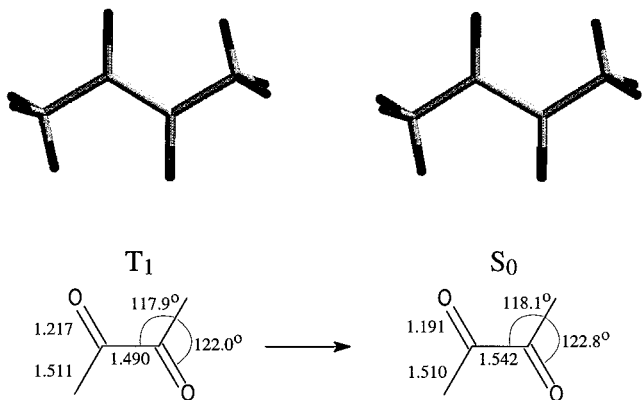


Figure 3. Singlet ground-state and lowest triplet-state geometries of biacetyl optimized at the RHF and UHF 6-31G** levels. Note the close similarity of the structures.

Rigid Aromatic Triplet Energy Acceptors. The planar aromatics constitute the most homogeneous class of acceptors in this study. Since the molecular orbitals of importance are fully delocalized in these molecules, the nuclear relaxation following the nonradiative formation of the triplet state is similarly distributed among small changes of bond lengths and bond angles, rather than being concentrated in a particular localized distortion. The overall magnitude of the internal reorganization energy is also modest. Table 1 shows that, for aromatic triplet energy acceptors, the maximum transfer rate occurs at a rather low −ΔG^o value between 5 and 9 kcal/mol. The experimentally determined activation energies (Table 1) indicate that already fluoranthene (FLA) enters the “inverted region” of the ΔG^o dependence. In accordance with these results, we assigned to the rigid aromatics an average value of internal reorganization energy of 0.12 eV (~2.8 kcal/mol). Since it is associated exclusively with the high-frequency skeletal modes, the value of $\nu = 1300 \text{ cm}^{-1}$ was used in the analysis.²⁵ The λ_{total} used to model triplet transfer from 1•biacetyl to aromatic

acceptors is 5.6 kcal/mol. The theoretical curve based on eq 2, and on the above parameters, was plotted together with the experimental data in Figure 4.

The amplitude of the curve, and hence the magnitude of the electronic coupling, were adjusted to give the best fit, thus yielding $|V| = 0.26 \text{ cm}^{-1} \pm 10\%$. This value represents the electronic interaction between the incarcerated donor and the acceptor averaged over all geometries of collision and over the distribution of lifetimes of the encounter complex. For these reasons, it is difficult to make a truly quantitative comparison between the electronic exchange coupling mediated by the walls of the hemiacarcerand cage and the coupling in a covalently bound system with a similar donor–acceptor separation. Nevertheless, it can be estimated that the off-diagonal matrix element is no more than 1 order of magnitude lower than that in a comparable system linked by C–C σ -bonds.²⁶ This is not surprising, considering that the trapped biacetyl interacts with the entire internal surface of the hemiacarcerand (Figure 1b), and thus the exchange coupling between the donor and the cage must be large.²⁷

Acyclic Olefin Triplet Energy Acceptors. It is well known that acyclic olefins in the lowest singlet and triplet excited states relax by twisting one of the >C=C< bonds until the minimum at 90° is achieved.²⁸ Naturally, such a dramatic change of geometry is associated with a very large nuclear reorganization energy which is partitioned primarily between the >C=C<

(25) Summation over two independent vibrational modes, $\nu = 1500 \text{ cm}^{-1}$ for the donor and $\nu = 1300 \text{ cm}^{-1}$ for the acceptor, was performed (eq 2). The fit is only weakly dependent on the volume of this parameter for $1000 < \nu < 1700 \text{ cm}^{-1}$. For the general multimode version of this expression and the simplified limiting cases, see ref 14b.

(26) For example, consider one of the systems in ref 9b, consisting of a benzophenone donor and a naphthalene acceptor attached to positions 1 and 4 of a cyclohexane spacer.

(27) In the standard superexchange approach, the overall donor/acceptor interaction is the result of a sequence of “donor/intervening medium” and “intervening medium/acceptor” couplings. Preliminary results on a larger hemiacarcerand, in which the biacetyl donor is not in van der Waals contact with the entire inner surface of the cage, indicate a significant reduction of the triplet-transfer rate and the electronic coupling.

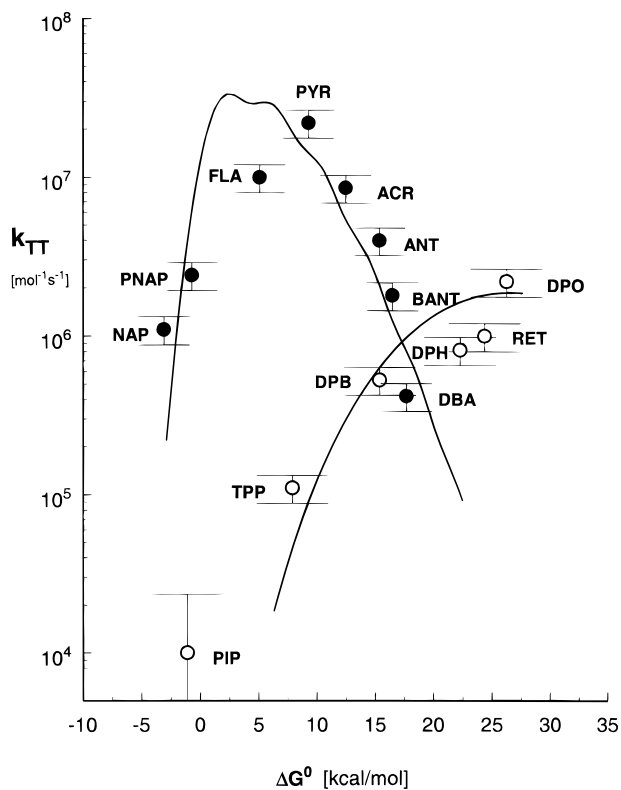


Figure 4. Rate constant vs driving force correlation of triplet energy transfer from $1\cdot$ biacetyl to aryl (●) and alkene (○) acceptors, plotted together with the theoretical curves generated using eq 1. See the text for details. The abbreviations are as follows: naphthalene (NAP), 2-phenylnaphthalene (PNAP), fluoranthene (FLA), pyrene (PYR), acridine (ACR), anthracene (ANT), 9-bromoanthracene (BANT), 9,10-dibromoanthracene (DBA), *cis*-piperylene (PIP), triphenylethylene (TPP), 1,4-diphenyl-1,3-butadiene (DPB), 1,6-diphenyl-1,3,5-hexatriene (DPH), *all-E*-retinol (RET) and 1,8-diphenyl-1,3,5,7-octatetraene (DPO).

torsional and stretching modes. The twisting mode always carries the main fraction of the reorganization energy; e.g., in the case of ethylene, less than 30% of the relaxation energy is associated with the $>C=C<$ stretch.²⁹

The analysis of the olefin data employed the same reorganization energy values for $1\cdot$ biacetyl and the solvent. However, the acceptor reorganization energy was increased to 6.9 kcal/mol in high-frequency vibrations (1300 cm^{-1}) and 17.3 kcal/mol in the low-frequency torsions, giving $\lambda_{\text{total}} = 27\text{ kcal/mol}$. The low-frequency contribution was treated classically; i.e., it was simply incorporated into the λ_s . We feel that this is well justified, since there is ample resonance Raman and computational evidence that the frequencies of the twisting modes of electronically excited olefins are below the value of kT at room temperature.³⁰ Furthermore, the normal-mode analysis reveals that, even in the ground state, the extended olefins exhibit a number of low-frequency vibrations of the $>C(=C-C)_n=C<$ backbone; e.g., in 1,4-diphenylbutadiene (DPB), there are seven modes at frequencies below 200 cm^{-1} , with the lowest one at $\sim 20\text{ cm}^{-1}$.³¹ This set of parameters, consistent with the accepted

(28) Salties, J.; Sun, Y. P. In *Photochromism—Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 64 and references therein.

(29) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415 and references therein.

(30) (a) Myers, A. B.; Mathies, R. A. *J. Chem. Phys.* **1984**, *81*, 1552. (b) Myers, A. B.; Harris, R. A.; Mathies, R. A. *J. Chem. Phys.* **1983**, *79*, 603. (c) Matousek, P.; Parker, A. W.; Phillips, D.; Scholes, G. D.; Toner, W. T.; Towrie, M. *Chem. Phys. Lett.* **1997**, *278*, 56.

(31) Geometry optimization and vibrational frequencies were obtained at the AM1 level without a correction factor.

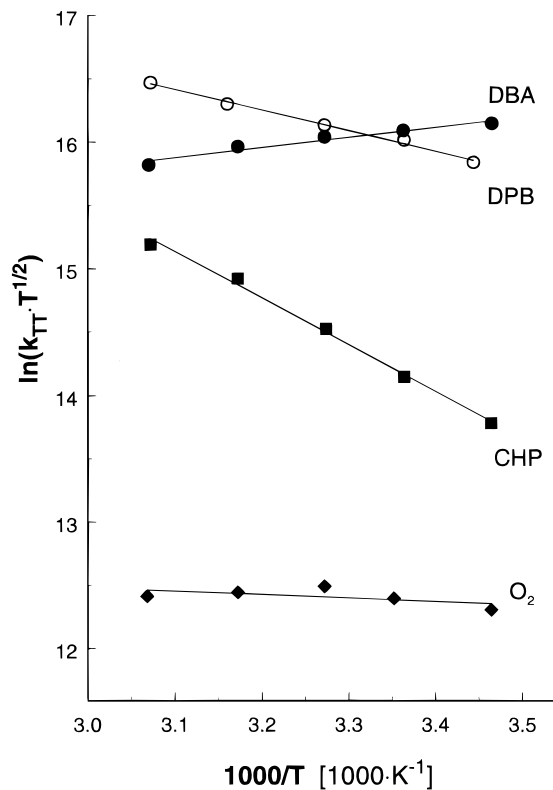


Figure 5. Comparison of the rate constant dependence on temperature between 9-dibromoanthracene (DBA), 1,3-diphenyl-1,3-butadiene (DPB), cycloheptatriene (CHP), and molecular oxygen.

picture of the excited-state conformation of alkenes, yielded the theoretical curve presented in Figure 4. Clearly, the basic trend observed in the experiments is satisfactorily reproduced, even if the overall correlation is not quite as good as it was in the case of rigid aromatics.³² It can be seen from Figure 4 that, as a result of the large internal reorganization energy, all olefin triplet acceptors appear to belong to the “normal region”, even at the very high driving forces exceeding 20 kcal/mol. This finding has been decisively confirmed by the variable-temperature measurements. In all cases, positive values of free energy of activation were found (Figure 5 and Table 1). The importance of the activation energy measurements is underscored by the examples of dibromoanthracene (DBA) and diphenylbutadiene (DPB). Both acceptors have similar triplet energies and, therefore, similar driving forces for triplet transfer from biacetyl (17.7 and 15.4 kcal/mol, respectively). The corresponding triplet-transfer rates of 4.2×10^5 and $5.3 \times 10^5\text{ mol}^{-1}\text{ s}^{-1}$ are within the experimental uncertainty (Figure 4). However, this coincidence of rates is purely fortuitous and potentially misleading. Triplet transfer to dibromoanthracene is characterized by rates decreasing with increasing temperature and a negative activation energy typical of the “inverted” region, while the transfer rates to diphenylcyclobutadiene increase with increasing temperature

(32) The experimental energies of the Franck–Condon and fully relaxed triplet states of olefins are much less reliable than those of aromatics or ketones. The energies of the nonemissive fully relaxed triplet states of olefins are usually obtained either by measuring equilibria with species whose triplet energies are well established, or via photoacoustic experiments. These approaches tend to be less reliable than simple phosphorescence measurements, especially in the case of such short-lived triplets. The Franck–Condon triplet energies are most often derived from the red edge of the extremely weak $T_1 \leftarrow S_0$ absorption induced either by a solvent containing heavy atoms (CH_3I or CH_2I_2) or by complexation with O_2 . Values obtained for molecules with $T_1 \leftarrow S_0$ spectra devoid of a sharp onset and without a clearly defined 0–0 peak, of which the olefins are a perfect example, carry a large margin of error and are best viewed as being highly approximate.

and yield a positive activation energy, confirming that it belongs to the “normal region” (Figure 5). It should be mentioned that the appearance of slightly negative activation free energies at driving forces exceeding λ_{total} originates primarily from the temperature dependence of the preexponential factor in eq 2. The semiclassical Franck–Condon term expressed as the sum over w in eq 2 is only very weakly temperature dependent. This is in contrast with the original Marcus theory, which predicts the emergence of a classical activation barrier and an unrealistically strong temperature dependence in the “inverted” region.²⁰

The analysis returns a somewhat lower value of the effective electronic coupling for the family of olefinic acceptors than in the case of rigid aromatics ($0.16 \text{ cm}^{-1} \pm 20\%$ versus $0.26 \text{ cm}^{-1} \pm 10\%$). This discrepancy is not surprising, since the average coupling experienced by the encounter complex will depend on the shape, the size, and the electron distribution of a particular acceptor. However, there is no obvious fundamental reason it should be consistently smaller in the case of olefins. At this point, we can only offer the following conjectures: (a) The commonly used models, including the one employed in this paper, represent all vibrational modes of the acceptor coupled to the reaction coordinate by one average frequency and, more importantly, by one value of coupling between the electronic and nuclear displacements. It is possible that olefins do not satisfy this approximation quite as well as other molecules do. While the magnitude of the nuclear relaxation energy is dominated by the twisting mode, the resonance Raman measurements (on the S_1 rather than T_1 state) indicate that the $>\text{C}=\text{C}<$ stretching mode is much more strongly coupled to the electronic transition than the $>\text{C}=\text{C}<$ twisting mode.³³ (b) The model assumes that the frequencies of the relevant donor and acceptor modes are the same for the reactants and the products. It is clear that olefins represent a major departure from this otherwise reasonable approximation. The twisting motion of the $>\text{C}=\text{C}<$ double bond on the reactant side is quantized, while on the product side it becomes an essentially free, unquantized rotation of a single $>\text{C}-\text{C}<$ bond. This mismatch of the crucial vibrational frequencies on the opposite sides of the transition state may be the source of the generally lower transfer rates observed for olefinic acceptors. (c) It is also possible that the encounter complex between the hemiacarplex and the acceptor survives for a longer time in the case of the aromatics than in the case of olefins. However, such preferential complex formation seems highly unlikely to occur in benzene.³⁴

Cyclic Dienes. While at first it seems natural to place cycloheptatriene and cyclohexadiene together with the other olefins, experimental and computational data show that these cyclic compounds have to be treated separately. Cycloheptatriene exhibits an exceptionally high internal reorganization energy of approximately 20 kcal/mol (Gorman et al. report 18 kcal/mol as the possible lower limit),³⁵ which is associated with

(33) Myers, A. B. Excited-State Electronic Properties from Ground-State Resonance Raman Intensities. In *Laser Techniques in Chemistry*; Myers, A. B., Rizzo, T. R., Eds.; John Wiley & Sons: New York, 1995; p 325 and references therein.

(34) The lifetime of the encounter complex, τ , becomes an important factor when $1/\tau$ approaches or exceeds $|V|$. Time-dependent perturbation theory predicts that, in this situation, the state mixing will not be able to reach its full magnitude. Interestingly, as the acceptor becomes larger, its diffusion rate, and hence the rate of encounters with the donor, decreases; however, the lifetime of the “solvent cage” around the encounter complex increases. This reverse size dependence will lead to at least partial cancellation of these two effects. Furthermore, since the size of the solvent cage is determined primarily by the hemiacarplex (Figure 1), in the absence of specific binding interactions the size of the acceptor is expected to have little influence on the lifetime of the encounter complex.

(35) Gorman, A. A.; Hamblett, I.; Irvine, M.; Raby, P.; Standen, M. C.; Yeates, S. *J. Am. Chem. Soc.* **1985**, *107*, 4404.

the planarization of the ring in the excited state (the nearly planar S_1 structure was probed experimentally by Mathies et al.).³⁶ Calculations predict³⁷ that, upon formation of the T_1 state, cycloheptatriene relaxes from the ground-state boatlike conformation to a fully planar geometry with a completely altered, bis-allylic bonding pattern (Figure 5, top). Despite the large driving force ($\Delta G^\circ = -19.9 \text{ kcal/mol}$), cycloheptatriene belongs to the “normal region” of its own ΔG° curve. Once again, this assignment is confirmed by the variable-temperature measurements of the free energy of activation (Figure 4).

Finally, one more aspect of cycloheptatriene’s behavior, namely its very fast quenching of the triplet of free biacetyl, must be noted (Table 1). The quenching occurs not due to rapid excitation transfer, but due to hydrogen abstraction by the triplet biacetyl. The formation of the cycloheptatrienyl radical and the corresponding ketyl radical is highly exothermic ($\Delta G^\circ > 25 \text{ kcal/mol}$) and proceeds at a diffusion-controlled rate.³⁸ Naturally, this deactivation channel becomes completely inoperative when biacetyl is enclosed inside the carcerand, as any direct contact with cycloheptatriene is then precluded.

The 1,3-cyclohexadiene triplet, instead of becoming planar, attempts to relax by twisting one of its double bonds, i.e., similarly to its acyclic equivalent, the 1,3-butadiene. Naturally, in a cyclic molecule this relaxation cannot reach the optimum 90° twist angle, and the resulting structure consisting of a planar allylic fragment and an alkyl radical is highly strained. Similarly as in the case of cycloheptatriene, the $S_0 \leftrightarrow T_1$ transition is accompanied by a complete change of the bond order (Figure 6, bottom).³⁷ Cyclohexadiene and cycloheptatriene correspond approximately to the last curve in Figure 2.

Molecular Oxygen. O_2 is a unique triplet energy acceptor in two aspects: (a) The triplet \leftrightarrow singlet transition corresponds to an intracconfigurational change in the electronic structure (i.e., there is no change in the occupancy of the spatial orbitals), and therefore it is associated with a remarkably small reorganization energy (0.006 kcal/mol on the basis of ab initio calculations at the 6-31G** HF and MP2 levels). (b) The molecule possesses only one vibrational mode. As a consequence, triplet energy transfer to oxygen reaches the “inverted region” at very low values of driving force. This behavior will be particularly pronounced for donors with small reorganization energy, for which the maximum rate will occur at a correspondingly lower ΔG° . Biacetyl, with λ_v of only $\sim 0.5 \text{ kcal/mol}$, provides an extreme example of this situation. The Franck–Condon factors for triplet excitation transfer between $1\cdot$ biacetyl and oxygen are very poor, and the quenching is the second slowest among all studied quenchers, even though the diffusion rate of the small O_2 molecule, and the resulting frequency of encounters, are considerably higher than those for any other acceptor. Indeed, Schmidt and co-workers³⁹ found that triplet energy transfer from a variety of organic donors is likely to occur primarily to the higher energy $^1\Sigma_g^+$ state of oxygen, rather than at the $^1\Delta_g$ lowest singlet, because of the more favorable Franck–Condon factors. Our observations strongly support this conclusion. The $1\cdot$ biacetyl/

(36) Reid, P. J.; Shreve, A. P.; Mathies, R. A. *J. Phys. Chem.* **1993**, *97*, 12691.

(37) Ab initio calculations were done at the MP2 level with the 6-31G** basis set.

(38) While there are no literature reports dealing specifically with the biacetyl/cycloheptatriene couple, the hydrogen abstracting ability of triplet biacetyl is well known (Turro, N. J.; Engel, R. *J. Am. Chem. Soc.* **1969**, *91*, 7113), and cycloheptatriene’s eagerness to serve as a H-radical donor has been clearly demonstrated (Green, I. G.; Walton J. C. *J. Chem. Soc., Perkin Trans.* **1984**, *2* (7), 1253. Paul, V.; Roberts, V. P.; Robinson, C. A. *S. J. Chem. Res.* **1988**, *8*, 264).

(39) Bodesheim, M.; Schütz, M.; Schmidt, R. *Chem. Phys. Lett.* **1994**, *221*, 7.

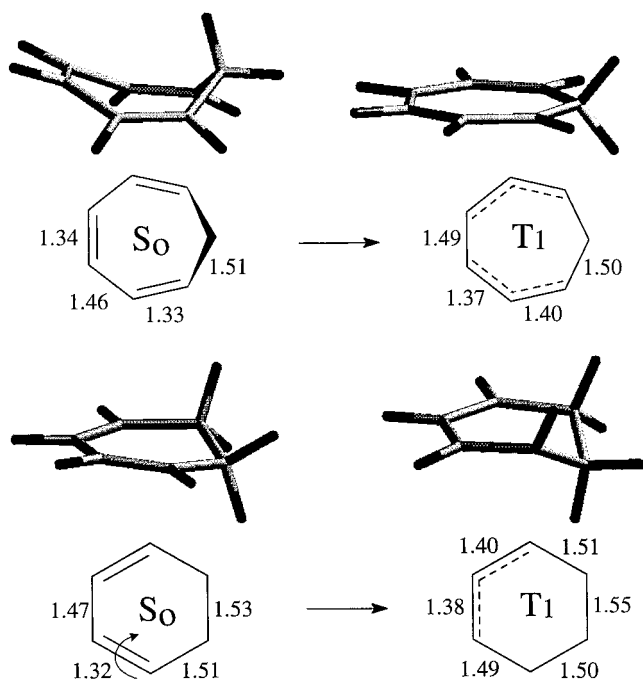


Figure 6. Optimized geometries of the S_0 and T_1 states for cycloheptatriene (top) and cyclohexadiene (bottom) calculated at the RHF and UHF 6-31G** levels. Bond lengths are shown in angstroms.

O_2 donor/acceptor pair, with $\lambda_{total} = 2.8$ kcal/mol (the fixed solvent component of 2.3 kcal/mol is most likely seriously exaggerated in the case of O_2),⁴⁰ corresponds approximately to the first curve in Figure 2, and approaches the “gap law” rather than the Marcus behavior.⁴¹

Summary

The presented results underscore the pronounced dependence of triplet excitation-transfer rates on the internal reorganization energy of the donor/acceptor pair. There are two principal reasons responsible for this behavior: (1) the medium reorganization energy is typically negligibly small in the case of excitation transfer, and (2) for many commonly used organic donors and acceptors, the absolute magnitude of the internal

(40) (a) Schmidt, R. *J. Phys. Chem.* **1996**, *100*, 8049. (b) Wessels, J. M.; Rodgers, M. A. J. *J. Phys. Chem.* **1995**, *99*, 17586. Both references report exceedingly small solvent-induced Stokes shifts of the O_2 emission.

(41) Patterson, L. K.; Porter, G.; Topp, M. R. *Chem. Phys. Lett.* **1970**, *7*, 612.

reorganization energy accompanying the $S_0 \leftrightarrow T_1$ and $S_0 \leftrightarrow S_1$ transitions is considerably larger than it is in the case of formation of the corresponding radical anions or cations. Because a triplet energy donor with a very small internal reorganization energy (biacetyl) was used in our work, the Franck–Condon factors and the measured rates were highly sensitive to the changes in the internal reorganization energy of the acceptor. The position of a particular donor–acceptor pair on the free energy/reorganization energy plot could be unequivocally determined only by variable-temperature measurements.

Naturally, there are factors other than the variation in internal reorganization energy which might influence the observed distribution of triplet-transfer rates. One would expect that the differences in size and shape of various triplet acceptors should be reflected in different effective electronic couplings in the corresponding encounter complexes between the acceptor and the incarcerated donor. Similarly, the diffusion rates of various acceptors must differ from one another, resulting in different frequency of encounters. Finally, the lifetime of the encounter complex may be different in the case of different acceptors.³⁴ These effects are most likely responsible for the scatter in the experimental data; however, they cannot account for the overall trends. Since there are no truly reliable methods of accounting for these effects in a quantitative manner, and there is no reason they should correlate with the triplet energy of the acceptor, the authors have chosen not discuss them in detail. Indeed, particularly in view of these possible additional factors, the obtained agreement between the experimental results and the standard theory of nonradiative electronic energy transfer (Figure 3) is very satisfying.

Further work on these systems, including the study of the dependence of the rate of triplet excitation transfer on the size of the hemarcerand cage, will be reported shortly.

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Supporting Information Available: Synthesis of 1•biacetyl, along with NMR and FAB-MS data; table of the AM1 calculated triplet reorganization energies (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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