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Free Energy and Entropy Changes in Vertical and Nonvertical Triplet Energy Transfer Processes between Rigid and Nonrigid Molecules. A Laser Photolysis Study

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Abstract: The free energy and entropy changes associated with intermolecular triplet energy transfer (TT) processes were determined by direct measurement of the equilibrium constant using a laser flash photolysis technique. 10,10-Dimethylanthrone and 9,9-dimethylfluorene were synthesized and used as a "rigid" donor and acceptor, respectively, in comparison with 4-methylbenzophenone, a "nonrigid" donor, and 4-methylbiphenyl, a "nonrigid" acceptor, in the TT reactions. Both the nonrigid donor and the nonrigid acceptor lose entropy while going from the twisted ground state to the planar triplet state. The ΔS values for 4-methylbenzophenone and 4-methylbiphenyl are 0.5–1.0 and 2.5–3.0 gibbs/mol, respectively.

Introduction

Although triplet energy transfer (TT) is an important process occurring in many systems ranging from photosynthesis to exciton theory,[1,2] the entropy term ΔS in TT reactions has been largely neglected and poorly studied. The importance of the entropy term in free energy change and transfer rate for TT started to be recognized only about 10 years ago.[3] The ΔS term is important in TT reactions because both its sign and magnitude can significantly affect the equilibrium constant by over an order of magnitude.[4] The first direct measurements of entropy changes in triplet energy transfer reactions were carried out by Gessner and Scaiano[4] only 7 years ago. The ΔS term, representing important changes in degrees of freedom, would help us understand the structure of both the ground state and the triplet state of the molecules involved in the process. Numerous studies exist on the ground state and excited triplet state of biphenyl[5-18] and benzophenone[19-26] molecules. Some additional understanding of these two molecules should be possible by measuring the entropy change in their TT reactions.

In addition, the ΔG values for intermolecular TT reactions are required for interpretation of the temperature dependence of the long-distance intramolecular TT reactions.[27] Since both electron transfer (ET) and TT can be treated as radiationless processes governed by "Fermi's golden rule", TT reactions can be used to test semiclassical electron transfer model for the rate constant developed by Jortner and others.[28] While their theory works very well for long-distance intramolecular ET experiments,[29] an intramolecular TT study should be a good test of the generality of the theory for radiationless processes. Since the covalently attached benzophenone and biphenyl molecules can have different triplet excited state and ground state energies from the benzophenone and biphenyl molecules themselves, the methyl-substituted benzophenone and biphenyl molecules should give more accurate ΔG values for these intramolecular TT processes.

That in TT reaction 1

$$D^T + A \rightleftarrows D + A^T \qquad (1)$$

an equilibrium can be readily established between two triplet states in solution has been known for almost three decades,[30] where D and A refer to donor and acceptor, respectively, and T refers to the triplet state. Because of the long lifetime of the triplet state relative to the TT reaction rates, direct observation of the equilibrium between the two excited triplet states is possible,

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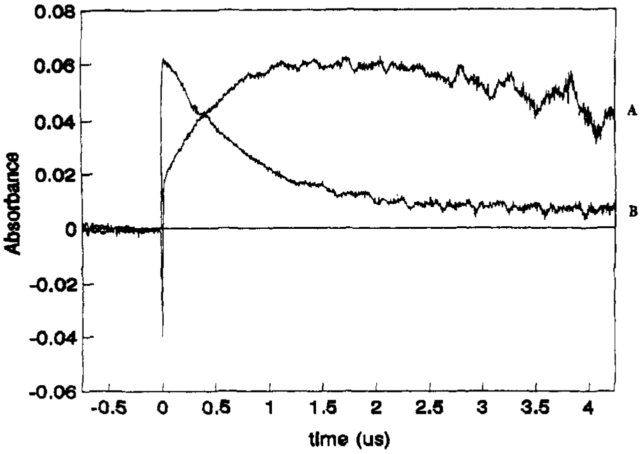

Figure 1. Representative traces for the 4-methylbenzophenone and 4-methylbiphenyl system at 333 K, monitored at 540 nm (A) where the decay of the donor triplet state predominates and at 400 nm (B) where the rise of the acceptor triplet state predominates. The concentrations are [4-methylbenzophenone] = 1.0 mM and [4-methylbiphenyl] = 0.5 mM.

and the equilibrium constant, K_{eq}, defined in eq 2 can be readily measured.[31-34] From the measured K_{eq}, the ΔG can be determined

$$K_{eq} = [A^T][D][A]^{-1}[D^T]^{-1} \qquad (2)$$

$$\ln K_{eq} = -\Delta G/RT \qquad (3)$$

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

using eq 3. From a study of the temperature dependence of K_{eq}, we can also determine the reaction's enthalpy and entropy changes using eq 4.

According to the Franck–Condon principle, when little change of conformation is involved upon excitation, then phosphorescence studies that measure the vertical transition between the ground state and the triplet excited state accurately represent the triplet state energy and therefore the ΔG of the TT reaction. However, some molecules have significant conformational differences between the two states resulting in what is sometimes called a "nonvertical" transition, and then the phosphorescence studies do not give the correct triplet energy, resulting in the incorrect ΔG. The laser flash photolysis technique used here measures the energy difference between the "relaxed" triplet state and the ground state. In other words, the "true" ΔG of these reactions is measured.

In this paper we report the free energy change of four TT reactions over a temperature range of 100 °C, along with ΔH and ΔS calculated from eq 4. In our study, 4-methylbenzophenone (mBz) and 10,10-dimethylanthrone (mAn) were chosen as the "nonrigid" and "rigid" donors, respectively, and 4-methylbiphenyl (mBi) and 9,9-dimethylfluorene (mFl) were chosen as the "nonrigid" and "rigid" acceptors, respectively. In order to determine K_{eq} successfully using the laser flash photolysis technique described below, the ratio of the observed optical densities at the two wavelength should be competitive. Thus, this technique works best for those reactions with small $|\Delta G|$. For reactions with very small or very large equilibrium constants, either the donor or the acceptor should be present in a large concentration. Such a large concentration raises the possibility of a triplet–triplet annihilation reaction. Unfortunately, the triplet–triplet annihilation unnecessarily complicates the study of the TT process. In order to avoid using high concentrations of either the donor or the acceptor, a potential problem in the Scaiano work, all the donor and acceptor pairs used in this work have small $|\Delta G|$ values, thus minimizing the possibility of the triplet–triplet annihilation process.

Results

The data analysis is the same as described by Kira and Thomas.[34] According to Beer's law and eq 2

$$(OD^a - mOD^d)(OD^d - nOD^a)^{-1} = K_{eq}\epsilon_A^a(\epsilon_D^d)^{-1}[A][D]^{-1} \qquad (5)$$

where ϵ_D and ϵ_A represent the extinction coefficient of the donor and acceptor triplet state, respectively, $m = \epsilon_D^a/\epsilon_D^d$ and $n = \epsilon_A^d/\epsilon_A^a$. The subscripts D and A indicate the triplet donor and triplet acceptor, respectively. The superscripts d and a indicate the wavelength chosen where the donor and acceptor, respectively, absorb predominantly.

The parameters m, n, and $\epsilon_A^a/\epsilon_D^d$ were determined by the ratios of the triplet state concentrations and the optical densities at the two selected wavelengths. Two assumptions were applied. (i) The same donor concentration results in the same triplet state concentration if the laser power is kept constant. (ii) The decay of the triplet state of the donor is much slower than the intermolecular TT when the acceptor has a much greater concentration than the donor.

According to eq 1, the kinetics of the donor and the acceptor triplet can be described by the following differential equations

$$d[D^T]/dt = -k_1[D^T][A] + k_{-1}[D][A^T] \qquad (6)$$

$$d[A^T]/dt = k_1[D^T][A] - k_{-1}[D][A^T] \qquad (7)$$

where k_1 and k_{-1} are the forward and back rate constants in reaction 1. Solving the differential equations using the initial condition $[D^T] = [D^T]_0$ and $[A^T] = 0$, it produces

$$[D^T](t) = \{[D^T]_0/(k_1[A] + k_{-1}[D])\}\{k_{-1}[D] + k_1[A]\exp[-(k_{-1}[D] + k_1[A])t]\} \qquad (8)$$

$$[A^T](t) = \{[D^T]_0 k_1[A]/(k_1[A] + k_{-1}[D])\} \times \{1 - \exp[-(k_{-1}[D] + k_1[A])t]\} \qquad (9)$$

when $t \rightarrow \infty$, $[D^T]/[A^T] = k_{-1}[D]/k_1[A]$, where equilibrium is established. However, when $k_{-1}[D] + k_1[A]$ in the exponential part is large enough, the equilibrium can be reached in a short time. In the reactions we studied, the equilibrium is reached within 2 μs as judged for example by Figure 2. The equilibrium point was determined by the criterion that the ratio does not decrease more than 5% over 30 points (150 ns). The average value of these 30 points right after the defined equilibrium point was used as the ratio in eq 5. Figure 3 is a plot of ln K_{eq} vs T^{-1} for the four reactions. Table I is a summary of our results.

Discussion

For biphenyl in the crystalline state the conformation is known to be planar at room temperature[5] and twisted at low temperature.[6,7] Several studies by electron diffraction have estimated the dihedral angle between the two phenyl rings to be 42–45°.[8-10] Optical studies reveal that in solution the twisted angle is about 15–30°.[11-14] The twisted structure of biphenyl is a result of the subtle balance between two opposite effects. The first, the hydrogen–hydrogen repulsion in the ortho positions of two phenyl rings, favors the rings to be orthogonal. The second, electron delocalization of the π system, prefers the rings to be planar.[17]

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Table I. Energy Transfer Data and Ratios of Extinction Coefficients

donor	acceptor	$m(\epsilon_D^a/\epsilon_D^d)$	$n(\epsilon_A^d/\epsilon_A^a)$	$\epsilon_D^a/\epsilon_D^d$	K_{eq}(20 °C)	ΔG(20 °C)	ΔH^a	ΔS^b
mBz	mBi	0.25	0.075	1.85	12.6	−1.48 ± 0.20	−2.0 ± 0.15	−2.1 ± 0.5
mBz	mFl	0.25	0.1	1.58	10.8	−1.39 ± 0.15	−1.28 ± 0.07	0.4 ± 0.2
mAn	mBi	0.6	0.075	4.2	7.6	−1.18 ± 0.20	−2.05 ± 0.11	−3.1 ± 0.35
mAn	mFl	0.6	0.1	3.7	4.8	−0.91 ± 0.30	−0.94 ± 0.13	−0.08 ± 0.15

[a] In kcal/mol. [b] In gibbs/mol.

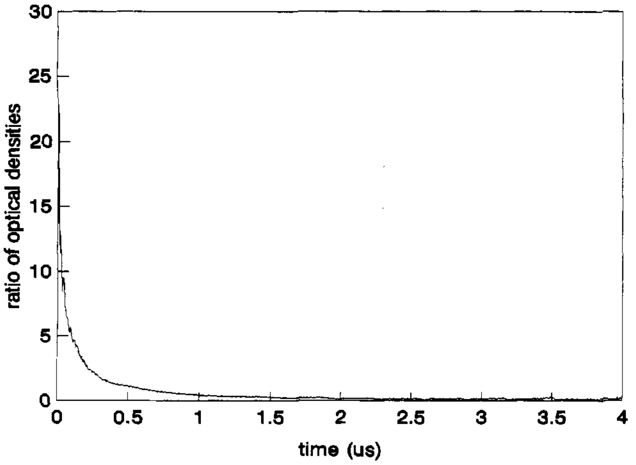


Figure 2. Representative trace of ($OD^d - nOD^a$)/($OD^a - mOD^d$) of the 4-methylbenzophenone and 4-methylbiphenyl system at 313 K. Equilibrium is reached approximately 2 μs after the donor triplet is generated.

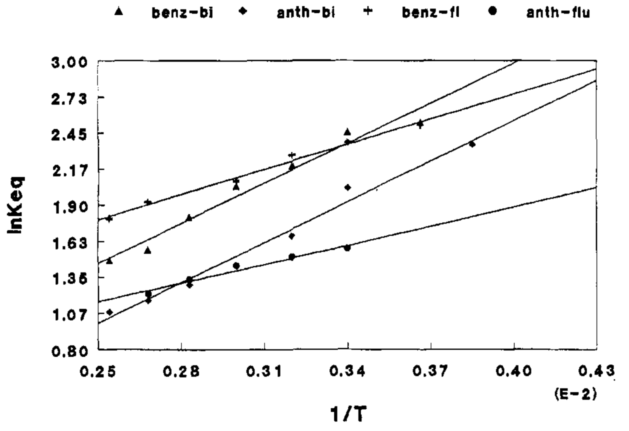


Figure 3. Semilogarithmic plot of the equilibrium constant against the reciprocal temperature for the mBz–mBi (▲), mBz–mFl (+), mAn–mBi (◆), and mAn–mFl (●) systems. The solid lines are the least-squares fits of the equation $y = kx + b$ for each system. The slope equals $-\Delta H/R$ and the intercept equals $\Delta S/R$.

An ab initio calculation predicts a relatively small barrier to torsional motion, ca. 2–2.5 kcal/mol.[15] According to EPR and ENDOR studies in crystals[16] and electronic excitation spectra study of the excited triplet in a supersonic jet,[17] the biphenyl molecule is in a planar conformation. In the gas phase the para-substituted biphenyls have a similar geometry to biphenyl in both the ground and excited states.[17] According to Wagner and Scheve[18] in liquid solution the ground states of 4-methylbiphenyl and biphenyl both have a twisted conformation and in the excited triplet state the methyl group in the para position does not affect the planarity of the two phenyl rings.

The benzophenone molecule is known to have a nonplanar C_2 symmetry conformation, with both phenyl rings twisted out of the phenyl carbonyl plane. The reported twist angles are 30° (by crystallography structure,[19] X-ray diffraction,[20] ^{1}H NMR,[21] and AM1 calculations[21,22]), 36° (by ab initio calculations[23]), and 42° (by ^{13}C NMR and force-field calculations[24]). An extended Hückel treatment predicts a twisted angle of 38°.[25] For excited state benzophenone molecules, the twisted angle is 28.5° according to optically detected ENDOR.[26] Semiempirical calculations also predicted a significant decrease of the twist angle in the excited state (32°) when compared with that in the ground state (38°).[25]

The entropy changes observed in the four TT reactions studied here can be interpreted in terms of the relative change in conformational freedom betwen the ground and excited states. If we suppose that the planar conformation has less freedom than the twisted conformation, then the nonrigid donor would contribute positively to entropy change since an increase in conformational freedom occurs when the donor goes from the planar conformation in the triplet state to the twisted one in the ground state. On the other hand, a nonrigid acceptor would contribute negatively in ΔS since a decrease in the conformational freedom results when the acceptor goes from the twisted ground state to the planar excited triplet state.

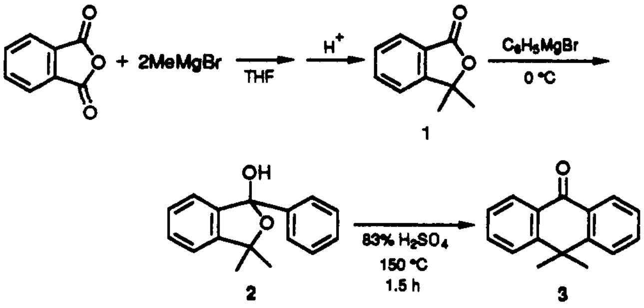
Qualitatively the data of Table I agree with the above interpretation. The mBz–mFl pair, which has a nonrigid donor and rigid acceptor, gives the highest ΔS, while the mAn–mBi pair, which has a rigid donor and nonrigid acceptor, gives the most negative ΔS. The nonrigid–nonrigid mBz–mBi pair and the rigid-rigid mAn–mFl pair give the ΔS values in between.

Quantitatively, the magnitude of ΔS resulting from the change in the conformational degrees of freedom in the 4-methylbiphenyl and 4-methylbenzophenone can be estimated from the ΔS values of the four reactions studied. Comparing the two ΔS values for the mBz–mBi pair and the mBz–mFl pair, the difference between these two numbers is an estimate of the entropy change of 4-methylbiphenyl upon excitation with the assumption that the "rigid" fluorene molecule has a zero entropy change during the energy transfer process. The same is true when comparing the ΔS of the mAn–mBi pair and the mAn–mFl pair. The two differences are ca. −2.5 and ca. −3.0 gibbs/mol, respectively. The same comparison between the mBz–mBi and mAn–mBi pairs and the mBz–mFl and mAn–mFl pairs gives values of 0.5 and 1.0 gibbs/mol, respectively. With the same assumption that the "rigid" 10,10-dimethylanthrone contributes zero entropy change in the reaction, these values are estimates of the entropy change for the 4-methylbenzophenone molecule undergoing de-excitation from the triplet state to the ground state during the energy transfer process. The equilibrium constant for the mBz–mBi pair (12.6) at room temperature agrees very well with the value of 12 for the benzophenone and biphenyl system reported by Gessner and Scaiano.[4] However, our calculated ΔS for mBz and mBi are both much smaller than the ones they got for benzophenone (4.3 gibbs/mol) and biphenyl (6.1 gibbs/mol). According to Wagner[18] the para-substituted biphenyl seems to require a smaller geometry change than biphenyl in the TT process. Even though this might lead to a smaller entropy change, we are not sure if this is the only cause. Finally, we note that the ΔG and ΔS values obtained from four different donor and acceptor pairs agree with each other quite well. Since any three ΔG values can be used to determined the fourth one, the results lead to a self-consistant and rather complete picture of the TT process.

Experimental Section

All the reactions were carried out in chlorobenzene as the solvent. Chlorobenzene was purchased from J. T. Baker without further purification. 4-Methylbenzophenone (Aldrich) and 4-methylbiphenyl (Al-

Scheme I



drich) were used as received. 9,9-Dimethylfluorene was synthesized in this lab. The detailed procedure was reported elsewhere.[35,36]

10,10-Dimethylanthrone is synthesized according to the procedure developed in this lab as shown in Scheme I.[37] The α,α-dimethylphthalide was prepared by published procedures[38] and purified by recrystallization from cyclohexane. The hemiketal was prepared by adding phenyl magnesium bromide to **1** in diethyl ether at 0 °C. No dialkylation was observed in the collected product. The hemiketal was obtained in 83% yield, after purification on silica gel column eluted with 20% CH_2Cl_2/hexane: mp 114–116 °C; ^{1}H-NMR 1.65 (3H, s, –CH_3), 1.71 (3H, s, –CH_3), 3.1 (1H, s, –OH), 7.14–7.16 (9H, m, –Ar). The hemiketal **2**, monitored by TLC, was stirred in H_2SO_4 at 150 °C for 1.5 h. The reaction did not proceed readily until the temperature rose to at least 150 °C. After 1.5 h, the aqueous solution was extracted three times with diethyl ether. The organic layers were combined and then washed with sodium bicarbonate. After being dried with magnesium sulfate, the solvent was removed using a rotor evaporator. The brownish crystalline product was purified on a silica gel column with CH_2Cl_2/hexane (50/50 v/v) as eluent and then recrystallized in ethanol twice. White flakes of **3**[39] were obtained from the recrystalline (20% yield): mass spectra, *m/z* 223 (90%), 208 (100%), and 178 (87%); ^{1}H-NMR 1.75 (6H, s, –CH_3), 7.40–7.48 (2H, t), 7.62–7.74 (4H, m), 8.36–8.40 (2H, d).

The measurements were performed using the laser flash photolysis technique. The sample was excited with the third harmonic (355 nm) from a Quantel Nd:YAG laser. The Hamamatsu L2439 super-quite xenon flash lamp was used as the analyzing light source. The beam passed through the sample contained in a suprasil cell and then an interference filter from Oriel. The output light was digitized by a LeCroy TR8828C digitizer which takes points every 5 ns. The data were transferred to an IBM-PC/AT via a CAMAC-GPIB interface. All the samples were deoxygenated 5 times by the "freeze–pump–thaw" cycle method before measurements. The temperature control was carried out by flowing nitrogen gas through a dewar with a homemade heater inside. A platinum RTD probe (Cole–Parmer) was placed right below the sample cell and connected to a digital temperature controller (Cole–Parmer) with a control accuracy of ±0.1 °C.

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